April 17, 1962
F. LEVI
3,029,496
METHODS OF PRODUCING MAGNETIC MATERIALS AND
TO THE MAGNETIC MATERIALS SO PRODUCED
Filed Nov. 14, 1958
3 Sheets-Sheet 1

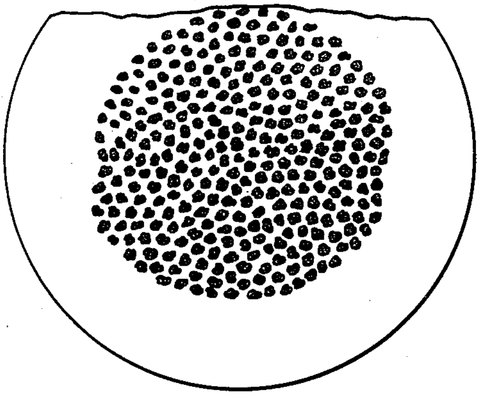

Fig. 1.

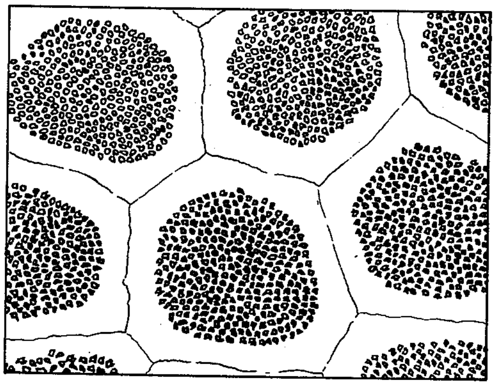

Fig. 2.

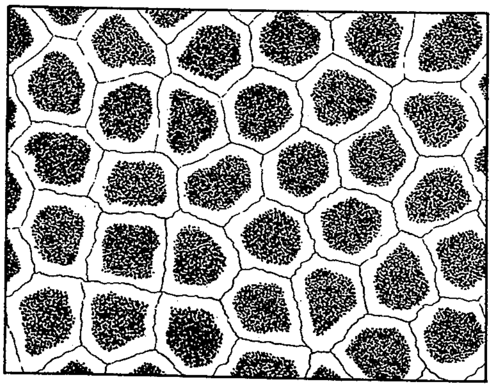

Fig. 3.

INVENTOR

FULVIO LEVI

Imirie & Smiley
Attys.

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3 Sheets-Sheet 2

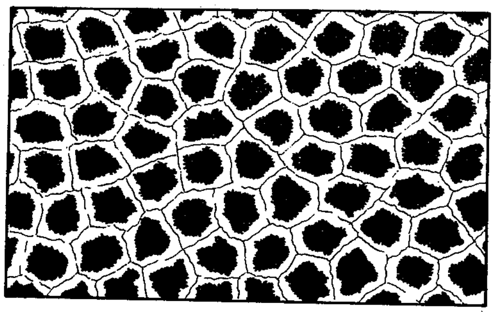

Fig. 4.

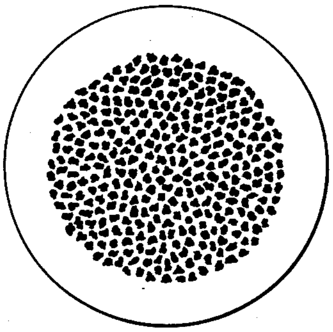

Fig. 5.

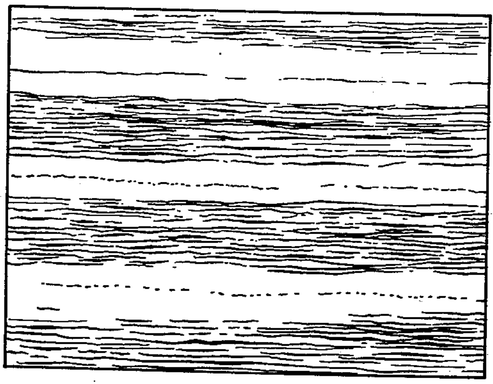

Fig. 6.

INVENTOR

FULVIO LEVI

Imirie & Smiley
Attys.

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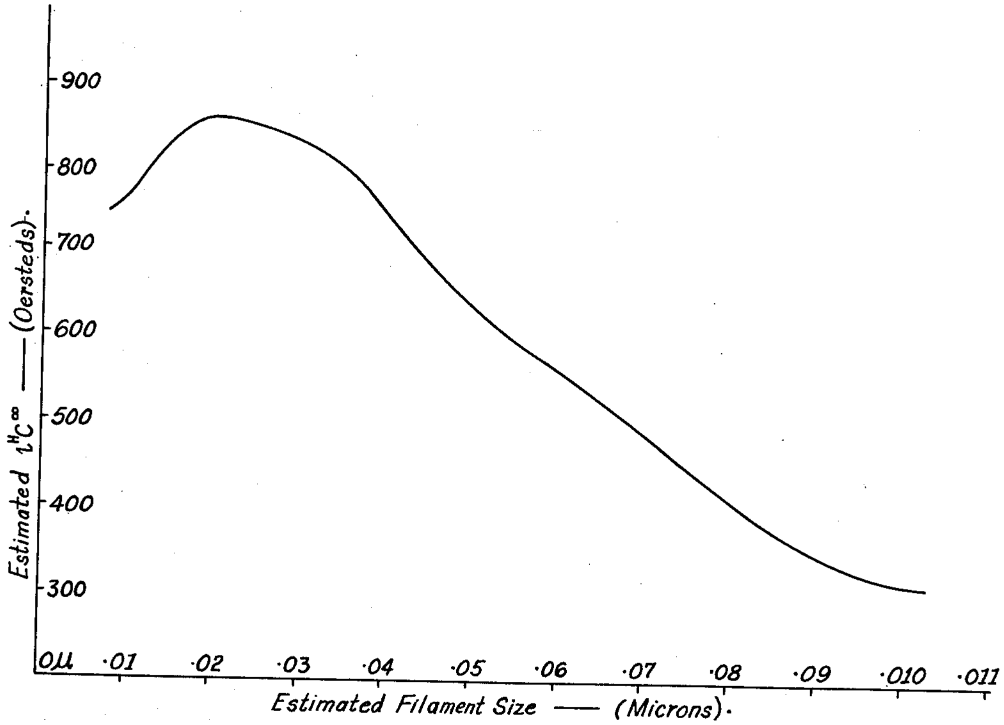

Fig. 7.

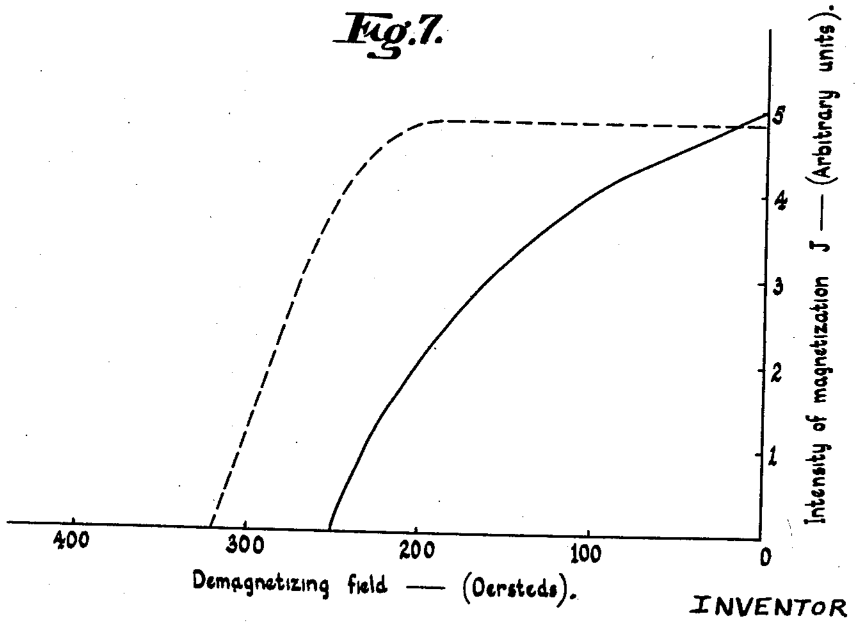

Fig. 8.

INVENTOR
FULVIO LEVI
Imrie & Smiley
Attys.

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METHODS OF PRODUCING MAGNETIC MATERIALS AND TO THE MAGNETIC MATERIALS SO PRODUCED

Fulvio Levi, Camberwell, Victoria, Australia, assignor to Rola Company (Australia) Proprietary Limited, Richmond, Victoria, Australia, a company of Australia

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Claims priority, application Australia Nov. 20, 1957
26 Claims. (Cl. 29—155.59)

The present invention relates to methods of producing permanent magnet materials and to the permanent magnet materials so produced.

The most widely used permanent magnets today are produced from cast alloys used under various trade names such as "Alnico," "Alcomax," "Ticonal." These permanent magnets are hard and brittle, and contain substantial percentages of scarce and expensive materials like cobalt and nickel.

Reasonably ductile permanent magnets are also available; these are particularly useful in instrumentation work, where magnets having a high coercive force and very small dimensions are often required. Permanent magnets of this class are, for example, those sold under the trade names of "Cunife" and "Vicalloy." "Cunife" contains about 20% nickel and "Vicalloy" about 50% of cobalt. Typical compositions are: 20% iron, 20% nickel, 60% copper for Cunife and 34% iron, 53% cobalt, 14% vanadium for Vicalloy. The optimum magnetic properties of these materials can be varied only slightly, owing to metallurgical reasons. The best magnetic properties are obtained after severe mechanical elongation of the materials, e.g. by means of drawing, and are found along the direction in which the materials have been elongated.

The permanent magnetic properties of all the foregoing materials are obtained by a process which includes, essentially: a solid solution heat treatment, a quench, and an ageing heat treatment. As a result of this process, the final material contains extremely fine particles of a main ferromagnetic phase dispersed within a non-ferromagnetic or secondary ferromagnetic phase.

According to a now widely accepted theory of permanent magnetism, this finely dispersed state is responsible for the high coercive forces—varying, broadly, from 400 to 800 oersteds—of the above materials.

Theory (see, e.g.: "Physical Theory of Ferromagnetic Domains" Charles Kittel—Reviews of Modern Physics, volume 21, No. 4, October 1949, pp. 541–583) also suggests that a body containing sufficiently small particles of a ferromagnetic material, having negligible coercive force in the bulk state like iron and cobalt, for example, separated one from another by a non-ferromagnetic material ought to be a permanent magnet, or, in other words, possess substantial coercive force. This condition is achieved with approximately spherical particles of iron when the diameter of each particle is less than about 0.1 of a micron (1 micron $=10^{-4}$ cm.). Each particle of iron is then considered to contain only one magnetic domain and is commonly called a "single-domain" particle. A single-domain particle is known as one having uniform magnetization in zero field and the references to a single-domain particle hereinafter appearing are to be interpreted accordingly. The critical diameter below which a spherical particle is a single-domain particle generally varies with the material of the particle.

Further development of the theory has led to the conclusion that the highest values of coercive force, and generally other desirable magnetic properties, should be found in a body composed of elongated ferromagnetic particles—of iron or of cobalt for example—of equal round cross-sections each having a diameter somewhat smaller than the critical diameter of a single-domain sphere of the same material, all particles being evenly spaced from each other, and all particles having parallel elongated axes. It is also considered that elongated particles of a given material can be single-domain when their diameter normal to the elongated axis is considerably larger than the critical diameter of a spherical particle of the same material.

Another important theoretical result is that the intrinsic coercive force $_iH_c$ of a body composed of single-domain particles, assumed of equal sizes and shapes and evenly spaced with non-ferromagnetic material, is given by the relation $_iH_c = {}_iH_{c\infty}(1-p)$ where p is the fraction of volume occupied by the single-domain particles and $_iH_{c\infty}$ is the intrinsic coercive force of an isolated single-domain particle. It follows from this relation, that the magnetic properties of the body can be modified by changing the spacing between the particles.

Most of these theoretical conclusions have been known for over ten years and a large amount of experimental work has been carried out in an endeavour to produce bodies having the required structure. This interest derives not only from the fact that it appears possible to produce powerful permanent magnets using only cheap and freely available materials like iron, but also because the predicted maximum values of the coercive force are much higher than those obtained so far in the above mentioned materials "Alnico," "Cunife" and "Vicalloy." Although the predicted theoretical maximum values for $_iH_{c\infty}$ of isolated elongated particles of iron having a cross-sectional diameter of about .02 of a micron and a length exceeding about .1 of a micron, vary between about 2500 and 10,000 oersteds (see, e.g.: Kittel, already quoted above and: "Reproducing the Properties of Alnico Permanent Magnet Alloys with Elongated Single-Domain Cobalt-Iron Particles" Lubersky, Mendelsohn, Paine; Conference on Magnetism and Magnetic Materials, Boston, 1956—published February 1957, pp. 133–144) properly compacted particles possessing even the lowest predicted maximum value would result in a permanent magnet more powerful than any magnet commercially produced today.

To the best of the applicant's knowledge, all previous methods of producing these composite bodies rely on the compacting of previously manufactured fine particles of ferromagnetic material. The resulting bodies are mechanically soft, but are not ductile and cannot be drawn or rolled to small dimensions.

Some of the methods used for the manufacture of the particles are: the decomposition of organic salts of iron or of iron and cobalt with subsequent hydrogen de-oxidation; electro-deposition of iron or of iron and cobalt on a mercury cathode, either moving or stationary, followed by removal of the mercury; casting alloys of iron or of iron and cobalt with aluminium under suitable conditions followed by chemical removal of the aluminium.

Many procedures have also been suggested and used to protect the fine particles from oxidation, since the materials become pyrophoric when subdivided to the required degree, and from coalescence during compacting.

It is obvious that, with all hitherto known processes, the shapes and dimensions of the particles are not uniform and it is extremely difficult to obtain a large percentage of particles having optimum properties. Furthermore the alignment of the particles, which is usually attempted by applying a magnetic field during some of the stages leading to, and including, the final compacting and eventual heat treatment, is only partially successful owing to frictional forces, to the presence of particles which are not susceptible to alignment and even to the permanent magnetic properties of the particles themselves which cause formation of particle clusters.

All the above difficulties are best appreciated when it is remembered that iron or cobalt powders having the desired properties are invisible with the best optical microscope, since they have cross-sectional dimensions smaller than the wave length of light, and are comparable to smoke particles. When all these factors are taken into consideration, the results achieved with know methods are indeed remarkable and a clear indication of the probable correctness of the theory.

The primary object of the present invention is to provide a novel method of preparing permanent magnet materials containing very finely dispersed elements, which substantially avoids the above mentioned difficulties.

According to the invention materials possessing desirable permanent magnet properties are produced by reducing the cross-section of a composite body containing multidomain ferromagnetic elements, separated from each other by suitable materials, until the ferromagnetic elements become single-domain owing to their reduced cross-sections.

For this purpose a starting material is employed which comprises a composite body containing a plurality of ferromagnetic elements each of an appropriate shape in cross-section and of a size in cross section substantially larger than that of the particles finally desired and each separated by a non-ferromagnetic material or a ferromagnetic material different from that of the ferromagnetic elements. The ferromagnetic elements may be separated from each other by more than one kind of material provided the material is a non-ferromagnetic material or is a ferromagnetic material different to that of the ferromagnetic elements. The composite body is then subjected to an elongation process by means of drawing, rolling, swaging or other similar techniques, until the ferromagnetic elements within the body each have a sufficiently small cross section to be single domain. It will be appreciated that, in this manner, elongation and alignment of all the elements is automatically achieved. The body containing the lements can be of substantial cross section for economy and ease of operation. When a given body becomes too small in cross section and further reduction is necessary, the body may be cut into shorter lengths which are then assembled to form a second composite body. The process may then be repeated.

The ferromagnetic elements may have substantially equal and like configurations in cross-section and may be substantially equispaced from each other in planes normal to the elongation direction.

Each ferromagnetic element may consist of a rod or wire which is encased in a sleeve of non-ferromagnetic material or a ferromagnetic material different to that of the rod or wire. The elements may each be subjected to elongation with or without heat treatment prior to assembly in the composite body.

During the elongation process the composite body may be annealed or otherwise heat treated at an appropriate temperature and for an appropriate period depending upon the materials forming the body and properties required for the final magnetic material. At no stage, however, should the temperature be sufficiently high to bring the elements into solid solution.

Although the method is not limited to the manufacture of bodies having a high coercive force as the only desirable magnetic property, the application of the method to this particular aim will now be described in detail.

As previously explained, a substantial coercive force can theoretically be obtained in a composite body containing parallel and equispaced iron filaments having round cross sections of about 0.1 of a micron diameter and lengths exceeding 0.5 of a micron.

In one practical embodiment of the invention a magnetic body was produced containing iron filaments estimated to satisfy the above conditions and having an approximate intrinsic coercive force of 100 oersteds in the hard drawn condition and of 200 oersteds after annealing. Although much higher coercive forces have been achieved in other embodiments, some of which are hereinafter described, the microphotographs relating to Example I are the most suitable for a clear understanding of the principles of the invention.

Example I

A tube of 5% tin bronze with 0.024" wall thickness was drawn over a 0.070" diameter iron wire. The resulting composite wire was drawn from the diameter of

$$0.070''+(2\times0.024'')=.118''$$

to a diameter of .005". The wire was annealed at approximately 420° C. for half an hour at stages corresponding to about 75% area reduction.

A bundle of 300 substantially parallel composite wires 0.005" diameter formed as above described was inserted in a 5% tin bronze tube with 0.014" wall thickness to form a first compact. The starting diameter of this first compact, after the outer tube had been drawn over the wires fairly tightly, was about 0.125". This first compact was drawn to 0.005" diameter. The compact was annealed at approximately 420° C. for half an hour at stages corresponding to about 50% area reduction.

FIGURE 1 shows a drawing of a microphotograph of a cross-section of this first compact at 0.030" diameter containing 300 iron filaments each of approximately 20 microns diameter.

A bundle of 300 substantially parallel first compacts of 0.005" diameter was inserted in a 5% tin bronze tube with 0.014" wall thickness to form a second compact. The starting diameter of this second compact, after the outer tube had been drawn over the bundle of first compacts fairly tightly, was about 0.125". This second compact was drawn to 0.005" diameter. The second compact was annealed at approximately 420° C. for half an hour at stages corresponding to about 50% area reduction.

FIGURES 2, 3 and 4 show drawings of microphotographs of portions of the cross-sections of this second compact at 0.035", 0.015" and 0.005" diameter respectively. The estimated equivalent cross-sectional diameters of the individual iron filaments are respectively approximately: 0.7 of a micron, 0.3 of a micron and 0.1 of a micron. The individual iron filaments are clearly visible in FIGURE 2 but are blurred in FIGURE 3 and indistinguishable in FIGURE 4. This is due to the fact that the diameters of the individual filaments cannot be resolved by optical microscopes when they are smaller than about 0.5 of a micron.

FIGURE 5 shows a drawing of a microphotograph of a complete cross-section of the second compact at 0.005" diameter. Each of the 300 dark areas contains an estimated 300 iron filaments, each about 0.1 of a micron diameter. The intrinsic coercive force at this stage was, as already mentioned, about 100 oersteds before anneal and 200 oersteds after anneal.

FIGURE 6 shows a drawing of a microphotograph of a longitudinal section of a portion of the second compact at 0.025" diameter. The iron filaments have an estimated equivalent diameter of 0.5 of a micron and can be seen in the figure running substantially parallel to each other inside each first compact.

Two complete first compacts can be seen in FIGURE 6. Although small misalignments are unavoidable, it can be seen that most of the filaments appear to be of uniform cross-section, are of considerable length and are equally spaced from each other.

Two other practical embodiments will now be described in which the spacing between the individual iron filaments corresponds to about 35% iron in Example II and 21% in Example III.

Example II

A tube of 5% tin bronze with 0.024" wall thickness was drawn over a 0.070" diameter iron wire. The resulting composite wire was drawn to 0.0025" diameter with anneals at approximately 460° C. for 10 minutes at stages corresponding to about 75% area reduction.

A first compact was made containing 1000 wires 0.0025" diameter, surrounded by a 0.014" wall thickness bronze tube and drawn to 0.003".

The first compact was annealed at approximately 460° C., for ten minutes after a reduction corresponding to about 95% area reduction and at reductions corresponding to about 50% area reduction after the first anneal.

A second compact was made containing 800 first compacts 0.003" diameter surrounded by a 0.014" wall thickness bronze tube and drawn to 0.005". The estimated individual iron filament equivalent diameter was then .05 of a micron.

The second compact was annealed at approximately 460° C. for ten minutes after a reduction corresponding to about 70% area reduction at reductions corresponding to about 50% area reduction following the first anneal. The approximate intrinsic coercive force of the second compact at 0.005" was 330 oersteds in the hard drawn state and 420 oersteds after anneal. The computed average intrinsic coercive force of the isolated particles after anneal is

$${}_iH_{coo}=\frac{420}{1-0.35}=650 \text{ oersteds}$$

Example III

A tube of 5% tin bronze with 0.024" wall thickness was drawn over 0.040" diameter iron wire. The resulting composite wire was drawn and first and second compacts made similarly to Example II.

When the second compact was drawn to 0.005" the estimated individual iron filament equivalent diameter was 0.04 of a micron.

The iron percentage inside the outer bronze tube in the first compact was 21%.

The approximate intrinsic coercive force of the second compact at 0.005" was 480 oersteds in the hard drawn state and 600 oersteds after anneal.

The computed average intrinsic coercive force of the isolated particles after anneal is

$${}_iH_{coo}=\frac{600}{1-0.21}=760 \text{ oersteds}$$

FIGURE 7 is a graph showing the relationship: average intrinsic coercive force of the isolated particles computed from the results of various selected embodiments, versus the estimated iron filament equivalent diameter in magnetic materials produced by the method of the invention.

It can be seen from this graph that the average intrinsic coercive force of the individual elements as computed from measured coercive forces of compacted materials made according to the invention can exceed the value of 800 oersteds. Whilst this result is sufficient to allow the manufacture of ductile materials having high coercive forces and using only cheap and freely available materials, like iron, a result which is believed to be both useful and novel, it is expected that the method of the invention is capable of producing magnetic materials with much higher coercive forces than those mentioned. In this regard it will be obvious that there are a great number of combinations of materials, compacting and reducing methods and annealing schedules which are possible.

Another feature of the material of the invention is that the demagnetizing curve of magnetic materials manufactured as in the examples previously described have a substantially square demagnetizing curve if they are subjected to an annealing treatment at temperatures of between 420° C. to 470° C. for about five to twenty minutes. As an example, FIGURE 8 shows the demagnetizing curves of a material produced as described in Example II in the hard drawn and in the annealed conditions, when the estimated iron filament diameter was about 0.07 of a micron.

The iron wire used in all the embodiments herein described was low carbon 0.1 manganese semikilled steel wire as used for the manufacture of nails and similar articles, hydrogen purified.

The 5% tin bronze tubing contained approximately 95% copper, 4.5% tin, plus minor additions of phosphorus, iron and zinc.

It is believed that a variety of other materials can be used to carry out the invention. Whilst it is not desired to be limited by any specific theory, experience suggests that the materials, temperatures and frequency of the interstage anneals have to be selected so as to achieve a suitable compromise between ductility of the compact and fine grain size of both the ferromagnetic filaments and of the spacing materials. Filament breaks result in uneven filament cross-sections; increase of grain size causes deformation of the cross section of the original ferromagnetic elements. Both faults reduce the coercive force of the compacts.

It should be noted that the times and temperatures quoted in the above examples, refer to a process where the composite bodies were placed inside a muffle containing a neutral atmosphere and the muffle heated in an air circulating oven set at the quoted temperature.

The actual time during which the composite body was annealed at the quoted temperature was somewhat less than the total quoted time owing to the presence of the muffle.

It has been found that a good guide as to the selection of suitable values of the process variables is obtained from an examination of the cross-sections of the ferromagnetic elements under a microscope. The ferromagnetic elements' cross-sections can then be checked for shape, size and uniformity of spacing at different stages of the process and the process modified to obtain the desired result.

Having now described my invention, what I claim as new and desire to secure by Letters Patent is:

1. A method of producing permanent magnets comprising the steps of providing a plurality of rod-like elements of a ductile ferromagnetic metal, enclosing each element in a casing of a different metal having substantially the same ductility assembling a plurality of the encased ferromagnetic elements together to form a composite body, and compacting the assembly to uniformly elongate the composite body by repeated compacting operations until substantially all of the ferromagnetic elements are single domain.

2. A permanent magnet comprising a plurality of laterally spaced ferromagnetic elements substantially all of which are single domain, and a metallic material different to the material of the elements separating said elements from each other, said permanent magnet being produced by the method of claim 1.

3. The method of producing permanent magnets according to claim 1 wherein said composite body is subjected to annealing steps between and after said repeated compacting operations at a temperature less than that which would bring said ferromagnetic elements into solid solution.

4. The method of producing permanent magnets according to claim 3 wherein said annealing steps are performed in the range of 420–470° C.

5. A method as claimed in claim 1, wherein the composite body is subjected to heat treatment during elongation, the duration and temperature of the heat treatment and the stage at which the heat treatment is effected being predetermined in accordance with the properties required for the permanent magnet material.

6. A method as claimed in claim 1, wherein the ferromagnetic elements and the separating enclosing metal

of the casings contained in the composite body are selected so that they will have similar hardness and recrystallization properties throughout the process in order that they may be uniformly elongated.

7. A method as claimed in claim 1, wherein each ferromagnetic element is subjected to elongation prior to assembly in the composite body.

8. A method of producing permanent magnets comprising the steps of providing a plurality of rod-like elements selected from the group consisting of ductile ferromagnetic metals and ferromagnetic alloys of metal, enclosing each element in a casing of a different metallic material having substantially the same ductility, assembling a plurality of the encased ferromagnetic elements together to form a composite body, and compacting the assembly to uniformly elongate the composite body by repeated operations until substantially all of the ferromagnetic elements are single domain.

9. A method as claimed in claim 8, wherein the ferromagnetic elements have substantially equal and like configurations in cross-section and are substantially equispaced from each other in planes normal to the elongation direction.

10. A method as claimed in claim 8, wherein the composite body is subjected to heat treatment during elongation, the duration and temperature of the heat treatment and the stage at which the heat treatment is effected being predetermined in accordance with the properties required for the permanent magnet material.

11. A method as claimed in claim 8, wherein the ferromagnetic elements and the enclosing metallic material are selected so that they will have similar hardness and recrystallization properties throughout the properties throughout the process in order that they may be uniformly elongated.

12. A method as claimed in claim 8, wherein the ferromagnetic elements are in the form of wires.

13. A method as claimed in claim 8, wherein each ferromagnetic element is subjected to elongation prior to assembly in the composite body.

14. A method of producing permanent magnets comprising the steps of providing a plurality of rod-like elements of a ductile ferromagnetic metal, enclosing each element in a casing of a different metal having substantially the same ductility, assembling a plurality of the encased ferromagnetic elements together to form a primary composite body, and compacting the assembly to uniformly elongate the primary composite body, repeating the preceding steps to form a plurality of elongated primary composite bodies; enclosing a plurality of elongated primary composite bodies in a casing of a metal different from the metal of the ferromagnetic elements and having substantially the same ductility to form a secondary composite body, and compacting the secondary composite body to uniformly elongate the secondary composite body by repeated compacting operations until all of the ferromagnetic elements contained therein are single domain.

15. A method as claimed in claim 14, wherein each primary composite body is encased prior to elongation in at least one sleeve composed of a metal different to that of the ferromagnetic elements but having substantially the same ductility.

16. A method as claimed in claim 14, wherein the secondary composite body is heat treated after elongation to develop optimum magnetic properties.

17. A method of producing a permanent magnet comprising the steps of providing a plurality of iron wires each having a diameter no smaller than 10 microns, enclosing each wire in a casing of metal other than iron having substantially the same ductility, assembling a plurality of the encased iron wires together to form a composite body, and compacting the composite body by repeated compacting operations until the diameter of each iron wire is less than 1 micron.

18. A permanent magnet having a plurality of substantially parallel iron wires each encased in a metal other than iron and constructed in accordance with the method of claim 17.

19. A method as claimed in claim 17, wherein the iron wire enclosing metal is 5% tin bronze.

20. A method as claimed in claim 17, wherein the iron wires have substantially equal and like configurations in cross section and are substantially equispaced from each other in planes normal to the elongation direction.

21. A method as claimed in claim 17, wherein the composite body is subjected to heat treatment during elongation, the duration and temperature of the heat treatment and the stage at which the heat treatment is effected being predetermined in accordance with the properties required for the permanent magnet.

22. A method as claimed in claim 17, wherein the iron wire enclosing metal is selected so that it will have similar hardness and recrystallization properties as the iron wires throughout the process.

23. A method as claimed in claim 17, wherein each iron wire is subjected to compacting for elongation prior to its assembly in the composite body.

24. A method as claimed in claim 17, wherein the composite body after elongation is heat treated to develop optimum magnetic properties.

25. A method of producing a permanent magnet comprising the steps of providing a plurality of iron wires each having a diameter no smaller than 10 microns, enclosing each wire in a casing of a metal other than iron and having substantially the same ductility, assembling a plurality of the encased iron wires together to form a primary composite body, compacting the assembly to uniformly elongate the primary composite body; repeating the preceding steps to form a plurality of elongated primary composite bodies; enclosing a plurality of elongated primary composite bodies in a casing of a metal other than iron and having substantially the same ductility to form a secondary composite body, and compacting the assembly to uniformly elongate the secondary composite body by repeated compacting operations until the diameter of each iron wire contained therein is less than 1 micron.

26. A method of producing a permanent magnet comprising the steps of selecting a plurality of rod-like elements from the group consisting of ferromagnetic metals and ferromagnetic alloys of metals, enclosing each ferromagnetic element in a casing of at least one non-ferromagnetic material selected from the group consisting of non-ferromagnetic metals and non-ferromagnetic alloys of metals and having substantially the same ductility as said ferromagnetic elements, assembling a plurality of the encased ferromagnetic elements together to form a composite body and compacting the assembly to uniformly elongate the composite body until substantially all of the ferromagnetic elements are single domain.

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