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METHOD OF MAKING MAGNETICALLY ANISOTROPIC PERMANENT MAGNETS

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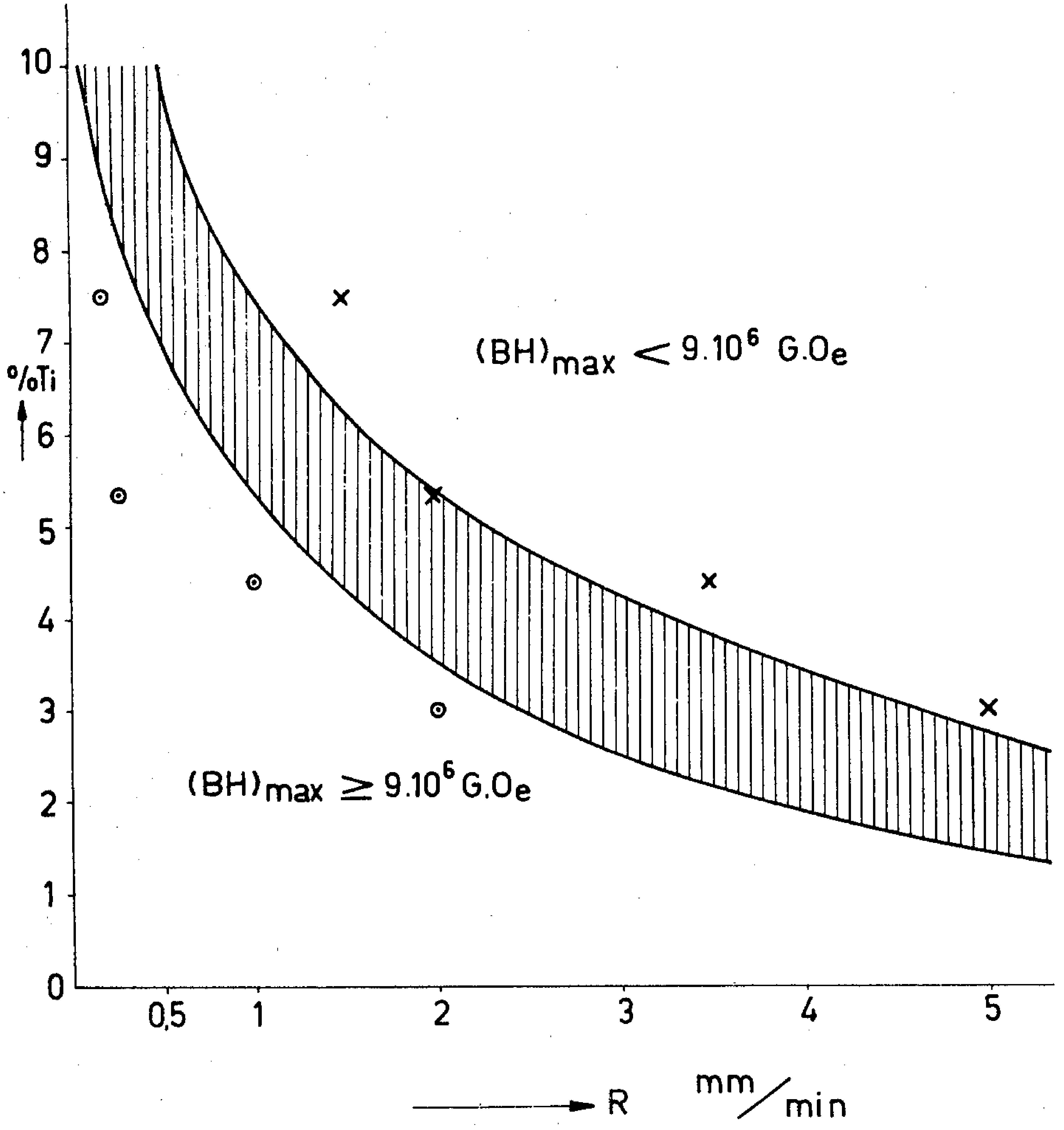

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# METHOD OF MAKING MAGNETICALLY ANISOTROPIC PERMANENT MAGNETS

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**Int. Cl. H01f** *1/04*

The invention relates to a method of manufacturing rod-shaped magnetically anisotropic permanent magnet bodies having a cubic crystal structure and a (100) direction of the crystals which is substantially axially oriented from an alloy containing, in addition to Fe and the normally present impurities, 16–42% of Co, 7–20% of Ni, 6–11% of Al, 0–10% of Cu, 1–10% of Ti, 0–4% of Nb, 0–8% of Ta, 0–1% of Si, 0–1% of S, a melt of the said alloy being cooled in a temperature gradient.

"Normally-present" impurities are to be understood to mean herein those impurities which are already present in the raw materials. In general they total approximately 0.5%.

Known methods of obtaining crystal orientation in magnets of the aforesaid type are all based on the principle that heat is withdrawn from the alloy during solidification only in one direction. From these alloys magnet bodies are formed which in accordance with the method used have a more or less pronounced crystal orientation in that direction. If it is ensured that the preferred direction of magnetization is located in the same direction by subjecting the magnet body to the action of a magnetic field during the thermal treatment, the direction of which field coincides with the (100) direction, it is possible, with the combination of these two factors (crystal-orientation and magnetic field treatment), to obtain magnetic properties in these alloys which far exceed the properties which are obtained if only one of these two factors is present. Consequently, in the manufacture of magnets it is sought to obtain optimum results in this manner and in particular by using methods which give reproducible results, and, in addition, are suitable for mass production. The end view in these endeavours is not so much an improvement of the magnetic field treatment, as an improvement of the crystal orientation. Naturally, the choice of the alloy to be used is also decisive for obtaining the desired specific magnetic properties, for example, a high $(BH)_{\text{max.}}$ value combined, or not combined, with a coercive force which is as high as possible. Moreover, the choice of the composition of the alloys determines the properties of the magnet. For example, it is generally known that alloys in the aforesaid range which contain given quantities of Co and Ti, may show very high coercive forces, (up to 2000 oersted).

To obtain the desired crystal orientation in alloys which have a titanium content and in which the (100) direction of the crystals is oriented axially, it is conventional to use vertically arranged molds which are provided in the bottom with a so-called chill-plate as a result of which the heat, during solidification of the alloy, is withdrawn substantially in a direction at right angles to said chill-plate. Further means are provided to avoid heat flowing away to an undesired extent in a lateral direction, for example, additional heat. It is possible in this manner to obtain a $(BH)_{\text{max.}}$ value of $5.5\times10^6$ g.o., which is reproducible in mass production.

With such alloys $(BH)_{\text{max.}}$ values of $7\text{–}9\times10^6$ g.o. can be obtained in a reproducible manner in mass production if rods of the such alloys are manufactured according to the so-called continuous casting process in

which the (100) direction of the crystals is oriented axially. For example, this method consists in that the molten alloy is continuously applied to the top of a vertically arranged pipe, the rod of the molten alloy being continuusly, or discontinuously, drawn out of the pipe on the lower side. The desired crystal orientation in axial direction is obtained by withdrawing the heat through the rod itself in one direction—the longitudinal direction of the rod—which can even be promoted by additionally cooling the part of the rod emerging out of the pipe. It is also preferable that the pipe be insulated in a transverse direction and/or heated by additional means so as to check the thermal losses.

In the range of the Ti-containing alloys from the group containing 16–42% of Co, 7–20% of Ni, 6–11% of Al, 0–10% of Cu, 1–10% of Ti, 0–4% of Nb, 0–8% of Ta, 0–1% of Si, 0–1% of S, rest Fe and the normally present impurities, magnets without crystal orientation can be mass produced which show high coercive forces of 1000 oe. and more in a reproducible manner. A very good representative of this group is, for example, the alloy consisting of 34% of Co, 14.5% of Ni, 7% of Al, 4.5% of Cu, 5% of Ti, rest Fe and the impurities normally present. With this alloy magnets can be mass-produced without crystal orientation having $(BH)_{\text{max.}}$ values of $4\text{–}5\times10^6$ g.o. and coercive forces of 1300–1500 oe.

The manufacture of magnets with crystal orientation from an alloy containing little or no Ti presents no difficulties in mass manufacture with reproducible results; this is not the case with magnets containing 1% or more of Ti. With alloys having a maximum Ti content up to 1% it is possible to use the above-described method of molding using a chill-plate. For alloys having higher Ti contents, which are required to obtain the desired very high coercive forces, this method, however, generally cannot be used, since the solidification rates which occur are too large. In addition the simultaneous presence of Ti and Al gives rise to undesired nuclei formation which disturbs the crystal orientation. Nuclei formation can be decreased, however, by adding S or Se to the alloy.

Obtaining crystal orientation in alloys having a high Ti content by means of the above described continuous casting process also presents difficulties. In fact, the high Ti content in the alloy has for its result that the melt more or less sticks to the ceramic material of the wall of the pipe. As a result thereof it is possible only to draw bars of a restricted length, while the very advantage of such a method is that unrestricted lengths can be produced so that continuous manufacture is possible.

Also suitable for mass manufacture is the known and useful but time-consuming and expensive methods of obtaining monocrystals and pseudo-monocrystals by drawing a rod from the Ti-containing melt in an upward direction. However, in this manner only rods a few mms. thick can be obtained and it requires care to be taken that the oxide skin floating on the melt does not disturb the desired crystal orientation. The highly pure atmosphere required for this method, however, requires special measures to be taken which are not very attractive for mass production. It should be noted that it is possible in this manner to obtain $(BH)_{\text{max.}}$ values of approximately $11\times10^6$ g.o. combined with coercive forces of 1300–1500 oersted.

An improvement with respect to mass manufacture was obtained using the so-called floating-zone melt method, in which rods of the alloy are moved through a heating zone. Heating is effected by means of a thin high-frequency coil through which the rod extends. In the heating zone the alloy melts after which on cooling in the known manner the desired axial crystal orientation is obtained. This method offers the possibility of using a semi- or fully-automatic plant suitable for various alloys.

However, a draw-back of this method, in particular in the method of floating-zone melting without the use of a crucible, is that during operation the center of the rod does not always coincide with the center of the space enclosed by the high-frequency coil as a result of which an inclined solidification front is obtained which results in that in some parts of the rod not the (100) direction of the crystals, but, for example, the (110) direction will be oriented axially.

A further drawback is that in spite of the precautions taken, heat will be dissipated in a radial direction which promotes an undesired direction of growth of the crystals, namely from without to within.

A very important drawback of such a magnet is that the molten zone shows convection flows as a result of the presence of the high frequency coil. As a result of this many new crystals are formed with arbitrary orientations, which is very undesirable.

A result of these draw-backs is that the energy product always is smaller than $9 \times 10^6$ g.o.

It is a principal object of the invention to provide a method of manufacturing a permanent magnet having a high $(BH)_{max.}$ value and a high coercive force using an alloy of the aforesaid type.

It is a further object of the invention to provide a method of manufacturing a permanent magnet using alloys of the aforesaid type but having an improved crystal orientation in the (100) direction whereby magnets are obtained which have a higher $(BH)_{max.}$ value and coercive force than hitherto obtainable.

Another object of the invention is to provide a method of manufacturing anisotropic permanent magnets consisting of a Co-Ni-Al-Me alloy having a $(BH)_{max.}$ value of at least $9.0 \times 10^6$ g.o.

These and further objects of the invention will appear as this specification progresses.

The invention is based on the discovery that in order to obtain magnetically anisotropic permanent magnets having a high $(BH)_{max.}$ value and a high coercive force from the aforesaid group of alloys, the conditions at the solidification front, or points at which solidification of the melt occurs, must be optimum. In addition to the withdrawal of heat in the axial direction, additional measures must be taken to insure formation of the desired crystal orientation, a criterion for which is that the $(BH)_{max.}$ value must be at least $9 \times 10^6$ gauss-oersted. Thus, it has been found that the solidification rate R must meet special requirements dependent upon the composition of the alloy and dependent upon quantities determined by the apparatus used.

Thus, in accordance with the invention the oxide skin which forms between a seed having a cubic crystal structure, the (100) direction of which is oriented axially, and which in the liquid phase is miscible with the melt, and the melt first is removed and then the melt is contacted with the seed during which contact the seed partially melts and forms a dendritic melting face having an axially oriented (100) direction of the crystals. While in contact with the seed, the solidification rate R (mm./min.) for a given Ti-content, a given temperature gradient G (° C/mm.), and for a given solidification front then is kept below a given maximum value.

According to this method it is possible to mass produce in a fully reproducible manner rods of magnet steel of any desired diameter, the energy product $(BH)_{max.}$ value of which has values of from $9\text{–}12 \times 10^6$ g.o. These high $(BH)_{max.}$ values moreover can be obtained with alloys having more than 1% of Ti. The value of the coercive force $H_c$, may even be 2000 oe. when the composition contains 40% of Co, and 7.5% of Ti.

Although the temperature gradient adjusts in a particular oven, the temperature gradient at the solidification front in the melt—which, ultimately, is decisive of the product to be manufactured—will differ considerably from the first mentioned gradient. This difference is determined principally by the rate R with which the solidification front moves so that this rate R is the most important variable quantity.

The invention will be described in greater detail with reference to the accompanying drawing, the sole figure of which shows the dependency of the energy product, $(BH)_{max.}$ value, in relation to the solidification rate, R.

The manner in which maximum admissible solidification rate R for a given temperature gradient G at the solidification front depends upon the percentage of the alloy is shown in the drawing. When combinations of the percentage of Ti and solidification rate R are chosen below the shaded area, a satisfactory crystal orientation is formed in the magnets. Above this area the resulting orientation is bad. With the combination in the shaded transition area, $(BH)_{max.}$ values of from $4\text{–}9 \times 10^6$ g.o. are obtained.

It is essential in the method according to the invention that the solidification of the alloy begin after the melt has been contacted with a seed which has a dendritically formed boundary surface oriented in the (100) direction. As a seed, for example, a cubic monocrystal of an alloy of the composition: 23% of Co, 14% of Ni, 3% of Cu, 8% of Al, and the balance Fe, may be used. Such an alloy is also known in the trade at Ticonal G/G. Once a part of the melt has solidified, this newly formed magnet steel itself may serve as a seed to obtain the desired crystal orientation in the melt which is still to be solidified.

When the melt has contacted with a seed, first the oxide skin which is always present on the surface of such a melt (both of a partially molten seed and on the molten alloy to be contacted therewith) must be removed. This oxide skin between the seed and the melt may be removed by means of cryolite ($Na_3AlF_6$) which can be provided on the boundary surface of the seed before the melt and the seed are contacted with one another. When the oxide skin is contacted with the cryolite, it dissolves therein after which a ready contact is formed between the melt and the seed.

According to a further embodiment of the method of the invention, the oxide skin may also be removed mechanically. This may be done, for example, with a stirring rod. Alternatively, according to another embodiment the skin can be removed by convection flows in the melt, but convection flows only will be sufficiently operative when the diameter of the melt is large (<10 mm.). The skin may be forced upwards by said flows.

## Example I

A rod, 2 cm. long, 20 mm. diameter, of an alloy having the composition:

35% of Co,
34.5% of Fe,
14.5% of Ni,
7.3% of Al,
4.5% of Cu,
5.2% of Ti,

was placed on a seed consisting of a few crystals oriented with their (100) direction in the direction of the axis of the rod and having the composition:

24% of Co,
14% of Ni,
3% of Cu,
8% of Al,
and the balance Fe.

A layer of cryolite was provided on the boundary surface between the seed and the rod.

A ceramic pipe was slid over the rod and the seat, after which the assembly was placed in a vertical oven. The rod was melted in an atmosphere of cleaned argon gas. The position of the pipe in the oven was chosen to be such that part of the oriented seed also melts.

The ceramic pipe was then lowered on the lower side of the oven at a rate $L=0.25$ mm./min. The temperature gradient at this radiation front was 5° C./mm.

After a thermal treatment in a magnetic field the magnetic properties were found to be:

$$(BH)_{max.}=10\times 10^6 \text{ g.o.}$$
$$H_c=1500 \text{ oe.}$$

If the rate R was 2 mm./min., these properties were found to be:

$$(BH)_{max.}=7.5\times 10^6 \text{ g.o.}$$
$$H_c=1450$$

## Example II

A rod, diameter 10 mm. of an alloy of the composition:

35.4% of Fe
34% of Co
14.5% of Ni
7.3% of Al
4.5% of Cu
4.3% of Ti

was treated in the same manner as described in Example I.

The rate R was 1.0 mm./min.

The resulting magnetic properties were:

$$(BH)_{max.}=9\times 10^6 \text{ g.o.}$$
$$H_c=1200 \text{ oe.}$$

If the rate $R=3.5$ mm./min., these properties were

$$(BH)_{max.}=6.8\times 10^6 \text{ g.o.}$$
$$H_c=1160 \text{ oe.}$$

## Example III

A rod diameter 20 mm., of an alloy of the composition:

40.0% of Co
27.5% of Fe
14.0% of Ni
8.0% of Al
7.5% of Ti
3.0% of Cu

was treated in the same manner as described in Example I.

The rate R was 0.15 mm./min.

The resulting magnetic properties were:

$$(BH)_{max.}=9.1\times 10^6 \text{ g.o.}$$
$$H_c=1980 \text{ oe.}$$

If the rate $R=1.5$ mm./min., the resulting magnetic properties were:

$$(BH)_{max.}=7.0\times 10^6 \text{ g.o.}$$
$$H_c=1870 \text{ oe.}$$

## Example IV

A rod, diameter 20 mm., of an alloy having the composition:

29% of Co
14% of Ni
8% of Al
3% of Cu
3% of Ti
2% of Nb
and the balance Fe

was treated in the same manner as described in Example I.

The rate R was 2 mm./min.

The resulting magnetic properties were:

$$(BH)_{max.}=9.2\times 10^6 \text{ g.o.}$$
$$H_c=1250 \text{ oe.}$$

If the rate R was 5 mm./min., the resulting magnetic properties were:

$$(BH)_{max.}=6.2\times 10^6 \text{ g.o.}$$
$$H_c=1210 \text{ oe.}$$

While the invention has been described in connection with specific examples and applications thereof, other modifications will be apparent to those skilled in this art without departing from the spirit and scope of the invention.

What is claimed is:

**1.** A method of manufacturing rod-shaped magnetically anisotropic permanent magnet bodies having a cubic crystal structure and a (100) direction of the crystals oriented substantially axially from an alloy consisting of 16–42% of Co, 7–20% of Ni, 6–11% of Al, 0–10% of Cu, 1–10% of Ti, 0–4% of Nb, 0–8% of Ta, 0–1% of Si, 0–1% of S and the balance principally Fe comprising the steps of forming a melt of the said alloy, contacting the melt with an oxide-free seed having a cubic crystal structure, the (100) direction of which is oriented axially and which is miscible in the liquid phase of the melt, the seed during contact with the melt partially melting and forming a dendritic boundary surface with an axially oriented (100) direction of the crystal, and cooling the melt at a predetermined solidification rate R (mm./min.), which for a given temperature gradient G (° C./min.) at the solidification front is kept below a predetermined maximum value, which increases as the Ti-content decreases, whereby the resulting alloy after thermal treatment in a magnetic field has a $(BH)_{max.}$ value of at least $9.0\times 10^6$ g.o.

**2.** A method as claimed in claim **1**, in which the oxide skin between the seed and the melt is removed with cryolite, ($Na_3AlF_6$).

**3.** A method as claimed in claim **1**, in which the oxide skin between the seed and the melt is removed mechanically.

**4.** A method as claimed in claim **1**, in which the oxide skin between the seed and the melt is removed by convection flows in the melt.

**5.** A method as claimed in claim **1**, in which the seed is an alloy of about 23% of Co, 14% of Ni, 3% of Cu, 8% of Al, and the balance Fe.

**6.** A method as claimed in claim **2**, in which the cryolite is provided on the boundary surface between the seed and the rod.

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