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(54) Sintering of permanent-magnet bodies of rare-earth alloys

(57) A permanent-magnet body is formed by sintering together grains of an alloy comprising at least one 3d transition element and at least one element selected from the rare-earth metal group (inclusive of yttrium). The size of the alloy grains (e.g. less than 0.3μm) and the sintering temperature are in a range which provides a desired coercivity Hcj. In accordance with the present invention before sintering, there is mixed together with the alloy grains a grain-growth inhibitor (e.g. granular alumina of less than 0.1μm) which is of a sufficiently small size and is sufficiently chemically inert in relation to the alloy at the sintering temperature as to form a physical barrier inhibiting inter-grain growth at the grain boundaries of the alloy during sintering. This enables the desired coercivity to be obtained over a wider temperature range for the sintering process. This is particularly useful for single-phase alloys of the RCO_5 type (where R is at least one element selected from the group Sm, Y, Ce, Pr and Nd). Thus, for $SmCo_5$, the sintering may be effected at a temperature in the range of 1125°C to 1150°C to provide a coercivity Hcj in excess of 1600 kA.m^{-1}.

At least one drawing originally filed was informal and the print reproduced here is taken from a later filed formal copy.

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Fig.1.

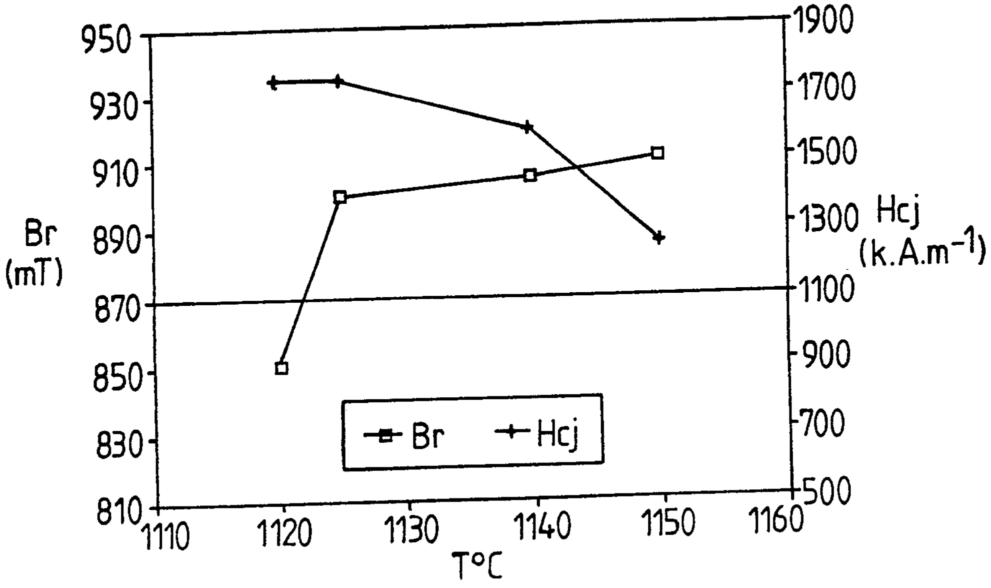


Fig.2.

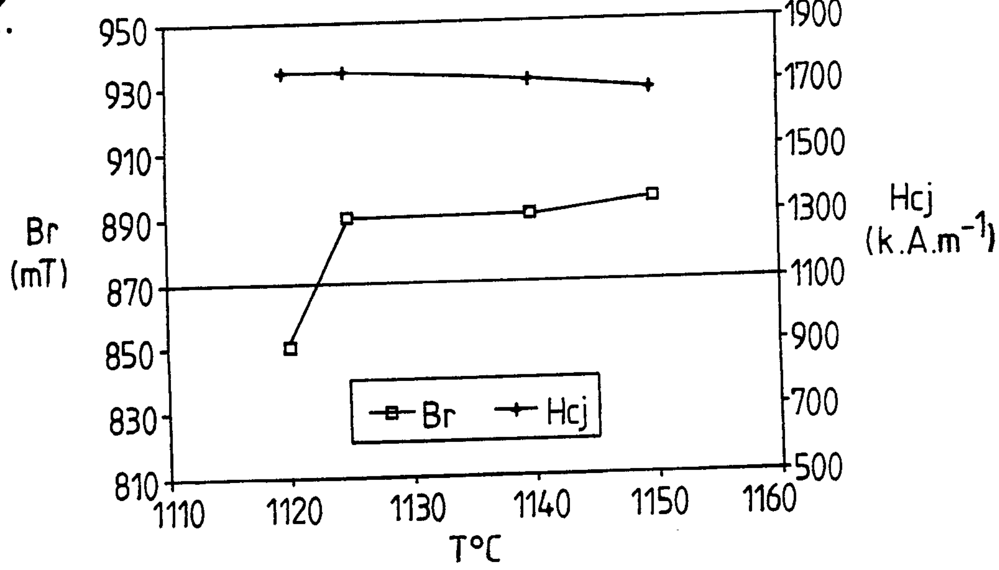
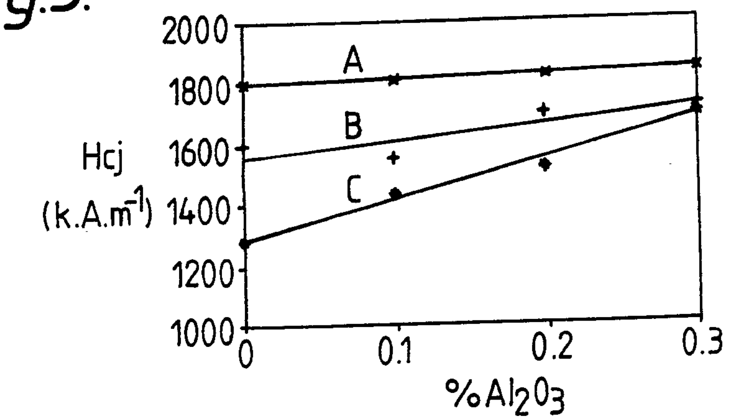


Fig.3.



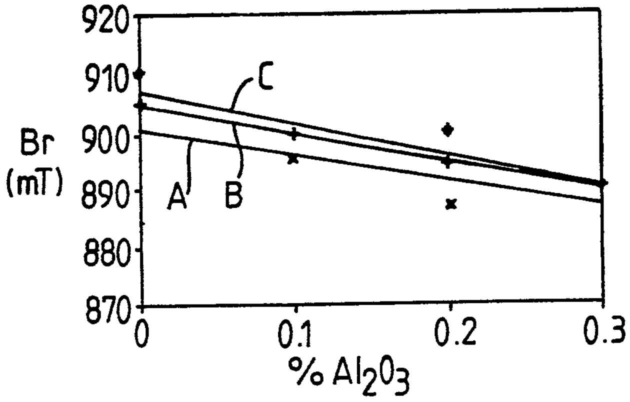


Fig.4.

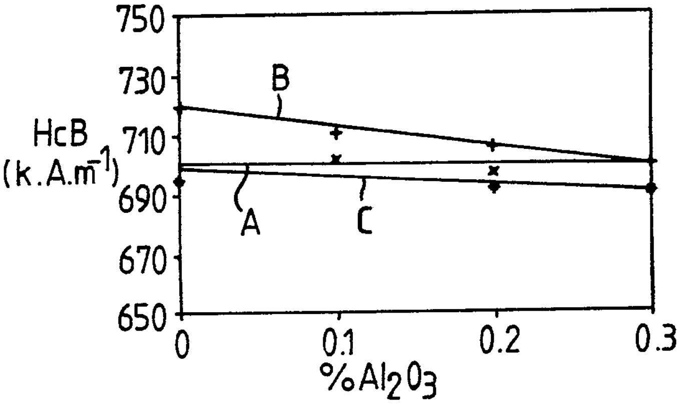


Fig.5.

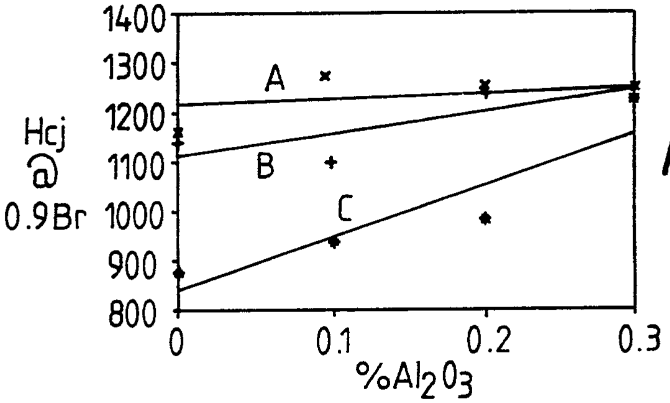


Fig.6.

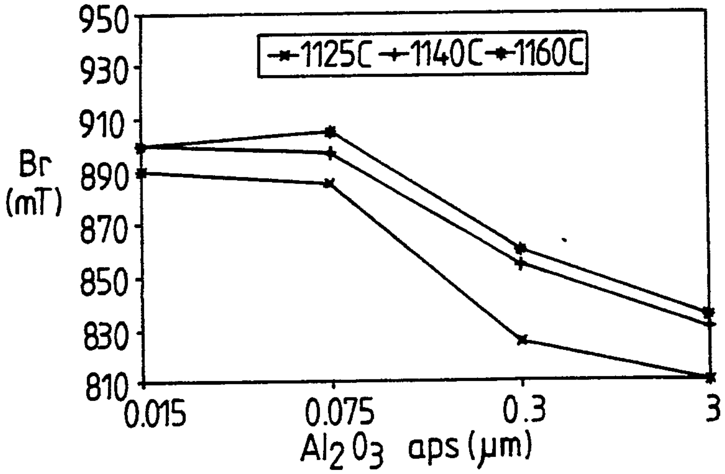


Fig.7.

DESCRIPTION

SINTERING OF PERMANENT-MAGNET BODIES OF RARE-EARTH ALLOYS

This invention relates to methods of forming a permanent-magnet body by sintering together grains of a rare-earth alloy, particularly but not exclusively $SmCo_5$, or for example the Nd-Fe-X alloy type. The invention further relates to sintered bodies formed by such methods.

Magnetic materials based on intermetallic compounds of certain rare-earth metals with transition metals may be formed into permanent magnets having coercive fields of considerable magnitude, for example in excess of 1000 $kA.m^{-1}$ and even 1600$kA.m^{-1}$. It is known to form a permanent-magnet body by sintering together grains of an alloy comprising at least one 3d transition element and at least one element selected from the rare-earth metal group (inclusive of yttrium). The most commonly used examples of such alloys are $SmCo_5$ and Nd-Fe-B types (for example $Nd_2Fe_{14}B$). $SmCo_5$ is essentially a single-phase alloy, although in practice even $SmCo_5$ magnets, like all commercially available sintered permanent magnets, have complex multiphase microstructures. The expression "single-phase" is used to denote such magnets in which within the grains of the sintered body there is for the most part an absence of precipitate phases which would inhibit movement of magnetic domain walls. Thus, in the case of sintered single-phase materials, domain walls may move easily within the grains, but the grain boundaries impede the motion of the domains from grain to grain. High coercivities are obtained by reducing the size of the sintered grains until each grain may be considered as corresponding to a single magnetic domain and by producing a microstructure having grain boundaries with strong pinning properties and a low density of defects; defects (such as Sm_2Co_{17} precipitates in $SmCo_5$, and oxide inclusions) may provide nucleation sites for reverse domains, so reducing the coercivity. A general overview of "The physical metallurgy and processing of sintered rare earth permanent magnets" is given in the paper of this title by Dr. J. Ormerod in Journal of the Less Common Metals, vol 111 (1985) pages 49 to 69, published by Elsevier Sequoia S.A., Lausanne, the whole contents of which are hereby incorporated herein as reference material.

Thus, in the formation of sintered permanent-magnet bodies of the rare-earth alloy type, it is common practice to choose both the sintering temperature and the grain size of the pre-sintered alloy grains to be in a range which provides a desired coercivity. With too large a grain size, for example more than 40μm (or even exceeding 10μm, the sintered grains are not single magnetic domains and include magnetic walls between domains which may permit comparatively easy inversion of magnetisation; however if the alloy grains produced by milling are very small the magnetic properties may degrade due to oxidation. With too high a sintering temperature the individual grains may grow together during the sintering step to form multiple-domain grains which lower the coercivity, whereas if the sintering temperature is too low insufficient sintering and a low density for the sintered body can result. The sintering temperature range for Nd-Fe-B type alloys is quite wide (for example a range of about 40°C from 1020°C to 1060°C) before coercivity is affected due to rapid grain growth. By contrast, the corresponding sintering temperature for $SmCo_5$ is higher, for example about 1130°C, and the temperature range for high coercivity is narrow, typically about 10°C.

According to the present invention, there is provided a method of forming a permanent-magnet body by sintering together grains of an alloy comprising at least one 3d transition element and at least one element selected from the rare-earth metal group (inclusive of yttrium), the size of the alloy grains and the sintering temperature being in a range which provides a desired coercivity for the permanent-magnet body, which method is characterised in that before sintering there is mixed together with the alloy grains a grain-growth inhibitor which is of a sufficiently smaller size than the size of the alloy grains and is sufficiently chemically inert in relation to the alloy at the sintering temperature as to form a physical barrier inhibiting inter-grain growth at the grain boundaries of the alloy during sintering, thereby enabling the desired coercivity to be obtained over a wider temperature range for the sintering process.

The present invention is based on a recognition by the inventor that, by mixing a grain-growth inhibitor of a sufficiently small size with the alloy grains before sintering, the rate of inter-grain growth can be reduced sufficiently to widen the temperature range over which the grains can be sintered while still achieving a high desired coercivity for given grain sizes of the alloy over that wider sintering temperature range.

Thus, for example, in order to achieve a high coercivity, the alloy grains may have an average grain size in the range of 1 to 40μm (and preferably less than 10μm). The grain-growth inhibitor may be in granular form having an average grain size of less than one tenth of the average grain size of the alloy grains; thus, it may be for example less than 0.3μm (even preferably less than 0.1μm).

So as not to degrade the magnetic properties of the sintered body, the total amount of the inhibitor which is mixed together with the alloy grains before sintering is preferably less than 0.5% by weight. A sufficient intergrain barrier is obtained (at least in the case of $SmCo_5$) with, for example, about 0.3% by weight of sufficiently small inhibitor grains.

It may be noted that it is known from, for example, published European patent application EP-A-0 101 552 that, in forming sintered magnet bodies with R-Fe-B alloys (where R is a rare earth such as Nd), further elements such as Ti,Ni,Bi,V,Nb,Ta,Cr,Mo,W, Mn,Al,Sb,Ge,Sn,Zr and Hf may be added to the alloy components. The addition of these elements contributes an increase in the coercivity of the magnet. However, no effect on the desired range of sintering temperature is disclosed. Furthermore in this known process, the additional elements are added as pure elements at the melt stage and form an alloy Fe-B-R-M with the other components (where M is one or more of these additional elements). This alloy is then cast and ground to form homogeneous grains for the sintering, and so these additional elements do not form any separate bodies of any size and cannot be distinguished from the alloy grains of the sintered body; they form a constituent of the alloy. The whole contents of EP-A-0 101 552 are hereby incorporated herein as reference material.

By way of contrast, the inhibitor which is added in accordance with the present invention is separate from but physically mixed together with the preformed alloy grains, is of a significantly smaller size than these alloy grains so that sintering is not prevented and is sufficiently chemically inert in relation to the alloy at the sintering temperature as not to become a part of the magnetic alloy but to form a physical barrier which reduces the intergrain growth rate of the alloy with temperature. Indeed, in observation of the sintered grain boundaries under a microscope, the physical presence of the inhibitor has been seen as very small barrier particles between the boundaries of neighbouring alloy grains. Furthermore, a grain-growth inhibitor in accordance with the invention may be added not only in the sintering of R-Fe-B type magnets, but more importantly also in R-Co type magnets such as $SmCo_5$ for which the acceptable range of sintering temperature is narrow in the absence of this inhibitor.

A variety of different chemically inert materials may be used as the grain-growth inhibitor in accordance with the invention. Oxides of Cr and of Al are very stable both chemically and physically and so are particularly suitable. Of these, alumina is a particularly convenient choice because it is readily commercially available and inexpensive.

These and other features in accordance with the present invention will now be illustrated with reference to a few examples in respect of $SmCo_5$ magnet bodies for which advantages of invention are particularly useful in the production of currently desired commercial magnets, and in respect of which the accompanying graphs depict experimental results as follows:-

Figure 1 is a graph showing the effect of sinter temperature T (in ^{o}C) on the magnetic properties of a $SmCo_5$ magnet in terms of its remanence Br (in mT) and its polarization coercivity Hcj (in kA/m) for a comparative example not in accordance with the invention;

Figure 2 is a similar graph of T and both Br and Hcj for an example having 0.3% of alumina in accordance with the invention;

Figures 3 to 6 are graphs showing the effect of varying percentages of alumina (% Al_2O_3) on the magnetic properties of a $SmCo_5$ magnet in terms of its polarization coercivity Hcj (Figure 3), remanence Br (Figure 4), coercivity HcB (Figure 5) and coercivity at 0.9Br (Figure 6), and

Figure 7 is a graph of the variation of remanence Br (in mT) with average particle size (aps) of the alumina (in μm), at three different sinter temperatures.

The same basic known process steps were used to form sintered $SmCo_5$ permanent magnets both for the comparative example of Figure 1 and for the examples in accordance with the invention to which Figures 2 to 6 relate. The resulting sintered body of $SmCo_5$ is one example (for which there is a very high commercial demand) of a substantially single-phase alloy comprising a 3d transition element (Co) and a rare-earth element (Sm). These basic known process steps are such as are normally used in the commercial production of rare-earth magnets (for example as described in the Ormerod 1985 J. Less Common Metals paper) and comprise:

(a) <u>alloy preparation</u>:

This involves mixing the constituent elements for the $SmCo_5$ alloy in the required proportions of, melting to form the alloy and then casting. For the examples leading to the Figures 1 to 6 results a commercially available $SmCo_5$ alloy from the company Th. Goldschmidt AG of Essen (DE) was used. It is customary to blend with the $SmCo_5$ a Sm-rich composition as a sinter aid, in order to reduce oxidation effects on the $SmCo_5$ composition. For the examples leading to the Figures 1 to 6 results a sinter aid available from Th. Goldschmidt was used, comprising about 40% by weight of Sm and 60% by weight of Co.

(b) <u>milling and composition adjustment</u>:

This may include a pre-milling step of crushing the cast alloy after which it is milled (for example by vibration ball milling or jet milling or attritor milling) under an inert atmosphere to granulate the alloy into appropriately sized grains for sintering. Being a single-phase magnet material, the grain size and surface condition play a critical role in determining the coercivity of the magnet. The average grain size is chosen to be less than a value at which multiple magnetic domains can be accommodated in each grain. Thus, the $SmCo_5$ material is milled to an average grain size of less than about 10μm. Overmilling, however, produces excess oxygen pick-up and causes excessive damage to the grain surface, so that the minimum average grain size to which the $SmCo_5$ material is milled normally exceeds 0.5μm and preferably 1 or 2μm. In the examples for which the Figures 1 to 6 results were taken, the average grain size to which the $SmCo_5$ was milled was 3μm. Attritor mill was used, and the size distribution was between about 2μm and 9 or 10μm. The Sm-rich sinter aid was milled together with the $SmCo_5$ material in a ratio of 1:4 (i.e. 4 times as much $SmCo_5$ as sinter aid) so that a homogeneously mixed basic powder of the same grain size for both the $SmCo_5$ and sinter-aid particles is obtained. Some sinter aid was also milled separately to the same grain size, for addition as extra sinter aid in the Figures 2 to 6 examples in accordance with the invention.

(c) <u>grain alignment and pressing</u>:

This involves magnetically aligning the grains of the powder such that the easy axes of magnetisation of the grains become parallel, and then pressing the aligned grains to a desired shape and density in the aligning field. In the examples for Figures 1 to 6, the grains were aligned in a field of about 1T and compacted to a density of about 4 $g.cm^{-3}$ under a pressure of about 1 $ton.cm^{-2}$ (about 10^8 Pa) parallel to the aligning field.

(d) <u>sintering and heat treatment</u>:

The sintering is carried out in an inert or reducing atmosphere. In the examples of Figures 1 to 6, a partial pressure of argon in a vacuum furnace was used. The sintering temperature

T and granular composition were as specified in the individual examples. After sintering, the bodies were annealed at a lower temperature (about 800°C). The density was about 8 g.cm^{-3}, depending on the sinter temperature.

(e) magnetising

Before magnetising to their full remanence value, sintered magnet bodies in commercial production may be machined to a final shape. This machining was not carried out on the sintered bodies in the examples of Figures 1 to 6. However, all the bodies in these examples were magnetised in a pulsed field of 3T.

FIGURE 1 COMPARATIVE EXAMPLE

The sinter grain composition in this case consisted of the 4:1 $SmCo_5$/sinter-aid basic powder without any addition of extra sinter. As can be seen from Figure 1, for the comparative example not in accordance with the invention, the high coercivity Hcj of the $SmCo_5$ magnet sintered at 1120°C decreases with increasing sinter temperature T from about 1125°C (and especially above 1140°C) whereas the remanence Br increases rapidly from about 1120°C to 1125° and less rapidly at higher temperatures. An optimum balance between the coercivity and the remanence can only be achieved over a narrow range of temperature, from about 1125°C to about 1135°C in the Figure 1 example. Above this range, the coercivity is degraded to below 1700 kA.m^{-1} due to rapid grain growth.

FIGURE 2 EXAMPLE

Figure 2 illustrates results obtained in accordance with the present invention in which after the milling step (b) and before steps (c) and (d) there is blended together with the 4:1 basic powder a grain-growth inhibitor in the form of alumina together with an extra addition of sinter aid to counteract oxidation effects on the $SmCo_5$ alloy due to the inclusion of the alumina. The alumina was in the form of a very fine powder whose grains are much smaller in size than the alloy grains. The alumina is sufficiently chemically inert in relation to the $SmCo_5$ alloy at the sintering temperature that the very small alumina grains form a physical barrier restricting intergrain growth at the grain boundaries of the $SmCo_5$ alloy during sintering. This enables the desired coercivity to be obtained over a wider temperature range for the sintering process, for example from about 1125°C to above 1150°C for Hcj in excess of $1600kA.m^{-1}$. In the example of Figure 2, 0.3% by weight of alumina with an average grain size of 0.075μm was added to the powder to be sintered. In order to obtain good mixing, the alumina powder was first thoroughly mixed with the extra sinter-aid power which was to be added, and then this mixture was thoroughly mixed with the 4:1 basic powder. The amount of extra sinter aid in the final powder composition to be sintered was about 10%.

The stabilisation of coercivity at higher sinter temperatures is attributed to the inhibition of grain growth brought about by the fine dispersion of alumina effectively physically pinning the grain boundaries. This is demonstrated by optical measurements of grain size both before and after sintering.

FIGURES 3 TO 6 EXAMPLES

The effect of alumina additions on the magnetic properties was recorded as a series of demagnetisation curves. The results of Figures 3 to 6 were obtained with the 4:1 basic powder into which upto 0.5% alumina was thoroughly mixed in 0.1% increments, together with extra sinter aid. The alumina had an average grain size of 0.075μm. A range of extra sinter aid of upto 15% was added in proportion to the percentage of alumina. Each composition was pressed into discs of 25mm diameter and 5mm thickness each. The discs were sintered under a partial pressure of argon at 1125°C, 1140°C and 1150°C in a vacuum furnace.

Demagnetisation curves were drawn for each of the test discs, and show a gradual tightening of the distribution of coercivity with increased sinter temperature. Data taken from these hysterisis curves was used to produce the summary graphs of Figures 3 to 6 showing how the magnetic properties were affected by the amount of alumina added. The Figure 6 coercivity at 0.9 Br is an indication of the shape of the hysterisis curve between Br and

Hcj. Curves A are for a sinter temperature of 1125°C, whereas curves B and C are respectively for sinter temperatures of 1140°C and 1150°C.

FURTHER EXAMPLES

Having obtained the composition for optimum magnetic properties, the experiment was repeated using different grades of alumina, with average grain sizes of 0.015μm to 0.3μm. Demagnetisation curves for the varying grades of alumina showed that the finest grades (0.075μm and less) were the most effective at stabilising coercivity and had least effect in reducing remanence (Br), see Figure 7. The 0.075μm aluminium is easier to mix with the larger alloy grains than is the 0.015μm powder, and so for this reason the 0.075μm grade is preferred.

A number of the discs formed in accordance with the invention were viewed under the optical microscope and grain size observations were made. The distribution of grain size was found to remain uniform over the range of sinter temperatures investigated for those examples to which additions of alumina had been made.

Thus, the addition of alumina has been seen to stabilise the coercivity with respect to sinter temperature. Additions of extra sinter aid are necessary to offset the increased oxygen content causing a slight loss in remanence, typically 20 mT. The best combination for $SmCo_5$ magnets appears to result with 0.3% alumina (average grain size of 0.075μm) and with 10% extra sinter aid. An optimum balance in magnetic properties is then obtained with the sintering effected at a temperature T in the range of 1125°C to about 1150°C to provide a coercivity Hcj in excess of 1600 $kA.m^{-1}$, and even 1700 $kA.m^{-1}$ or more.

$SmCo_5$ is currently the most important commercially of all the $R-Co_5$ type alloys. However the present invention may be used to increase the optimum sintering temperature range for other single-phase alloys of the RCo_5 type, where R is at least one element selected from the group Y, Ce, Pr and Nd.

A method in accordance with the present invention may also be used in the formation of sintered magnet bodies of which the alloy is of the rare-earth iron type, for example comprising Nd and Fe, and preferably also comprising boron or carbon. Thus the alloy may be an intermetallic compound of the Nd-Fe-X type, where X is for example boron or carbon.

From reading the present disclosure, other variations will be apparent to persons skilled in the art. Such variations may involve other features which are already known in the design, manufacture and use of permanent magnets, especially sintered rare-earth magnets and which may be used instead of or in addition to features already described herein. Although claims have been formulated in this application to particular combinations of features, it should be understood that the scope of the disclosure of the present application also includes any novel feature or any novel combination of features disclosed herein either explicitly or implicitly or any generalisation thereof, whether or not it relates to the same invention as presently claimed in any claim and whether or not it mitigates any or all of the same technical problems as does the present invention. The applicants hereby give notice that new claims may be formulated to such features and/or combinations of such features during the prosecution of the present application or of any further application derived therefrom.

CLAIM(S)

1. A method of forming a permanent-magnet body by sintering together grains of an alloy comprising at least one 3d transition element and at least one element selected from the rare-earth metal group (inclusive of yttrium), the size of the alloy grains and the sintering temperature being in a range which provides a desired coercivity for the permanent-magnet body, characterised in that before sintering there is mixed together with the alloy grains a grain-growth inhibitor which is of a sufficiently smaller size than the size of the alloy grains and is sufficiently chemically inert in relation to the alloy at the sintering temperature as to form a physical barrier inhibiting inter-grain growth at the grain boundaries of the alloy during sintering.

2. A method as claimed in claim 1, further characterised in that the alloy grains have an average grain size in the range of 1μm to 40μm (micrometres) and preferably less than 10μm, and in that the grain-growth inhibitor is in granular form having an average grain size of less than 0.3μm and less than one tenth of the average grain size of the alloy grains.

3. A method as claimed in claim 2, further characterised in that the inhibitor has an average grain size of less than 0.1μm (for example of about 0.075μm).

4. A method as claimed in any one of the preceding claims, further characterised in that less than 0.5% by weight of the inhibitor (for example of about 0.3% by weight) is mixed together with the grains to be sintered.

5. A method as claimed in any one of the preceding claims, further characterised in that the inhibitor is granular alumina.

6. A method as claimed in any one of the preceding claims, further characterised in that the alloy is of the single-phase RCo_5 type (where R is at least one element selected from the group Sm,Y,Ce,Pr and Nd), and is preferably $SmCo_5$.

7. A method as claimed in claim 6, further characterised in that the sintering is effected at a temperature in the range of 1125°C to 1150°C (Celsius) to provide a coercivity Hcj in

excess of 1600 $kA.m^{-1}$.

8. A method as claimed in any one of claims 1 to 5, further characterised in that the alloy is of the type comprising Nd and Fe, and preferably also comprising boron or carbon.

9. A sintered permanent-magnet body formed by a method claimed in any one of the preceding claims.

10. A magnet body or a method of forming a magnet body having any one of the novel features described herein and/or illustrated in the accompanying drawings.

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