

[54] **METHOD OF MANUFACTURING A BODY HAVING ANISOTROPIC PERMANENT MAGNETIC PROPERTIES BY GRINDING WITH FATTY LIQUID**

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[52] **U.S. Cl.**..... **148/103, 148/31.57, 148/100, 148/105**

[51] **Int. Cl.**..... **H01f 1/02**

[58] **Field of Search**..... 148/103, 113, 100, 148/101, 102, 105, 108, 31.57

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Assistant Examiner—W. R. Satterfield
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[57] **ABSTRACT**

A method of manufacturing a non-ageing sintered rare earth-cobalt magnet having an optimum coercive force and shape of the demagnetization curve, by sintering above a given critical temperature and by maintaining during the whole manufacturing process the oxygen content of the product below a particular critical value. This is realized in particular by starting from a powder which has been ground in the presence of a fatty liquid having the property of readily wetting metal surfaces, as a result of which the powder grains are enveloped by a layer protecting against oxidation.

3 Claims, 6 Drawing Figures

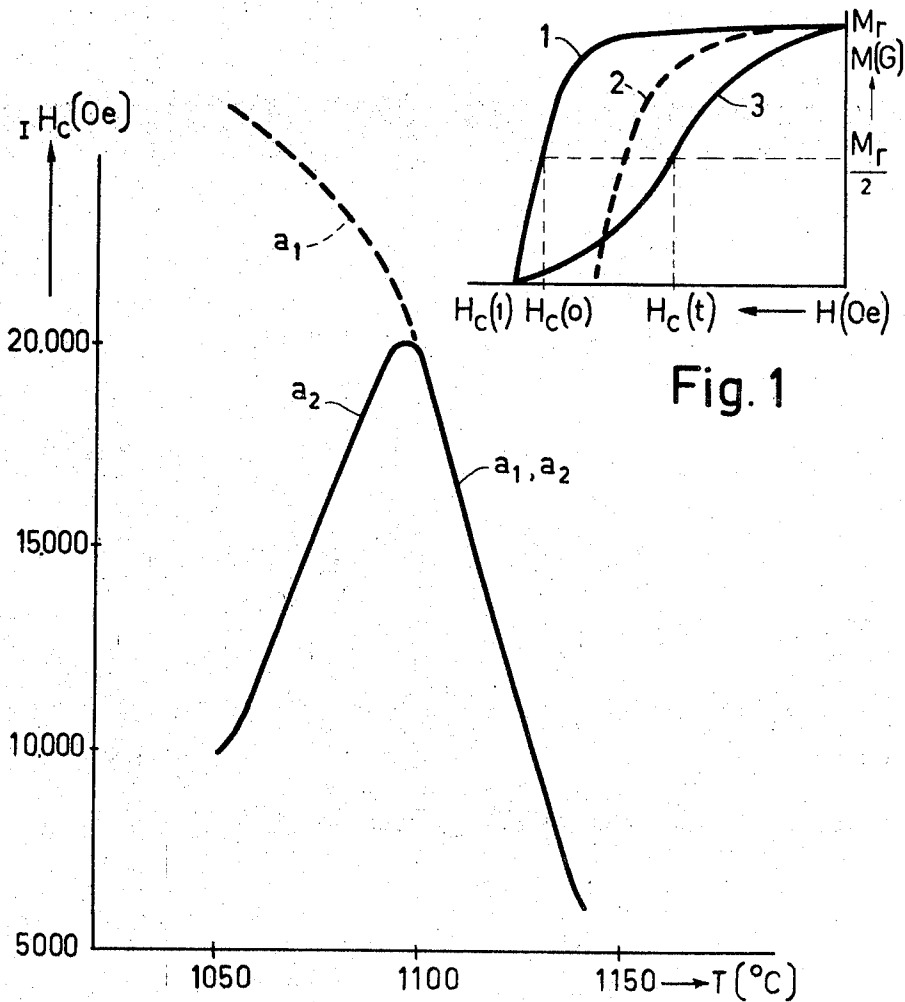


Fig. 2

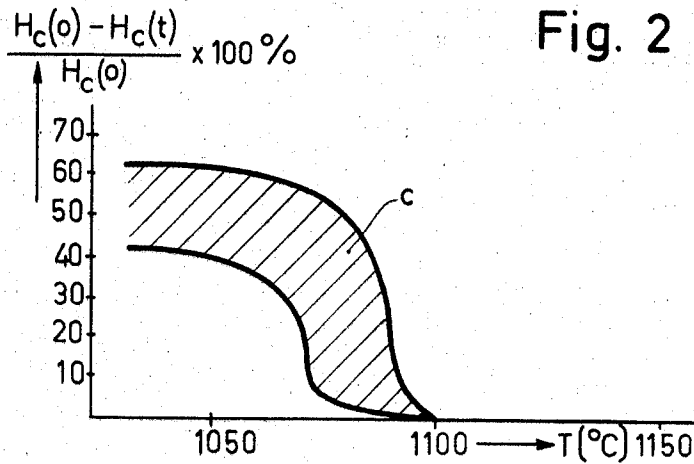
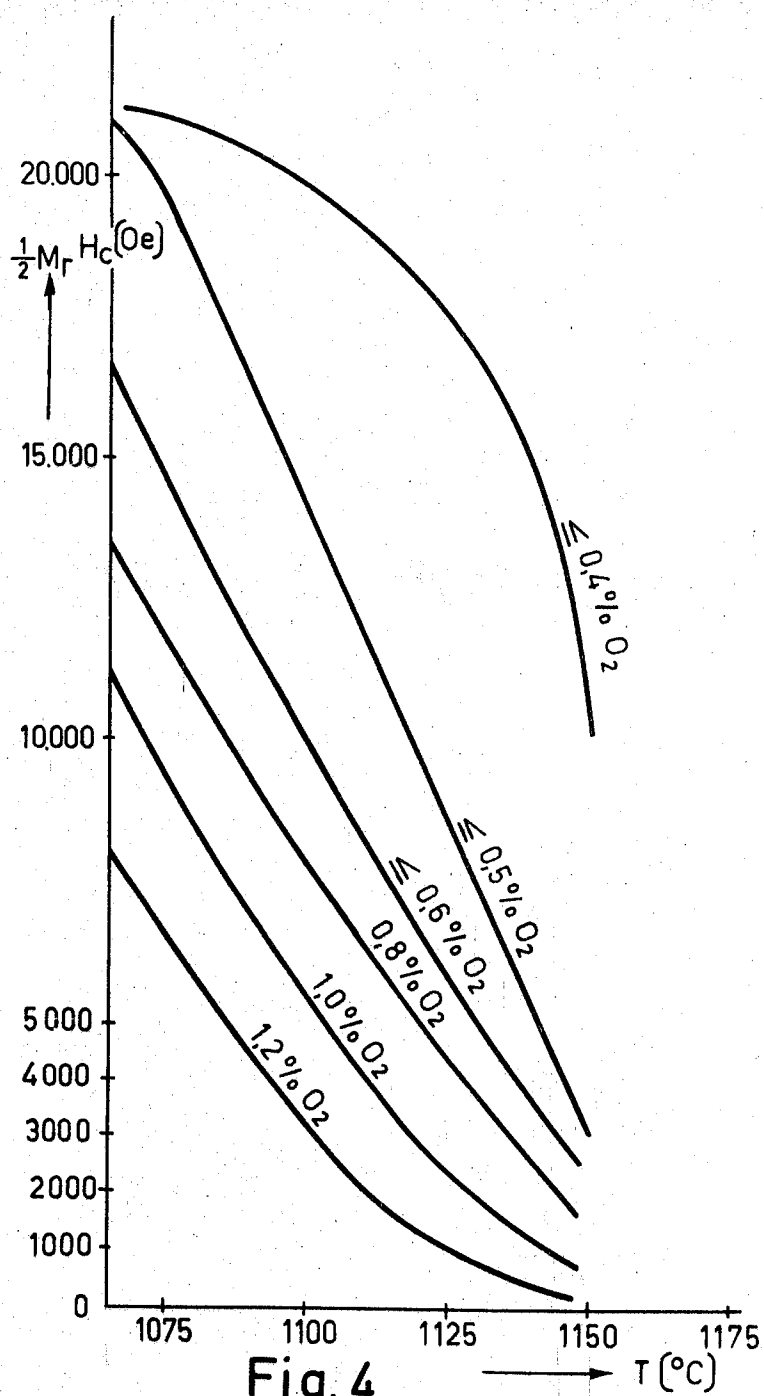


Fig. 3



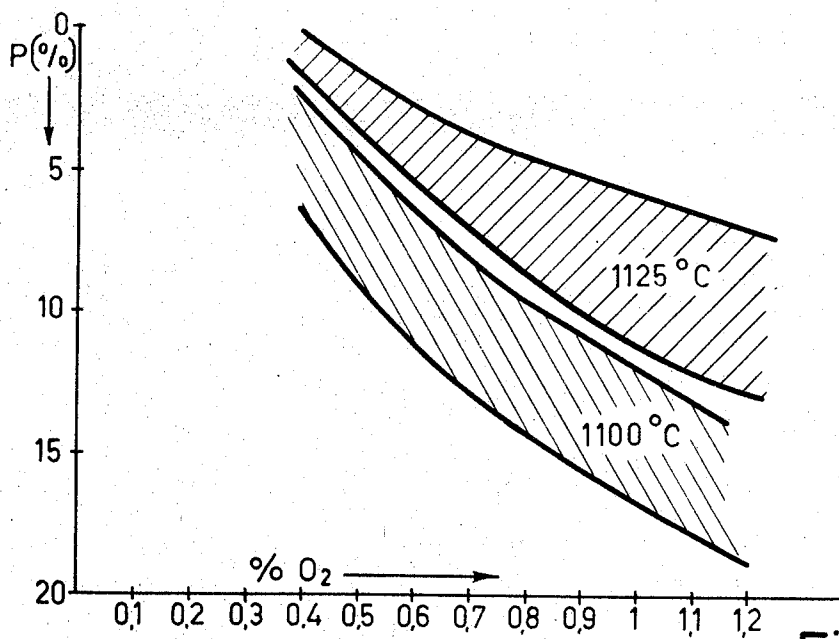


Fig. 5

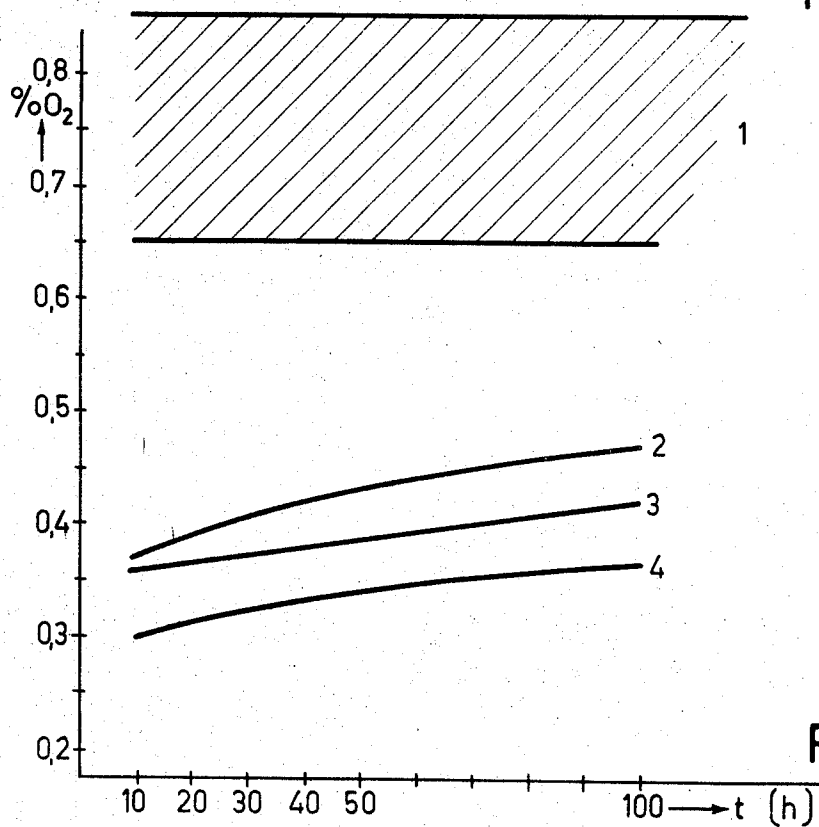


Fig. 6

METHOD OF MANUFACTURING A BODY HAVING ANISOTROPIC PERMANENT MAGNETIC PROPERTIES BY GRINDING WITH FATTY LIQUID

The invention relates to a method of manufacturing a body having anisotropic permanent magnetic properties of which the component essential for said properties is constituted by one or more compounds of M and R, with hexagonal crystal structure, in which M is Co or a combination of Co with one or more of the elements Fe, Ni and Cu, and in which R is one or more of the elements of the rare earths yttrium and thorium, of which compounds the existence range forms one assembly with the existence range of the compound M_5R in the system M-R, in which a crude body which consists of one or more of the said compounds of M and R is formed, pulverised, oriented in a magnetic field, compressed and sintered.

It is to be noted that, in addition to a main constituent which only contains compounds which form one assembly with the existence range of the compound M_5R , the final product may also comprise a constituent which consists of compounds which comprise a larger content of R than the compound M_5R itself, for example M_7R_2 . A method of the type described is known from the Dutch published Pat. application No. 6907;499. In addition it may be concluded from the publication by F. Westendorp in Solid State Communications, volume 8, pp. 139 - 141, 1970, that the sintering temperature must lie within a very particular temperature range to obtain high coercive forces, since it appears from said publication that the coercive force H_c of sintered material as a function of the sintering temperature strongly increases from a certain temperature - for $SmCo_5$ approximately 800°C -, reaches a maximum (for $SmCo_5$ at approximately 1,075°C) and then decreases again rapidly. It is therefore obvious to sinter at such a temperature that a product having a maximum H_c is obtained.

It is found, however, that a magnet manufactured in this manner generally has a great drawback: the coercive force and/or the shape of the demagnetization curve which is measured on the magnet, varies with time in that the coercive force of a part or of the whole of the permanent magnetic material from which said magnet body is constructed, decreases in course of time. This phenomenon, which is expressed in that demagnetization curves measured at 2 different instants on a magnet body do not overlap each other, is termed the "ageing" of the magnet body.

Experiments have proved that the extent to which ageing occurs depends upon the temperature at which sintering is carried out. It was also established that above a given high sintering temperature ageing does not occur at all. All this on the condition that sintering is carried out for a given minimum period of time. In order to obtain a non-ageing magnet body, sintering should therefore be carried out at a temperature which is higher than the critical sintering temperature of the chosen composition. The critical sintering temperature of a powder having a given composition is to be understood to mean herein the highest temperature of which it is found that the powder sintered at said temperature still shows ageing.

Since, as already explained, at higher sintering temperatures the maximum coercive force which, starting from a given M-R compound, can be achieved strongly

decreases from a certain sintering temperature, and since just at high sintering temperatures the desired non-ageing is reached, it does not seem possible at first sight to manufacture a magnet body which does not age and in addition has an optimum coercive force.

As will be explained hereinafter with reference to a figure, a decrease of the coercive force and/or a change of the shape of the demagnetisation curve (the "convexity") occurs upon ageing. A variation of one of the said quantities, or of both quantities, is reflected in the quantity $\frac{1}{2}M_r H_c$. $\frac{1}{2}M_r H_c$ is to be understood to mean the value of the field which has to be applied to reduce the retentivity M_r to half. As a measure of the combination of coercive force and "convexity" the value $\frac{1}{2}M_r H_c$ will be used hereinafter.

The method according to the invention is characterized in that, in order to obtain a non-ageing sintered magnet body having an optimum combination of coercive force and shape of the demagnetization curve, the sintering is carried out at a temperature which is higher than the critical sintering temperature of the chosen composition, while both during sintering and during the manufacturing steps preceding the sintering, measures are taken to prevent the oxygen content of the final product to exceed a critical value to be determined with reference to a graph showing the relationship between the coercive force and the sintering temperature at various oxygen contents.

As a matter of fact, it has surprisingly been found in experiments that the quantity $\frac{1}{2}M_r H_c$ is not only a function of the sintering temperature but also of the oxygen content of the final product and that this relation is such that the higher the sintering temperature, the smaller is the amount of oxygen admissible to obtain an optimum combination of coercive force and "convexity". This has two consequences. On the one hand, at a fixed sintering temperature required to manufacture a non-ageing magnet, a higher $\frac{1}{2}M_r H_c$ and in particular a higher coercive force can be reached than was initially assumed, provided the oxygen content is maintained sufficiently low. On the other hand, provided the oxygen content is maintained sufficiently low, sintering may be carried at a higher temperature than in the preceding case, while maintaining an acceptable value of combination of coercive force and "convexity". The temperature at which a powder of a given composition is to be sintered thus is not so critical as would be assumed, for example, on the basis of said article in Solid State Communications, if only a sufficiently low oxygen content is ensured.

It has also been found that the achievable density depends upon the oxygen content. The lower the oxygen content of the material to be sintered, the denser it can be sintered at one and the same temperature.

It is known from the published Dutch Pat. application No. 6,907,499 to carry out sintering in an inert gas atmosphere in the presence of an oxygen getter. In addition, measures are known, for example from literature, which prescribe during sintering the admixture of Ca or Sm-hydride to the powder to be sintered so as to bind any oxygen. An exact relationship between oxygen content and sintering temperature on the one hand, and density and coercive force and "convexity", respectively, on the other hand is not known so far, however.

It is usual to pre-compress the ground powder at a pressure below 1kB (for example 0.3 kB) and to com-

press it isostatically afterwards at a high pressure (15 to 20 kB) to a density of approximately 80 percent of the theoretical density. According to an embodiment of the method according to the invention, the compression should be carried out at a pressure of 0 - 15 kB, preferably between 5 and 10 kB. As a matter of fact, it has surprisingly been found that when the oxygen content remains below the above-indicated critical value, the density of the sintered final product always is above 90 percent of the theoretical density, independent of the value of isostatic pressure. This means notably that if the oxygen content is controlled, a considerable saving of apparatus to be used in the method can be obtained since, instead of a press which can supply a pressure of 15 to 20 kB, a press which can supply a pressure of, for example, 5 to 10 kB, will do.

Although the known measures to be taken notably during sintering may in incidental cases lead to good results, according to a further aspect of the invention, however, it is an essential condition for manufacturing good magnets that measures be taken already during the stages preceding sintering and in particular during grinding the powder to maintain the oxygen content below a critical value which depends upon the requirements to be imposed upon the final product.

It has up till now been usual in general to use in the preparation of M_5R powders grinding devices in which grinding is carried out in volatile organic liquids (that is to say liquids having a boiling point below 120°C), such, for example, as hexane, CCl_4 , benzene, acetone or toluene. Dried toluene is often used in particular. In this connection it is to be noted that the so-called "wet" grinding in grinding liquids in general gives powders having better and better reproducible directivities than the so-called "dry" grinding in gases such as argon and hydrogen.

According to a further embodiment of the method according to the invention, however, the grinding to a fine powder should be carried out in the presence of a liquid which readily wets metal surfaces.

According to still a further embodiment of the method according to the invention, it is advantageous if an organic liquid having a boiling point below 120°C is used as a grinding liquid and which comprises a component having the property of preferentially wetting metal surfaces.

It has been found that by using grinding liquids as above mentioned, an effective protection of the powder particles against oxidation is obtained during and after grinding since a skin is formed around the particles.

A preferred embodiment of the method according to the invention is characterized in that the liquid having the property of readily or preferentially, respectively, wetting metal surfaces is a fatty substance, such as a mineral, vegetable or animal oil. Fatty substances are to be understood to mean herein fats, oils and waxes, that is to say: non-volatile, non-water-soluble, organic substances. The application hereof during grinding turned out in general to result in sintered magnet bodies having a low oxygen content.

Such an application is the more surprising because in itself it seems to involve a contradiction that in a grinding process use is made of a liquid of which it may be expected to have a more or less lubricating effect. It has consequently proved that the use of a liquid which readily or preferentially, respectively, wets grain sur-

faces according to the invention requires a longer grinding time than the use of the conventional grinding liquids.

The methods according to the invention is characterized in particular in that M is Co and R is Sm, and the oxygen content is maintained below 0.5 percent and in particular below 0.45 percent.

The invention also relates to a sintered magnet body manufactured by means of any of the above methods.

The invention will now be described with reference to the accompanying drawing, in which:

FIG. 1 is a graph in which the magnetisation M is plotted against the externally applied demagnetizing field H for different magnet bodies

FIG. 2 is a graph showing the relationship between sintering temperature and coercive force

FIG. 3 is a graph showing the relative ageing as a function of the sintering temperature

FIG. 4 is a graph showing the relationship between $\frac{1}{2}M_r/H_c$ and the sintering temperature at various oxygen contents

FIG. 5 is a graph showing the relationship between pore volume and oxygen content of final products sintered at different temperatures and

FIG. 6 is a graph showing the variation against time of the oxygen content of powders ground in different grinding liquids.

The invention is illustrated by means of investigations performed on Sm-Co magnets but the present invention is based on the fact that a critical sintering temperature and a critical oxygen content can be found in general for any M-R compound.

A number of Sm-Co powder samples, for example, with an atomic ratio Sm : Co equal to 4.4, obtained by pulverizing in a vibratory mill moldings under varying conditions influencing the oxygen contents to a size of from 2 to 20 μ , were compressed after precompression at a pressure of 0.3 kB, under an isostatic pressure of 15 kB, the orientation taking place in a magnetic field of approximately 8,000 Oe. The samples were then sintered for 30 minutes at several temperatures, varying from 1,050° to 1,150°C. It is to be noted that sintering may be carried out under varying conditions. It may be carried out in a space which is maintained at a given vacuum (for example between 10^{-3} and 10^{-5} Torr) by means of a pump. Another possibility is to sinter in an inert gas atmosphere, either by leading a constant gas flow over the sample, or by placing the sample in a closed space which is evacuated prior to sintering and then filled with an inert gas, for example, argon. The demagnetisation curves were subsequently measured on the bodies obtained in the above-described manner. Each of the said bodies was then maintained at a temperature of 150°C in air for 1,000 hours, after which the demagnetisation curves were determined again. The temperature of 150°C was necessary for the accelerated demonstration of any ageing phenomena.

This ageing of the magnet body is expressed in the demagnetisation curve which can be measured in the magnetized magnet body. FIG. 1 of the drawing shows such a curve. The magnetization M is plotted on the vertical and the external magnetic field H on the horizontal. The curve 1 is a demagnetisation curve characteristic of a permanent magnetisable body. In a field H_c - the coercive force - the direction of which is opposite to the direction of magnetisation in the body, the mag-

netisation M is equal to zero. The demagnetisation curve 2 is characteristic of a magnet body having a coercive force (H_{c2}), lower than the (H_{c1}) associated with curve 1. When both curves have been measured in the same manner on the same magnet body, but the second a time t after the first, we call (H_{c1}) - (H_{c2}) the ageing during the time t .

However, when not all the permanently magnetisable material of which the body is composed ages, - for example because the body is constructed from several compounds - (either differing in M and/or R , or differing in stoichiometry) of which one does show and the other does not show a deterioration in H_c - a demagnetisation curve of the type 3 can be measured in a magnet body after ageing during a time t . Such a curve shows a smaller "convexity", while nevertheless the coercive force (H_c) remains the same. In such a case also it is called ageing of the magnet. Besides it is possible that both the coercive force and the "convexity" decrease upon ageing.

In the graph shown in FIG. 2 are plotted the coercive forces both prior to a thermal treatment at 150°C (curve a_1) and after that (curve a_2) measured on Sm-Co magnet bodies sintered at different temperatures and all showing a substantially equal oxygen content. The sintering time was always 30 minutes.

It may be seen from this graph that at sintering temperatures below $1,100^\circ\text{C}$ the curves a_1 and a_2 do not coincide. Magnets sintered at said temperatures thus still show ageing. At sintering temperatures above $1,100^\circ\text{C}$ the curves a_1 and a_2 coincide: magnets sintered at said temperatures thus do not show any ageing.

In the graph of FIG. 3 is plotted the relative ageing

$$[H_c(o) - H_c(t)]/[H_c(o)] \times 100 \text{ percent}$$

as a function of the sintering temperature T . In this case H_c is the external field which is to be applied to save a magnetisation $\frac{1}{2}M_r$, and $H_c(o)$ is H_c measured prior to and $H_c(t)$ is H_c measured after a thermal treatment of the magnet body at 150°C in air for a time t . The spreading of the measured results is represented by not showing the said relationship as a single line but as a shaded - area. From this graph also a critical sintering temperature (that is to say a temperature above which sintering is to be carried out so that no ageing occurs) of $1,100^\circ\text{C}$ may be derived.

In the graph of FIG. 4, $\frac{1}{2}M_r H_c$ is plotted as a function of the sintering temperature at different oxygen contents. In this connection it is to be noted that in order to be able to represent the influence of the oxygen content on the magnetic properties as fully as possible, also values are recorded in the graph which are measured in magnets sintered at such temperatures that they may show ageing phenomena. In order to be able to compare the various values all measurements have been performed immediately after sintering before ageing has occurred in magnets sintered at too low temperatures.

It is to be noted that in order to be able to also include the "convexity" of the demagnetisation curves in the equation, the values $\frac{1}{2}M_r H_c$ in FIG. 4 have been plotted as a function of the sintering temperature instead of the H_c as in FIG. 2.

It appears from the graph that in order to obtain a good combination of coercive force and "convexity" (represented by $\frac{1}{2}M_r H_c$), a certain oxygen content is

admissible which depends upon the requirements to be imposed. For example, if a magnet is to be manufactured with a $\frac{1}{2}M_r H_c$ of 10,000 Oe by sintering at $1,120^\circ\text{C}$, the oxygen content may not be higher than 0.5 percent (the critical value). This enables the manufacture of sintered M-R magnets according to conventional manufacturing methods. Without proceeding in conditioned circumstances (for example working in a special space with an oxygen- and water vapour-free atmosphere protecting against oxidation) good magnets can be manufactured nevertheless.

A comparison of the oxygen contents and pore volumes of several final products turned out to give the surprising result that not only material sintered at a higher temperature shows a greater density, as was to be expected, but that in addition the density to be reached depends upon the oxygen content. The lower the oxygen content, the more densely the material can be sintered with the temperature remaining the same. This result is shown in FIG. 5 in which the pore volume is plotted as a function of the oxygen content. The spreading in the measured results is shown by showing the said relationship not as a single line but as a shaded area.

The manufacture of magnet bodies having different oxygen contents was carried out in the scope of the present invention as follows. Sm-Co mouldings were pulverised in a vibratory mill while using different grinding liquids influencing the oxygen content of the power. In order to demonstrate the effect of the various grinding liquids, the resulting powders were exposed to air for 100 hours and the oxygen content was measured at regular intervals. The measured results are plotted in FIG. 6. Grinding in toluene technical quality turned out to produce a high oxygen level (1) with an upper limit of 0.8 to 0.9 and a lower limit of 0.6 to 0.7. Grinding in toluene pro analysis gave a considerably better result (2) as well as grinding in a mixture of toluene technical quality + 10 percent by volume of mineral oil or oleic acid (3). A minimum oxygen level was reached by grinding in exclusively mineral oil, for example the oils available in trade as "Tellus 33" and "Tellus 15" (4). Since the oil remains on the powder particle and does not evaporate away, a good protection was obtained also after grinding. The -excessive - oil may be removed (washed away) in a later stage of the manufacturing process. When not all the oil is removed, the final product may contain Sm-carbide. However, this has no influence on the magnetic properties.

The effect of the control of the oxygen content on the density of the final product is shown in the following table:

Pressure (kB)	Density relative to the theoretical	Sintering temp. ($^\circ\text{C}$)	Sintering time (minutes)	Sintered density	O ₂ (%)
20	85	1100	15	89	0.8
15	83	1100	15	86.3	1
15	84	1100	15	98	0.39
10	76	1085	15	96.5	0.41
10	75	1100	15	96	0.43
4	62	1085	20	98	0.40
4	63	1085	15	97	0.42
0	50	1095	10	97	0.34
0	50	1085	15	64	1.5

All the samples were pre-compressed at a pressure of 0.3 kB. The pressure during the isostatic compression

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varied from 0 to 20 kB (column 1). The densities after the isostatic compression are recorded in column 2, the sintering temperatures in column 3 (these are temperatures measured in a place as close as possible to the sample to be sintered. The actual sintering temperatures may deviate from these temperatures by $\pm 10^{\circ}\text{C}$), and the sintering times in column 4. The density (column 5) and the oxygen content (column 6) were measured in the sintered final products. It is obvious that, even at a pressure of 15 to 20 kB, the density of the final product is insufficient when the oxygen content is not sufficiently controlled. On the other hand it is found that, even without isostatic compression (0 kB), a sufficiently dense final product can be obtained if the oxygen content is controlled. It is to be noted that sintering was carried out in a closed evacuated space which was filled, prior to sintering, with an inert gas (argon) to a pressure of maximum 0.08 atm.

What is claimed is:

1. In the method of manufacturing a body having anisotropic permanent magnetic properties of which the component essential for said properties is a compound

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of M and R, with a hexagonal crystal structure, in which M is Co or a combination of Co with one or more of the elements Fe, Ni and Cu and in which R is one or more of the elements of the rare earths including yttrium and thorium, of which compounds the existence range forms one assembly with the existence range of the compound M_2R in the system M-R, in which a crude body consisting of one or more of the said compounds of M and R is formed, pulverised, oriented in a magnetic field, compressed and sintered, the improvement comprising pulverizing said crude body in the presence of a non-volatile, water insoluble fatty substance capable of preferentially wetting metal surfaces and thereby effectively preventing oxidation of the metal, after which the so-obtained powder is compressed and sintered at a temperature which is higher than $1,100^{\circ}\text{C}$ to produce a magnet having an oxygen content not exceeding 0.5 percent.

2. A method as claimed in claim 1, wherein the fatty substance has a boiling point below 120°C .

3. A method as claimed in claim 2, wherein the fatty substance is a mineral, vegetable or animal oil.

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UNITED STATES PATENT OFFICE
CERTIFICATE OF CORRECTION

Patent No. 3,785,881 Dated January 15, 1974

Inventor(s) PIETER A. NAASTEPAD ET AL

It is certified that error appears in the above-identified patent and that said Letters Patent are hereby corrected as shown below:

Column 1, line 35, "SMCo₅" should read --SmCo₅--;

Column 2, line 11, after " $\frac{1}{2}M_rH_c$ " 1st occurrence, insert
a period --.--;

Signed and sealed this 10th day of December 1974.

(SEAL)
Attest:

McCOY M. GIBSON JR.
Attesting Officer

C. MARSHALL DANN
Commissioner of Patents