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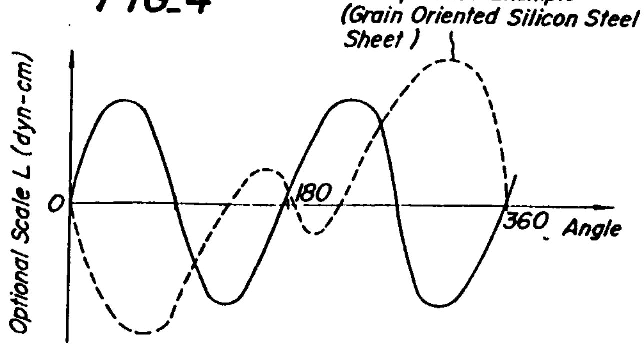
(54) **Method of producing two-phase separation type Fe-Cr-Co series permanent magnets.**

(57) A method of producing a two-phase separation type Fe-Cr-Co series permanent magnet is disclosed, which comprises forming a rapidly solidified tape or a thin sheet from a melt having an alloy composition of $Fe_{100-x-y}Cr_xCo_y$ or $Fe_{100-x-y-z}Cr_xCo_yM_z$ and subjecting to a heat treatment. In this case, permanent magnets having excellent magnetic properties in any direction among the longitudinal, widthwise and thickness directions can be produced by performing the heat treatment under particular conditions.

FIG_4



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METHOD OF PRODUCING TWO-PHASE SEPARATION TYPE Fe-Cr-Co SERIES PERMANENT MAGNETS

This invention relates to a method of producing permanent magnets, and more particularly to a method of producing a two-phase separation type Fe-Cr-Co series permanent magnet having improved workability and magnetic properties.

Permanent magnets are materials capable of generating a magnetic field without the supply of electrical energy from the outside, which are usually evaluated by a maximum energy product (BH)max. In order to increase the value of (BH)max, it is necessary to make a coercive force Hc and a residual magnetic flux density Br as large as possible.

In this connection, the relation among these parameters is shown in Fig. 1, from which it can be seen that the larger values of Br and Hc become better in the permanent magnet. Hc is a measure for magnetic force retaining Br against demagnetizing field. (BH)max is a maximum value on an energy product curve obtained by calculating product of B and H at a demagnetization curve in a second quadrant of Fig. 1, which means a maximum value of energy per unit volume born by the magnet.

Lately, the production of permanent magnets is on the increase with the advance of electron technics.

Further, these permanent magnets are used over wide applications for acoustic instruments, communication equipments, measuring apparatuses and electrical machines and instruments such as speaker, microphone, telephone, magnetron, klystron, microwave guide, ammeter, voltmeter, wattmeter, electric motor, generator, micrometer, hysteresis motor and so on.

In general, high-performance permanent magnets are poor in the workability because they are hard and brittle as in alnico magnet, ferrite magnet and rare earth series magnet. For this reason, there is a great restriction on the method of producing these permanent magnets. For instance, the production of alnico magnet is restricted to a casting process, while the production of ferrite and rare earth series magnets is restricted to a powder sintering process. For this reason, these high-performance permanent magnets are frequently shaped into blocks from a viewpoint of production restriction.

Therefore, magnets capable of shaping into a plate-like form without restricting the production method are limited to only easy-workable cunife, cunico and vicalloy magnets. However, these magnets are fairly poor in the magnetic properties as compared with the alnico, ferrite and rare earth series magnets.

Recently, Fe-Cr-Co series alloys are described in Japanese Patent laid open No. 59-83751 are largely watched because they are rich in the workability and have an energy product (BH)max larger than that of the conventional easy-workable cunife, cunico and vicalloy magnets. However, (BH)max of the Fe-Cr-Co series alloy is still low as compared with that of the alnico and ferrite magnets, so that it is strongly demanded to further improve the properties of the Fe-Cr-Co series alloy.

It is, therefore, an object of the invention to advantageously solve the aforementioned problems of the prior art and to provide a method of producing two-phase separation type Fe-Cr-Co series permanent magnets having a good workability and improved magnetic properties.

According to the invention, there is the provision of a method of producing a two-phase separation type Fe-Cr-Co series permanent magnet, which comprises melting a two-phase separation type alloy of the following formula:

$$Fe_{100-x-y}Cr_xCo_y \quad \text{or}$$

$$Fe_{100-x-y-z}Cr_xCo_yM_z$$

, wherein M is at least one element selected from the group consisting of Ti, Zr, V, Nb, Ta, Mo, B, W, Aℓ, Cu, Si, Sn, P, Mn, Zn, Be, Hf and rare earth elements, x is 3 to 40 wt%, y is 2 to 40 wt% and z is 0.01 to 35 wt% in total, subjecting the resulting melt to a rapid solidification process to form a metallic tape or to usual ingot making-slabbing or continuous casting, hot rolling and cold rolling process to form a thin sheet, and then subjecting the resulting tape or sheet to a heat treatment within a given temperature range.

In a first preferred embodiment of the invention, the Fe-Cr-Co series permanent magnets having a highly aligned {110}<001> orientation are produced by rolling the tape or sheet of the above alloy composition at a draft of 30-95% prior to the heat treatment and then performing the heat treatment that the rolled tape or sheet is subjected to a recrystallization annealing at a temperature of 800-1300°C, a two-phase separation annealing in a magnetic field at a temperature of 600-750°C and an age annealing at a temperature below the separation annealing temperature in this order.

In the second preferred embodiment of the invention, the Fe-Cr-Co series permanent magnets having a highly aligned {100}<011> orientation are produced by rolling the tape or sheet of the above alloy composition at a draft of not less than 40% prior to the heat treatment and then subjecting the rolled tape or sheet to an annealing inclusive of two-phase separation annealing at a temperature of 500-750°C as the heat treatment.

In a third preferred embodiment of the invention, the Fe-Cr-Co series permanent magnets having easy magnetization axes in radial direction of their plane are produced by subjecting the tape or sheet of the above alloy composition to a two-phase separation annealing at a temperature of 600-750°C in a magnetic field while rotating a direction of magnetic field applied to the tape or sheet in a plane parallel thereto and an age annealing at a temperature below the separation annealing temperature in this order as the heat treatment.

In a fourth preferred embodiment of the invention, the Fe-Cr-Co series permanent magnets having a highly aligned {100}<001> orientation are produced by subjecting the tape or hot-rolled sheet of the above alloy composition to two-stage cold rolling through an intermediate annealing at a first draft of not less than 10% and a second draft of 50-80% prior to the heat treatment and then performing the heat treatment that the rolled tape or sheet is subjected to a recrystallization annealing at a temperature of 800-1300°C and an annealing inclusive of two-phase separation annealing at a temperature of 500-750°C.

In a fifth preferred embodiment of the invention, the Fe-Cr-Co series permanent magnets having an easy magnetization axis in a direction perpendicular to plane are produced by subjecting the tape of the above alloy composition to a two-phase separation annealing in a magnetic field at a temperature of 600-750°C while applying the magnetic field in a direction perpendicular to the plane of the tape and an age annealing at a temperature below the separation annealing temperature in this order as the heat treatment.

The invention will be described with reference to the accompanying drawings, wherein:

Fig. 1 is a graph showing demagnetization curve and energy product curve of a permanent magnet;

Fig. 2 is (200) pole figures illustrating crystal texture of Fe_{60}-Cr_{25}-Co_{15} alloy tape after the rolling and annealing as a parameter of draft;

Figs. 3a-3d are pole figures showing a change of crystal texture of Fe-Co-Cr series alloy in accordance with the change of draft at cold rolling, respectively;

Fig. 4 is a magnetic torque curve of a permanent magnet having a highly aligned {100}<011> orientation according to the invention;

Figs. 5a-5c and Figs. 6a-6c are demagnetizing curves of ring-like tape and sheet after the two-phase separation annealing in a rotating magnetic field, a unidirectional magnetic field and non-magnetic field, respectively;

Fig. 7 is a graph showing influences of first draft and second draft in the rolling on crystal orientation of the tape;

Fig. 8 is a graph showing a relation between the revolution number of the cooling roll and the tape thickness;

Fig. 9 is a graph showing a relation between the tape thickness and the columnar grain rate;

Figs. 10a and 10b are microphotograph in section and (200) pole figure of crystal texture of Fe_{62}-Cr_{22}-Co_{15}-Mn_1 alloy tape having a columnar grain rate of more than 90% at as-cast state, respectively;

Figs. 11a and 11b are microphotograph in section and (200) pole figure of crystal texture after the tape of Fig. 10 is subjected to recrystallization annealing at 1100°C for 10 minutes, respectively;

Figs. 12a and 12b are microphotograph in section and (200) pole figure of crystal texture of Fe_{62}-Cr_{22}-Co_{15}-Mn_1 alloy tape having a columnar grain rate of less than 30% at as cast state, respectively; and

Figs. 13a and 13b are microphotograph in section and (200) pole figure of crystal texture after the tape of Fig. 12 is subjected to recrystallization annealing at 1100°C for 10 minutes, respectively.

The invention will be described in detail below.

At first, the reason why the chemical composition of the Fe-Cr-Co series alloy according to the invention is limited to the above range is as follows.

Cr: 3-40%

Cr is an effective element for the formation of a matrix being Cr-rich nonmagnetic α_2 phase. When the Cr amount is less than 3%, the α_2 phase is not a matrix but is a precipitation phase after the two-phase separation, while Fe-rich α_1 phase is a matrix, so that satisfactory properties as a permanent magnet can not be obtained. Further, the spinodal decomposition temperature lowers, so that a long time is required for the two-phase separation through spinodal decomposition. On the other hand, when the Cr amount exceeds 40%, Fe-Cr series σ phase begins to locally precipitate in the Fe-Cr-Co series alloy and the resulting tape or sheet is very brittle and difficult in the workability. Further, the spinodal decomposition temperature lowers to require a long time for two-phase separation, and also Fe-rich α_1 phase becomes smaller to degrade the properties of the permanent magnet. Therefore, the Cr amount is restricted to a range of 3-40%.

Co: 2-40%

Co effectively contributes not only to raise the spinodal decomposition temperature of the Fe-Cr-Co series alloy for completing two-phase separation in a short time but also to raise the Curie temperature for more enhancing the effect of magnetic field applied in the spinodal decomposition. When the Co amount is less than 2%, satisfactory treating effect in magnetic field based on the sufficient rising of spinodal decomposition temperature and Curie temperature can not be obtained. While, when the Cr amount exceeds 40%, Fe and Co ordered phases are locally precipitated to degrade the workability, and the addition effect is saturated to cause the cost-up. Therefore, the Co amount is restricted to a range of 2-40%.

M: 0.01-35% in total

M is at least one element selected from Ti, Zr, V, Nb, Ta, Mo, B, W, Aℓ, Cu, Si, Sn, P, Mn, Zn, Be, Hf and rare earth elements, which forms α phase by reacting with Fe to prevent the enlargement of γ phase loop in the Fe-Cr-Co series alloy and narrow the range of γ→α transformation in the cooling. Moreover, the rare earth element means to include Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb and Lu. In these Fe-Cr-Co series alloys, single α phase is necessary to exist as a supersaturation coolant prior to spinodal decomposition because the incorporation of γ phase can not give good properties as a permanent magnet. When the amount of M is less than 0.01% in total, γ phase remains during the cooling down to room temperature and the supersaturated solid solution of single α phase can not be attained, so that it is difficult to separate the single α phase into α_1 phase and α_2 phase through the spinodal decomposition and γ phase is locally existent in the α phase to degrade the magnetic properties. While, when the amount of M exceeds 35% in total, the resulting tape or sheet becomes brittle and the workability is degraded, and also the saturated magnetic flux density lowers to finally degrade (BH)max. Therefore, the amount of M is restricted to a range of 0.01-35% in total.

The production of the permanent magnets according to the invention will be described every step below.

At first, the melt of the aforementioned fundamental alloy composition is subjected to a rapid solidification process or to usual ingot making or continuous casting and hot and cold rollings to form a metallic tape or thin sheet having a thickness of about 0.05-5.0 mm (hereinafter referred to as a base plate).

When the thickness of the base plate is less than 0.05 mm, it is difficult to perform finish rolling, which is carried out prior to subsequent heat treatment if necessary, at a sufficient draft, while when the thickness exceeds 5.0 mm, the cracking is apt to be caused and the handling is difficult.

In case of producing permanent magnets having a highly aligned {110}<001> orientation or so-called unidirectionally oriented permanent magnets, the base plate is subjected to warm or cold rolling at a final draft of 30-95% so as to provide a final product thickness prior to the subsequent heat treatment. When the final draft is less than 30%, the alignment of {110}<001> orientation with respect to the rolling direction after secondary recrystallization annealing as mentioned later is poor and the improved magnetic properties can not be obtained, while when it exceeds 95%, the alignment of {110}<001> orientation with respect to the rolling direction is insufficient and the rolling itself becomes difficult and the cost-up is caused.

After the above rolling, the rolled base plate is subjected to a heat treatment as mentioned below.

Firstly, the rolled base plate is subjected to recrystallization annealing at a temperature of 800-1300°C to highly align {110}<001> orientation with respect to the rolling direction. When the recrystallization annealing temperature is lower than 800°C, a long time is required for the recrystallization and the alignment of {110}<001> orientation is apt to be dispersed, while when it exceeds 1300°C, the surface of the base plate may solute depending upon the alloy composition and the disadvantages in the equipment and operation become conspicuous.

In this connection, the melt of Fe_{60}-Cr_{25}-Co_{15} alloy was shaped into a rapidly solidified metallic tape of 0.5 mm in thickness through twin roll process, rolled at a given draft ranging from 10% to 95% and then subjected to recrystallization annealing at 1250°C for 30 minutes. Thereafter, the crystal texture of the resulting tape was examined to obtain (200) pole figures shown in Fig. 2.

As seen from Fig. 2, when the draft is not less than 30%, the good alignment of {110}<001> orientation is observed, and particularly the better results are obtained at a draft of 40-70%.

Although the permanent magnet material having a highly aligned {110}<001> orientation with respect to the rolling direction is formed at the steps of rolling → recrystallization annealing, the magnetic properties are more improved by subjecting to two-phase separation annealing in magnetic field and age annealing as the heat treatment.

The two-phase separation annealing is to cause the so-called spinodal decomposition. When the separation annealing temperature is lower than 600°C, a long time is uneconomically required for the spinodal decomposition, while when it exceeds 750°C, it is very difficult to separate the single α phase into α_1 and α_2 phases, and also the separation annealing temperature approaches to the Curie point of the alloy, so that the α_1 phase produced by the spinodal decomposition is not aligned in the direction of magnetic field when the magnetic field is applied to the alloy. Therefore, the separation annealing temperature in the magnetic field is restricted to a range of 600-750°C. In this case, the intensity of magnetic field is desired to be not less than 0.5 kOe.

Following to the two-phase separation annealing in magnetic field, age annealing is carried out at a temperature below the separation annealing temperature, for example at a temperature below 600°C. This age annealing is to achieve the equilibrium state in each of α_1 and α_2 phases separated by the spinodal decomposition and provide nonmagnetization of α_2 phase (M-rich phase) at room temperature. When the age annealing temperature is higher than the separation annealing temperature, the resulting α_2 phase exhibits a strong magnetism at room temperature and the difference in magnetization intensity between α_1 phase (Fe-rich phase) and α_2 phase, resulting in the decrease of coercive force represented by $Hc \propto (Is_{Fe}-Is_{M})$.

In the production of the aforementioned unidirectionally oriented permanent magnet, 0.005-0.06 wt% of C, 0.005 -0.10 wt% in total of at least one element selected from S, Se and Te and/or 0.003-0.30 wt% in total of at least one element selected from Bi, Sb and As may be added to the melt of the Fe-Cr-Co series fundamental alloy composition. In this case, the reason on the restricted range of such an additional element is as follows:

C: 0.005-0.06%

C produces a Cottrell effect by acting with dislocation introduced during the rolling to cause the locking or tangling of dislocation, resulting in the increase of dislocation density for promoting the formation of primary recrystallization fine grains. When the C amount is less than 0.005%, the tangling of dislocation is insufficient, while when it exceeds 0.06%, the transformation to γ phase is locally caused to degrade the magnetic properties. Therefore, the C amount is restricted to a range of 0.005-0.06%.

S, Se, Te: 0.005-0.10% in total

S, Se and Te are elements useful for forming inhibitors such as MnS, MnSe, MnTe and the like by reacting with Mn. When the amount of these elements is less than 0.005% in total, the given amount of the inhibitor can not be maintained, while when it exceeds 0.10% in total, the coarsening of the inhibitor is caused to damage the effect of controlling normal growth of primary recrystallization grains. Therefore, the amount of these elements is limited to a range of 0.005-0.10% in total. Moreover, in case of the $Fe_{100-x-y}Cr_xCo_y$ composition, it is necessary to add 0.01-0.15% of Mn separately.

Bi, As, Sb: 0.003-0.30% in total

These elements segregate in the vicinity of grain boundary between the primary recrystallization grains to exhibit the effect of controlling normal growth of the primary recrystallization grain.

When the amount of these elements is less than 0.003% in total, the effect of controlling such a normal growth is poor, while when it exceeds 0.30% in total, the segregation amount in the vicinity of the grain boundary becomes larger, resulting in the occurrence of grain boundary cracking, which renders the base plate into a brittle state. Therefore, the amount of these elements is restricted to a range of 0.003-0.30% in total.

The base plate of Fe-Cr-Co series alloy composition further containing the above additional elements was rolled at a final draft of 30-95%, and then the relation between the final draft and (BH)max was examined to obtain results as shown in the following Table 1. In this case, the molten alloy containing 25% of Cr, 15% of Co, 1% of Si, 0.035% of C, 0.06% of Mn, 0.018% of Se and 0.005% of Te was shaped into an ingot of 10 kg, which was hot rolled to a thickness of 3.0 mm. Then, the resulting hot rolled plate was subjected to a cold rolling at a final draft shown in Table 1 to form a cold rolled sheet of 0.5 mm in thickness. This sheet was subjected to decarburization annealing at 900°C and further to recrystallization annealing at 1200°C for 2 hours and then forcedly cooled in air. Thereafter, the sheet was subjected to two-phase separation annealing at 665°C for 15 minutes while applying a magnetic field of 2 kOe to the sheet in the rolling direction and further to multi-stage age annealing at 600°C for 5 hours, at 575°C for 5 hours, at 550°C for 5 hours and at 500°C for 10 hours.

Table 1

Draft (%)	0	20	30	40	50	60	70	80	95
(BH)max (MGOe)	2.4	3.2	5.3	6.5	8.2	9.0	8.7	7.2	5.8

As seen from Table 1, the excellent value of (BH)max is obtained within a final draft range of 30-95%.

Moreover, it is effective that the base plate of 0.1-5.0 mm in thickness prior to the rolling is subjected to normalizing annealing at a temperature of about 800-1100°C in order to improve the magnetic properties. And also, it is justifiable to perform intermediate rolling and intermediate annealing prior to the final rolling.

In the Fe-Cr-Co series alloy containing the additional elements, it is necessary to perform the decarburization annealing at a temperature of 800-1300°C after the final annealing and before the heat treatment. This decarburization annealing reduces the C amount to less than 0.005% degrading no magnetic properties. In this case, when the decarburization annealing temperature is lower than 800°C, the long annealing time is much taken to raise the cost, while when it exceeds 1300°C, the base plate is at a fused state in accordance with the kind of the alloy, so that the decarburization annealing temperature is restricted to a range of 800-1300°C.

After the decarburization annealing, the secondary recrystallization annealing is carried out at a temperature of 800-1300°C, wherein crystal grains having {110}<001> orientation are preferentially grown two times or more from the primary recrystallization grains as compared with crystal grains having the other orientations and then coarsened. When the treating temperature is lower than 800°C, a long time is taken for the growth of secondary grains, while when it exceeds 1300°C, the dissociation is started according to the kind of the inhibitor and it is difficult to control the growth of primary crystal grains having an orientation other than {110}<001> orientation and consequently the secondary recrystallization can not sufficiently been completed and the surface of the sheet or tape may be fused according to the alloy composition.

Moreover, when the age annealing is carried out after the two-phase separation annealing in magnetic field as previously mentioned, it is particularly preferable to perform multi-stage age annealing by gradually lowering the age annealing temperature.

In the permanent magnet of the aforementioned Fe-Cr-Co series alloy composition, high coercive force is obtained by utilizing two-phase separation phenomenon called as spinodal decomposition. Especially, the permanent magnets having {110}<001> orientation and more improved magnetic properties can be obtained by applying a higher magnetic field at the initial stage of the two-phase separation annealing.

Such an anisotropic magnetization of two-phase separation in the direction of magnetic field is attained by growing the separated α_1 phase in <100> direction near the magnetic field direction longer. It is said that the above anisotropic magnetization results from the fact that crystal grains growing in the direction near the magnetic field direction have a magnetostatic energy lower than that of crystal growth growing in a direction perpendicular to the above direction.

Lately, it is strongly demanded to develop permanent magnets having a so-called multi-pole magnetization in addition to the above unidirectionally oriented ones.

In general, the finally stable orientation of body-centered cubic crystal after the rolling is {100}<011> orientation called as a slant cube. In this connection, the inventors have examined with respect to the worked crystal texture of Fe-Co-Cr series alloy after the cold rolling and found that (100) crystal face of the alloy is parallel to the rolled plane thereof and [010] and [100] orientations as an easy magnetization axis of this crystal face are existent in two directions inclined at 45° with respect to the rolling direction.

Now, the base plate of the aforementioned fundamental alloy composition is subjected to hot, warm or cold rolling in order to highly align {100}<011> orientation. In this case, the draft in the rolling is required to be at least 40%.

The change of crystal texture in the Fe-Cr-Co series alloy was examined by varying the draft in the cold rolling to obtain results shown as a pole figure in Figs. 3a-3d.

As apparent from Fig. 3, the {100}<011> orientation is highly aligned with the increase of the draft. According to the invention, the draft is restricted to at least 40% in view of the developing effects.

Then, the as-rolled tape or sheet is subjected to an annealing inclusive of two-phase separation annealing as a heat treatment. In this case, the annealing temperature is somewhat varied according to the alloy composition, but it is preferable within a range of 500-750°C. When the annealing temperature is lower than 500°C, a long annealing time is required, while when it exceeds 750°C, it is difficult to obtain fine two separated phases.

Fig. 4 shows a magnetic torque curve of the plate-like permanent magnet produced by a series of the above production steps. As seen from Fig. 4, the solid line shows a magnetic torque having a bidirectional orientation, which means that the permanent magnet has bidirectionally easy magnetization axes. Moreover, dotted lines shows a magnetic torque curve of grain oriented silicon steel sheet produced by the usual production process.

In addition to the {100}<011> orientation, the easy magnetization axis may be formed in radial direction in plane. In this case, it is sufficient to control the growth direction of different phase in the two-phase separation. For this purpose, the two-phase separation annealing is carried out in a rotating magnetic field or while rotating the rolled plate in a magnetic field.

For example, the melt of $Fe_{59}Cr_{24}Co_{15}W_2$ alloy composition was rapidly solidified by continuously feeding into a contact portion between the two rotating rolls to form a tape of 0.50 mm in thickness. A ring-like sample of 30 mm in outer diameter and 10 mm in inner diameter was punched out from the tape, and subjected to two-phase separation annealing at 660°C in a rotating magnetic field with an intensity of 10 kOe or in a unidirectional magnetic field with an intensity of 10 kOe or in the absence of magnetic field for 10 minutes, held at 610°C for 24 hours without applying the magnetic field, cooled down to 500°C at a rate of 10°C/hr, and then subjected to age annealing at 500°C for 24 hours.

The magnetic properties of the thus obtained ring-like samples were measured to obtain results as shown in Figs. 5a-5c, wherein Fig. 5a is the case of annealing in the rotating magnetic field, Fig. 5b is the case of annealing in the unidirectional magnetic field and Fig. 5c is the case of annealing in the non-magnetic field. In Fig. 5b, $H_{/\!/}$ is a case that the measurement is performed in a direction parallel to the direction of the magnetic field applied, and $H_{\perp}$ is a case that the measurement is performed in a direction perpendicular to the direction of the magnetic field applied.

As apparent from Fig. 5, the excellent magnetic properties are obtained when applying the rotating magnetic field.

On the other hand, the melt of $Fe_{48}Cr_{24}Co_{15}W_4$ alloy composition was poured into a mold to form an ingot, which was heated at 1280°C for 30 minutes and hot rolled to form a hot rolled sheet of 0.65 mm in thickness. This sheet was subjected to a solution treatment at 1280°C, from which a ring-like sample of 30 mm in outer diameter and 10 mm in inner diameter was punched out. The resulting sample was subjected to the same heat treatment as described above (i.e. two-phase separation annealing in the presence or absence of magnetic field and further age annealing), and thereafter the magnetic properties were measured to obtain results shown in Figs. 6a-6c, wherein $R_{/\!/}$ is a case that the measurement is performed in a direction parallel to the rolling direction and $R_{\perp}$ is a case that the measurement is performed in a direction perpendicular to the rolling direction.

As seen from Fig. 6, the magnetic properties are largely improved by applying the rotating magnetic field. On the contrary, in case of the annealing in the unidirectional magnetic field, there is a great difference in the coercive force between $H_{/\!/}$ or $R_{/\!/}$ and $H_{\perp}$ or $R_{\perp}$, while in case of the annealing in non-magnetic field, large coercive force can not be obtained.

In the production of the permanent magnet having easy magnetization axes in radial direction of plane, according to the invention, the base plate of the fundamental alloy composition is shaped into a ring or disc by punching, etching or wire cutting before the heat treatment, if necessary. Thereafter, the base plate or its ring or disc is subjected to two-phase separation annealing in magnetic field as the heat treatment while rotating the magnetic field applied to the plate in a plane parallel thereto or rotating the plate under the application of unidirectional magnetic field. In this case, the direction of major axis in α_1 phase is influenced by the direction of magnetic field to form a so-called radial anisotropy wherein the major axis radially extends in the plane. Thereafter, the age annealing is performed as the heat treatment for more improving the magnetic properties obtained by the two-phase separation annealing. Thus, there are obtained permanent magnets having easy magnetization axes in radial direction of plane.

From a viewpoint of the improvement on the magnetic properties of the permanent magnet having radial anisotropy as mentioned above, it is more advantageous that the base plate or its ring or disc is subjected to a solution treatment prior to the two-phase separation annealing.

This solution treatment is to render the structure of the base plate into single α phase. When the treating temperature is lower than 900°C, a long time is taken for the solution treatment, while when it exceeds 1300°C, the surface of the base plate may be fused. Therefore, the solution treatment is necessary to be carried out at a temperature of 900-1300°C.

As the base plate, it is particularly preferable to use the tape obtained by rapidly solidifying the melt of the fundamental alloy composition as apparent from the following:

(i) The single α phase is obtained without the solution treatment because α phase is supercooled;

(ii) Since the solution treatment at high temperature is unnecessary, the two-phase separation annealing is easily performed to fine crystal grains of the tape; and

(iii) Since the orientation in plane of the tape is {100}<0vw>, many easy magnetization axes are existent in the tape plane.

In case of using such a tape, when the cooling rate during rapid solidification is lower than 10^3°C/sec, a partial transformation is induced after the rapid solidification to obtain no single α phase, so that the cooling rate is necessary to be not lower than 10^3°C/sec. Further, when the thickness of the tape is less than 0.05 mm, there are caused many defects and it is difficult to obtain satisfactory properties, while when it exceeds 1.0 mm, unsolidified portion remains in the tape and the cooling rate of not lower than 10^3°C/sec is hardly achieved, so that the thickness is restricted to a range of 0.05-1.0 mm.

Then, the invention will be described with respect to two-phase separation type Fe-Cr-Co series permanent magnets having good magnetic properties in the crystal texture of {100}<001> orientation.

At first, the production step of such a magnet is described in detail based on the following experimental data.

Molten steel comprising 23% of Cr, 12% of Co, 0.1% of Ti, 0.1% of Si and the balance of Fe was shaped into a tape of 0.05 mm, 0.1 mm, 0.15 mm, 0.2 mm, 0.3 mm or 0.5 mm in thickness by a twin roll process. Each of the resulting tapes other than the tape of 0.05 mm in thickness was subjected to a first rolling at various draft, annealed in a non-oxidizing atmosphere at 850°C for 5 minutes and then rolled to a thickness of 0.05 mm. Separately, each of the above tapes was rolled to a thickness of 0.05 mm at once. Moreover, the as-cast tape of 0.05 mm in thickness was not subjected to a rolling.

These tapes were piled one upon the other through $A\ell_2O_3$ powder as a parting agent, annealed in a hydrogen atmosphere at 1200°C for 60 minutes, and immediately cooled with water. After the surface of each of the tapes was cleaned, it was cut out in the longitudinal direction to measure (200) pole figure. The measured results on the alignment degree of {100}<001> orientation in each tape are shown in Fig. 7, wherein marks ◎ and ○ are a case that the displacement angle from {100}<001> orientation is within 10° and show a good alignment degree.

As apparent from Fig. 7, when the displacement angle from {100}<001> orientation is within 10°, the combination of first and second drafts is that the first draft is not less than 10% and the second draft is within a range of 50-80%.

In general, it is known that when the tape of about 0.1-0.2 mm in thickness is annealed at a high temperature of about 1200°C, crystal grains having (100) face parallel to the plane of the tape grow abnormally, but the orientation in plane is random and exhibits {100}<0kℓ> orientation. However, when the aforementioned rolling-intermediate annealing are carried out before the occurrence of abnormal growth, the rate of crystal grains having {100}<001> orientation can particularly be increased among grains of {100}<0kℓ> orientation.

In this embodiment, the rolled tape is subjected to recrystallization annealing at a temperature of 800-1300°C as a heat treatment. When the temperature is lower than 800°C, the growth of crystal grains of {100}<001> orientation is insufficient and it is difficult to obtain a highly aligned texture of {100}<001> orientation, while when it exceeds 1300°C, the industrialization is difficult from a viewpoint of technique and cost.

Then, the thus treated tape is subjected to an annealing inclusive of two-phase separation annealing at a temperature of 500-750°C as a further heat treatment, whereby spinodal decomposition is caused to enhance the coercive force. When the temperature is lower than 500°C, the decomposition rate is slow and the ageability is considerably degraded, while when it exceeds 750°C, γ and σ phases are included in α phase to deteriorate the magnetic properties.

Moreover, the latter annealing may be carried out in a magnetic field. In this case, it is desirable that the intensity of magnetic field is not less than 1 kOe and the direction of magnetic field applied is <100> orientation.

The thus obtained tape has {100}<001> orientation, so that the improving effect of magnetic properties is obtained even when the magnetic field is applied to the tape in any direction selected from the longitudinal direction of the tape, direction perpendicular to the longitudinal direction and direction perpendicular to the plane of the tape.

In order to more improve the magnetic properties, multi-stage age annealing may be carried out after the separation annealing in magnetic field.

Further, the invention will be described with respect to the production of two-phase separation type permanent magnets having an easy magnetization axis in a direction perpendicular to the plane or <001> axis in the direction perpendicular to plane.

At first, the melt of the fundamental alloy composition is shaped into a tape by a rapid solidification process. As the rapid solidification process, there may be used the conventionally well-known processes such as single roll process, twin roll process and the like.

In this embodiment, columnar structure produced in the rapid solidification of the alloy melt is positively utilized for aligning the easy magnetization axis in the direction perpendicular to the plane of the tape, and in this case it is important to control the crystal texture so that the solidification structure of the rapidly solidified tape contains at least 30% of columnar grain.

As the factor controlling the rate of columnar grain in the tape, there are tape thickness, cooling rate, thermal conductivity of roll, heat transfer rate between melt and roll and so on. For instance, when the pressure and amount of the alloy melt injected on the same cooling roll are constant, the rate of columnar grain in the resulting tape is substantially determined by the cooling rate to the tape thickness. Under such conditions, therefore, there can be found simple relations between the revolution number of the cooling roll and the tape thickness and between the tape thickness and the rate of columnar grain in the production of rapidly solidified tape. In case of $Fe_{63}Cr_{22}Co_{15}$ alloy, for example, the above relations are as shown in Figs. 8 and 9, from which it can be seen that when the tape has a thickness of not more than 0.5 mm and a columnar grain rate of at least 30%, the cooling may be performed at a revolution number of cooling roll of not less than 10^3 rpm. Since the cooling rate is proportional to the revolution number of cooling roll, the cooling rate in this example is at least 10^3°C/sec. Moreover, when the tape thickness is more than 0.5 mm at the columnar grain rate of at least 30%, it is sufficient to change the cooling rate into not less than 10^4°C/sec.

Here, the columnar structure at as-cast state means a structure that {100} face is parallel to the plane of the tape and <001> orientation is perpendicular to the plane.

Fig. 10a is a microphotograph in section of a rapidly solidified tape of $Fe_{62}Cr_{22}Co_{15}Mn_1$ alloy composition with a thickness of 0.3 mm at as-cast state and Fig. 10b is (200) pole figure thereof, wherein the rate of columnar grain is more than 90%. When this tape is subjected to recrystallization annealing at 1100°C for 10 minutes, the crystal grains are coarsened to form a macrograin passing through the thickness of the tape as shown in Fig. 11a. In this case, as shown in Fig. 11b, the aligned texture viewed from the pole figure is {100}<0uw>, so that <001> orientation is necessarily aligned in the direction perpendicular to the plane of the tape. Such <001> orientation is an easy magnetization axis likewise the case of BCC alloys represented by Fe.

On the contrary, when the rapidly solidified tape obtained by the same method as mentioned above has a columnar grain rate of less than 30% (or a rate of cubic system of more than 70%) as shown in Fig. 12a, even if the recrystallization annealing is carried out at 1100°C for 10 minutes, the crystal grain does not pass through the thickness of the tape as shown in Fig. 13a. Moreover, as seen from the pole figure of Fig. 12b, the aligned texture at as-cast state is {100}<0vw>, but the texture after the recrystallization annealing is rendered into random direction as shown in

Fig. 13b. That is, the latter texture is random to the plane of the tape but not perpendicular to the plane. Such a behavior of crystal grain growth is due to the fact that the rate of cubic system included in a central portion of the tape at as-cast state is large.

According to the invention, it is important that the columnar grain rate is not less than 30% or the rate of cubic system is less than 70% in order to align the easy magnetization axis in the direction perpendicular to the plane of the tape. Moreover, the thus obtained tape may be subjected to a skin pass rolling without troubles.

Then, the rapidly solidified tape having a columnar grain rate of not less than 30% may be subjected to a recrystallization annealing at a temperature of 800-1300°C to grow crystal grains. After the recrystallization annealing, the tape is subjected to two-phase separation annealing in magnetic field at a temperature of 600-750°C and age annealing at a temperature below the separation annealing temperature as a heat treatment to thereby improve the magnetic properties. In the two-phase separation annealing, it is required to apply the magnetic field to the tape in a direction perpendicular to the plane of the tape and the intensity of magnetic field is desirable to be not less than about 0.5 kOe. In the actual operation, it is preferable that spinodal decomposition is carried out in a continuous furnace or the like capable of applying the magnetic field in the direction perpendicular to the plane of the tape.

The following examples are given in the illustration of the invention and are not intended as limitations thereof.

Example 1

A melt of $Fe_{60}Cr_{25}Co_{15}$ alloy composition was injected from an injection nozzle onto a contact portion between two rotating cooled rolls to form a tape of 0.5 mm in thickness. Then, the resulting tape was subjected to a cold rolling at a draft varying from 0% to 95% and further to recrystallization annealing at 1250°C for about 30 minutes. The tapes obtained by rolling at a draft of 30-95% among the above tapes were confirmed to have {110}<001> orientation and then subjected to two-phase separation annealing at 660°C for 20 minutes while applying a magnetic field of 2 kOe to the tape toward <001> orientation. Thereafter, the tape was immediately cooled down to 600°C and subjected to age annealing from 600°C to 500°C at a cooling rate of 5°C/hr.

The coercive force Hc and maximum energy product (BH)max were measured with respect to the thus treated tapes to obtain results as shown in the following Table 2.

Table 2

Draft (%)	0	10	20	30	40	50	60	70	80	90	95
Hc(kOe)	0.40	0.41	0.43	0.51	0.55	0.79	0.98	0.92	0.88	0.80	0.76
(BH)max (MGOe)	4.2	4.5	5.2	5.5	6.7	9.2	11.8	10.1	9.5	8.9	8.2

As seen from Table 2, when the draft is within the range defined in the invention, better magnetic properties are particularly obtained.

Example 2

A melt of $Fe_{60}Cr_{23}Co_{15}Si_2$ alloy composition was injected from an injection nozzle onto a contact portion between two rotating cooled rolls to form a tape of 0.5 mm in thickness. The resulting tape was rolled at a draft of 65% and then subjected to recrystallization annealing at 1000°C for 40 minutes. Thereafter, the tape was subjected to two-phase separation annealing in a magnetic field of 2 kOe at 655°C for 30 minutes, immediately cooled down to 600°C and then subjected to age annealing from 600°C to 500°C at a cooling rate of 5°C/hr. The coercive force and maximum energy product of the thus obtained tape were measured to obtain results as shown in the following Table 3.

For the comparison, the non-rolled tape was subjected to the same heat treatment as described above and then the magnetic properties were measured to obtain results shown in Table 3.

Table 3

	Comparative Example	Example 2
Draft (%)	-	65
Hc(kOe)	0.40	0.96
(BH)max(MGOe)	4.2	10.9

Example 3

A melt of $Fe_{58.887}Cr_{25}Co_{15}Al_{1}C_{0.035}Mn_{0.06}Se_{0.018}$ alloy composition was shaped into an ingot of 10 kg, which was hot rolled to form a sheet of 3.0 mm in thickness. This sheet was annealed at 900°C for 5 minutes, cold rolled at a draft of 70% to a thickness of 0.9 mm and then subjected to an intermediate annealing at 950°C for 5 minutes. The thus treated sheet was subjected to a cold rolling at a second draft of 60% to form a thin sheet of 0.36 mm in final thickness, which was subjected to decarburization annealing at 850°C for 5 minutes and further to recrystallization annealing at 900°C for 5 hours. The thus treated thin sheet was subjected to two-phase separation annealing at 660°C for 10 minutes while applying a magnetic field of 2 kOe in the rolling direction and further to multi-stage age annealing at 600°C for 5 hours, at 575°C for 5 hours, at 550°C for 5 hours and at 500°C for 10 hours.

The magnetic properties of the thus obtained permanent magnet tape were measured together with those of the non-rolled tape containing no C, Mn and Se to obtain results as shown in the following Table 4.

Table 4

	Magnetic properties		
	Hc(Oe)	Br(kG)	(BH)max(MGOe)
Comparative Example	480	11	4.75
Example 3	870	14	10.96

Example 4

A melt of $Fe_{59.821}Cr_{23}Co_{15}W_2C_{0.033}Bi_{0.066}Sb_{0.08}$ alloy composition was shaped into an ingot of 10 kg, which was hot rolled to form a sheet of 2.7 mm in thickness. This sheet was annealed at 900°C for 5 minutes, cold rolled at a draft of about 88% to a thickness of 0.325 mm and then subjected to decarburization annealing at 850°C and further to recrystallization annealing at 1100°C for 2 hours. Then, the thus treated thin sheet was subjected to two-phase separation annealing at 660°C for 10 minutes while applying a magnetic field of 2 kOe in the rolling direction and further to multi-stage age annealing at 600°C for 5 hours, at 575°C for 5 hours and at 550°C for 10 hours.

The thus obtained thin sheet had a maximum energy product (BH)max of 8.9 MGOe.

Example 5

A rapidly solidified tape of 0.70 mm in thickness was produced from a melt of $Fe_{62.808}Cr_{22}Co_{14}Ti_1C_{0.030}Mn_{0.06}S_{0.022}Sb_{0.080}$ alloy composition by a twin roll process. This tape was annealed at 900°C for 5 minutes, rolled at a draft of 60% to a thickness of 0.28 mm, subjected to decarburization annealing in a hydrogen atmosphere at 850°C, recrystallization annealing at 800-900°C for 30 hours and normalizing annealing at 1200°C for 3 hours, and then cooled with water. The thus treated tape was subjected to two-phase separation annealing at 670°C for 15 minutes while applying a magnetic field of 2 kOe in the rolling direction and further to multi-stage age annealing at 600°C for 5 hours, at 575°C for 5 hours, at 550°C for 5 hours and at 500°C for 10 hours without the application of magnetic field.

The thus obtained tape had a maximum energy product (BH)max of 8.5 MGOe.

Example 6

A melt having an alloy composition as shown in the following Table 5 was injected from an injection nozzle onto a contact portion between two rotating rolls to form a rapidly solidified tape of about 0.5 mm in thickness and about 10 cm in width. This tape was immediately cold rolled at a draft of 60% to a thickness of about 0.2 mm, annealed at 1200°C for 1 hour and rapidly cooled.

Then, a set of 20 tapes piled one upon the other was subjected to two-phase separation annealing at 670°C for about 1 hour while applying a magnetic field of 3 kOe in the rolling direction, rapidly cooled down to 620°C, slowly cooled from 600°C to 500°C over 50 hours and then cooled in air. The magnetic properties of the thus obtained tape set were measured together with those of non-rolled tape set as a comparative example to obtain results as shown in Table 5.

Table 5

	Chemical composition (wt%)	Magnetic properties		
		Hc(Oe)	Br(kG)	(BH)max (MGOe)
Acceptable Example	$Fe_{61}Cr_{28}Co_{11}$	680	13.5	8.3
	$Fe_{60}Cr_{25}Co_{11}Zr_{2}V_{1}Ti_{1}$	720	13.2	8.6
	$Fe_{62}Cr_{25}Co_{11}Nb_{1.5}Cu_{0.5}$	660	13.7	8.2
	$Fe_{61}Cr_{25}Co_{11}Sn_{2.5}Mn_{0.5}$	670	13.5	8.1
	$Fe_{61.8}Cr_{25}Co_{11}A\ell_{2}Si_{0.1}Ta_{0.1}$	820	13.1	9.7
	$Fe_{61}Cr_{25}Co_{11}Zn_{2.5}Be_{0.5}$	990	13.2	11.5
	$Fe_{60}Cr_{25}Co_{11}Mn_{0.5}P_{0.5}A\ell_{3}$	690	14.2	8.8
	$Fe_{60}Cr_{25}Co_{11}Mo_{2}W_{2}$	700	13.9	8.7
	$Fe_{59}Cr_{25}Co_{11}Mo_{3}Hf_{2}$	920	12.5	10.2
	$Fe_{56}Cr_{23.5}Co_{11}MM_{9.0}B_{0.5}$	800	12.7	9.0
	$Fe_{63}Cr_{10}Co_{11}Nd_{15.7}B_{0.3}$	690	13.0	8.2
	$Fe_{48}Cr_{10}Co_{11}Ce_{30}A\ell_{1}$	600	11.5	6.3
	$Fe_{46}Cr_{10}Co_{20}Sm_{20}A\ell_{2.5}B_{1.5}$	580	10.6	5.5
Comparative Example	$Fe_{61}Cr_{25}Co_{11}A\ell_{2}Si_{1}$	420	13.1	3.3
	$Fe_{60}Cr_{25}Co_{11}Mo_{2}W_{2}$	410	13.5	2.8
	$Fe_{56}Cr_{23.5}Co_{11}MM_{9.0}B_{0.5}$	400	12.1	3.2

* Note) MM ··· Misch Metal

Example 7

An ingot was produced from a metl of $Fe_{61}Cr_{25}Co_{11}A\ell_{2}Si_{1}$ alloy composition in the usual manner, which was hot rolled to a thickness of 2 mm. The resulting hot rolled sheet was annealed at 900°C for 5 minutes, cold rolled at a draft shown in the following Table 6, subjected to recrystallization annealing at a temperature shown in Table 6 for about 1 hour, and then rapidly cooled. Then, a set of 20 to 50 cold rolled sheets piled one upon the other was subjected to two-phase separation annealing at 670°C for about 1 hour while applying a magnetic field of 3 kOe in the rolling direction, rapidly cooled down to 620°C, slowly cooled from 620°C to 500°C over 50 hours and then cooled in air. The maximum energy product (BH)max of the thus obtained sheet set was measured to obtain results as shown in Table 6.

Table 6

Annealing condition / Draft (%)	(BH)max (MGOe) recrystallization temperature (°C) (annealing time: 1 hr)					
	700	800	1000	1200	1300	1350
0	1.8	2.5	3.1	2.9	3.2	3.2
10	1.8	2.6	3.0	2.8	2.8	3.2
20	2.0	2.6	3.1	2.9	3.0	2.9
30	3.0	4.5	4.9	5.3	4.8	3.5
50	3.1	5.5	8.2	9.8	6.1	3.8
70	3.5	5.6	10.7	9.0	6.8	3.1
90	3.4	4.9	8.8	8.8	5.2	3.1
95	3.4	4.5	5.8	5.5	4.7	3.0
97	3.3	3.0	2.9	2.8	2.5	2.7

Example 8

An ingot was produced from a melt of $Fe_{61.8}Cr_{25}Co_{10}Mo_{3}Sb_{0.07}Mn_{0.07}Se_{0.03}C_{0.03}$ alloy composition, which was hot rolled to a thickness of 2 mm in the usual manner. Then, the resulting hot rolled sheet was annealed at 900°C for 5 minutes, cold rolled at a draft shown in the following Table 7 and then subjected to recrystallization annealing under conditions shown in Table 7. Then, a set of 20 to 50 cold rolled sheets piled one upon the other was subjected to two-phase separation annealing at 680°C for about 1 hour while applying a magnetic field of 3 kOe in the rolling direction, rapidly cooled down to 640°C, slowly cooled from 640°C to 500°C over 50 hours, and then cooled in air. The maximum energy product (BH)max of the thus obtained sheet set was measured to obtain results as shown in Table 7.

Table 7

Annealing condition / Draft (%)	(BH)max (MGOe) recrystallization temperature (°C) (annealing time: 1 hr)					
	700	800	1000	1200	1300	1350
0	2.5	2.7	2.7	3.0	2.5	2.5
10	2.5	2.5	2.5	2.6	2.4	2.5
20	2.6	2.6	3.2	3.0	2.5	2.4
30	3.0	4.5	5.0	6.1	4.8	3.2
50	3.1	5.3	8.1	9.0	5.0	3.1
70	3.0	6.0	11.1	9.5	5.3	2.8
90	3.2	5.0	9.0	7.8	4.5	2.9
95	3.2	4.8	5.2	5.1	4.3	2.5
97	3.1	3.2	2.5	2.8	3.0	2.6

Example 9

A melt having an alloy composition shown in the following Table 8 was injected from an injection nozzle onto a contact portion between two rotating cooled rolls to form a rapidly solidified tape of about 0.5 mm in thickness and about 10 cm in width. Then, the resulting tape was immediately cold rolled to a thickness of about 0.1 mm, subjected to decarburization annealing at 1000°C, quenched and then subjected to normalizing annealing at 1200°C for 2 hours, whereby the content of each of C, S, Se and Te was reduced to not more than 0.003%. Thereafter, a set of 50 cold rolled tapes piled one upon the other was subjected to two-phase separation annealing at 670°C for about 1 hour while applying a magnetic field of 3 kOe in the rolling direction, rapidly cooled down to 600°C, slowly cooled from 600°C to 500°C over 50 hours and then cooled in air. The magnetic properties of the thus treated tape set were measured to obtain results as shown in Table 8.

Table 8

Chemical composition (wt%)	Magnetic properties		
	Hc (Oe)	Br (kG)	(BH)max (MGOe)
$Fe_{62.81}Cr_{25}Co_{10}A\ell_{1}Si_{1}Mn_{0.07}S_{0.04}C_{0.08}$	860	12.8	9.9
$Fe_{60.84}Cr_{25}Co_{10}Sn_{3}Mo_{1}Mn_{0.07}Se_{0.02}Te_{0.01}C_{0.06}$	1020	13.2	11.5
$Fe_{61.85}Cr_{25}Co_{10}Mo_{3}Sb_{0.05}As_{0.04}Bi_{0.01}C_{0.05}$	980	13.5	11.2
$Fe_{62.81}Cr_{24}Co_{9}W_{2}V_{1}Zr_{1}Mn_{0.06}S_{0.04}Sb_{0.08}C_{0.01}$	960	14.1	10.5
$Fe_{63.8}Cr_{24}Co_{9}Ti_{1}Nb_{1}Zn_{1}Mn_{0.06}S_{0.04}Se_{0.02}As_{0.04}C_{0.04}$	890	14.0	9.5
$Fe_{63.37}Cr_{10}Co_{10}Nd_{15.7}B_{0.3}Bi_{0.5}Sb_{0.1}C_{0.03}$	820	11.5	8.4

As seen from Examples 1-9, the crystal texture of $\{110\}\langle 001\rangle$ is highly aligned by the combination of rolling and heat treatment to effectively produce unidirectional magnetic anisotropy having a higher value of (BH)max.

Example 10

An ingot was produced from a melt of $Fe_{60}Cr_{25}Co_{15}$ alloy composition, which was hot rolled to a thickness of 3.0 mm in the usual manner. Then, the resulting hot rolled sheet was annealed at 1300°C for 30 minutes, cooled with water and then cold rolled at a draft of 90% to form a cold rolled sheet of 0.30 mm in thickness. A disc of 20 mm in diameter was punched out from the cold rolled sheet, which was subjected to two-phase separation annealing at 660°C for 60 minutes and further to age annealing at 600°C for 5 hours.

The thus obtained sheet had a higher value of coercive force Hc of 620 Oe in a direction of two easy magnetization directions and a magnetic torque curve shown in Fig. 4.

Example 11

A melt of $Fe_{60}Cr_{20}Co_{13}B_{0.5}Si_{6.5}$ alloy composition was injected from an injection nozzle onto a contact portion between two rotating rolls to form a rapidly solidified tape of 0.50 mm in thickness. This tape was cold rolled at a draft of 82% to a thickness of 0.09 mm, from which was punched out a disc of 20 mm in diameter. The resulting disc was subjected to two-phase separation annealing at 670°C for 60 minutes and further to multi-stage age annealing at 620°C for 1 hour and at 600°C for 2 hours.

The thus obtained disc-like tape had a higher value of coercive force Hc of 590 Oe in a direction of two easy magnetization directions and had the same magnetic torque curve as shown in Fig. 4.

Example 12

An ingot having an alloy composition as shown in the following Table 9 was hot rolled to a thickness of 3 mm in the usual manner. After the removal of scale, the hot rolled sheet was cold rolled at a draft of about 90% to a final thickness of 0.3 mm. As a result of an X-ray analysis, the crystal texture of the resulting cold rolled sheet had {100}<011> orientation. Thereafter, the cold rolled sheet was subjected to age annealing at 680°C for 90 minutes as a heat treatment. The magnetic properties of the thus treated sheet were measured in a clockwise direction at an angle of 45° with respect to the rolling direction to obtain results as shown in Table 9. Moreover, the measured results of non-rolled sheet as a comparative example are also shown in Table 9.

Table 9

	Chemical composition (wt%)	Br(kG)	Hc(Oe)	(BH)max (MGOe)
Comparative Example	$Fe_{47}Cr_{30}Co_{23}$	8.5	360	2.5
	$Fe_{46}Cr_{30}Co_{23}Al_{1}$	8.2	410	2.8
	$Fe_{44}Cr_{30}Co_{23}W_{3}$	9.1	400	3.1
	$Fe_{46.5}Cr_{30}Co_{23}V_{0.5}$	9.5	380	3.1
	$Fe_{45}Cr_{30}Co_{23}Nb_{2}$	8.9	385	2.9
	$Fe_{46}Cr_{30}Co_{23}Zr_{1}$	8.8	450	3.5
	$Fe_{55}Cr_{25}Co_{10}Sm_{10}$	9.6	430	3.7
	$Fe_{35}Cr_{25}Co_{10}Pr_{10}$	8.5	425	3.1
	$Fe_{50}Cr_{25}Co_{5}Pr_{10}Nd_{10}$	9.4	450	3.7
Acceptable Example	$Fe_{47}Cr_{30}Co_{23}$	12.1	610	6.8
	$Fe_{46}Cr_{30}Co_{23}Al_{1}$	12.7	650	7.6
	$Fe_{44}Cr_{30}Co_{23}W_{3}$	12.0	620	6.9
	$Fe_{46.5}Cr_{30}Co_{23}V_{0.5}$	12.9	650	5.7
	$Fe_{45}Cr_{30}Co_{23}Nb_{2}$	12.1	730	6.2
	$Fe_{46}Cr_{30}Co_{23}Zr_{1}$	11.9	750	6.4
	$Fe_{40}Cr_{28}C_{22}Mn_{1}$	10.9	750	5.5
	$Fe_{49.5}Cr_{28}Co_{22}Zn_{0.5}$	11.5	680	5.3
	$Fe_{49}Cr_{28}Co_{22}Sn_{1}$	12.0	630	5.0
	$Fe_{49.5}Cr_{28}Co_{22}P_{0.5}$	12.5	610	5.2
	$Fe_{48}Cr_{28}Co_{22}Ta_{2}$	11.6	620	4.8
	$Fe_{34}Cr_{35}Co_{30}Si_{1}$	11.1	750	5.8
	$Fe_{33.5}Cr_{35}Co_{30}Cu_{1.5}$	11.5	760	6.1
	$Fe_{34.5}Cr_{35}Co_{30}Be_{0.5}$	11.8	790	6.6
	$Fe_{62}Cr_{22}Co_{15}B_{1}$	12.9	660	6.0
	$Fe_{60}Cr_{22}Co_{15}Mo_{3}$	14.5	780	7.5
	$Fe_{61}Cr_{22}Co_{15}Hf_{2}$	14.9	760	7.6
	$Fe_{60}Cr_{22}Co_{15}Mo_{2}Ti_{1}$	14.5	800	8.2
	$Fe_{63}Cr_{25}Co_{10}Si_{1}Ti_{1}$	13.8	720	7.1
	$Fe_{55}Cr_{25}Co_{10}Sm_{10}$	13.8	660	6.6
	$Fe_{55}Cr_{25}Co_{10}Pr_{10}$	13.5	640	5.9
	$Fe_{50}Cr_{25}Co_{5}Pr_{10}Nd_{10}$	13.1	690	6.5

Example 13

An ingot of 10 kg was produced from a melt of $Fe_{57}Cr_{23}Co_{15}A\ell_3Ti_2$ alloy composition, which was hot rolled to a thickness of 3.0 mm. The resulting hot rolled sheet was cold rolled in a direction perpendicular to the longitudinal direction of the sheet to form a cold rolled sheet of 0.30 mm in thickness. A disc of 20 mm in diameter was immediately punched out from the cold rolled sheet without solution treatment, and subjected to two-phase separation annealing in a rotating magnetic field of 10 kOe at 660°C for 30 minutes and further to multi-stage age annealing at 580°C for 1 hour, at 560°C for 1 hour, at 540°C for 1 hour, at 520°C for 1 hour and at 500°C for 5 hours.

The coercive force Hc of the thus treated disc was measured together with the case of applying the magnetic field in one direction to obtain results as shown in the following Table 10.

Table 10

	Magnetic field	Hc(Oe)		
		$H_{/\!/}$	$H_{\perp}$	H_{rot}
Example 13	rotation	-	-	530
Comparative Example	unidirection	540	420	-

Example 14

A melt of $Fe_{61}Cr_{23}Co_{14}Mo_2$ alloy composition was injected from an injection nozzle onto a contact portion between two rotating rolls at a cooling rate of 10^4°C/sec to form a rapidly solidified tape of 0.50 mm in thickness. A ring of 30 mm in outer diameter and 10 mm in inner diameter was punched out from the tape, subjected to two-phase separation annealing in a rotating magnetic field of 10 kOe or a unidirectional magnetic field of 10 kOe or in the absence of magnetic field at 650°C for 60 minutes, held at 600°C for 24 hours without the application of magnetic field, cooled down to 500°C at a cooling rate of 10°C/hr and then subjected to age annealing at 500°C for 24 hours.

The measured results on the coercive force Hc of the thus treated ring are shown in the following Table 11.

Table 11

	Magnetic field	Hc(Oe)			
		none	$H_{/\!/}$	$H_{\perp}$	H_{rot}
Comparative Example	none	300	-	-	-
Comparative Example	unidirection	-	520	470	-
Example 14	rotation	-	-	-	500

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Example 15

A melt of $Fe_{57}Cr_{24}Co_{15}V_4$ alloy composition was rapidly solidified by a twin roll process to form a tape of 0.40 mm in thickness. A disc of 30 mm in diameter was punched out from the tape, subjected to two-phase separation annealing in a rotating magnetic field of 10 kOe or a unidirectional magnetic field of 10 kOe or in the absence of magnetic field at 680°C for 20 minutes, held at 600°C for 24 hours without the application of magnetic field, cooled down to 500°C at a cooling rate of 10°C/hr and then subjected to age annealing at 500°C for 24 hours.

The coercive forces Hc of the thus treated discs are shown in the following Table 12.

Table 12

	Magnetic field	Hc(Oe)			
		none	$H_{//}$	$H_{\perp}$	H_{rot}
Comparative Example	none	310	-	-	-
Comparative Example	unidirection	-	550	400	-
Example 15	rotation	-	-	-	510

Example 16

A melt of $Fe_{57}Cr_{24}Co_{15}W_4$ alloy composition was poured from a melting furnace into a mold. The resulting ingot was heated at 1300°C and then subjected to the usual hot rolling and cold rolling to form a thin sheet of 0.65 mm in thickness. After the thin sheet was subjected to a solution treatment at 1300°C, a ring of 30 mm in outer diameter and 10 mm in inner diameter was punched out therefrom, subjected to two-phase separation annealing in a rotating magnetic field of 10 kOe at 660°C for 10 minutes, held at 610°C for 24 hours without the application of magnetic field, cooled down to 500°C at a cooling rate of 10°C/hr and then subjected to age annealing at 500°C for 24 hours. The coercive force Hc of the thus treated ring is shown in the following Table 13.

For the comparison, the ring was subjected to the same two-phase separation annealing as described above in a unidirectional magnetic field or in the absence of magnetic field instead of the rotating magnetic field and then the coercive force of the thus treated ring was measured to obtain results as shown in Table 13.

Table 13

	Magnetic field	Hc(Oe)			
		$H_{/\!/}$	$H_{\perp}$	H_{rot}	none
Comparative Example	none	-	-	-	400-410
Comparative Example	unidirection	510	470	-	-
Example 16	rotation	-	-	490-500	-

Example 17

An ingot of 10 kg was produced from a melt of $Fe_{58}Cr_{22}Co_{15}V_5$ alloy composition, which was heated at 1300°C for 30 minutes and then subjected to the usual hot rolling and cold rolling to form a thin sheet of 0.40 mm in thickness. After the thin sheet was subjected to a solution treatment at 1250°C, a disc of 30 mm in diameter was punched out therefrom, subjected to two-phase separation annealing in a rotating magnetic field of 10 kOe or a unidirectional magnetic field of 10 kOe or in the absence of magnetic field at 650°C for 20 minutes, held at 600°C for 24 hours without the application of magnetic field, cooled down to 500°C at a cooling rate of 10°C/sec and then subjected to age annealing at 500°C for 12 hours.

The measured results on the coercive force of the thus treated discs are shown in the following Table 14.

Table 14

	Magnetic field	Hc(Oe)			
		$H_{//}$	$H_{\perp}$	H_{rot}	none
Comparative Example	none	-	-	-	350-400
Comparative Example	unidirection	480	400	-	-
Example 17	rotation	-	-	510-520	-

Example 18

A melt having an alloy composition as shown in the following Table 15 was injected from an injection nozzle onto a contact portion between two rotating cooled rolls to form a rapidly solidified tape of about 0.5 mm in thickness and about 10 cm in width. After the tape was shaped into a disc, a set of about 10 discs piled one upon the other was subjected to two-phase separation annealing in a rotating magnetic field of about 3 kOe at 670°C for about 1 hour, cooled from 600°C to 500°C over about 50 hours and then cooled in air. The magnetic properties of the thus treated disc set were measured to obtain results as shown in Table 15. For the comparison, the magnetic properties of the disc set subjected to the two-phase separation annealing in the absence of magnetic field are also shown in Table 15.

Table 15

	Chemical composition (wt%)	Magnetic properties		
		Hc(Oe)	Br(kG)	(BH)max (MGOe)
Acceptable Example	$Fe_{55}Cr_{30}Co_{15}$	510	11.5	4.0
	$Fe_{55}Cr_{25}Co_{15}Al_4Zn_1$	520	9.8	4.2
	$Fe_{55}Cr_{25}Co_{15}Al_3Sn_2$	530	8.7	5.0
	$Fe_{55}Cr_{25}Co_{15}Zr_3Ti_2$	510	8.9	4.0
	$Fe_{55}Cr_{25}Co_{15}Ta_3Mo_2$	490	9.0	3.6
	$Fe_{55}Cr_{25}Co_{15}Nb_3W_2$	490	10.2	3.8
	$Fe_{61.5}Cr_{25}Co_{12}B_{1.0}Cu_{0.5}$	480	11.8	3.5
	$Fe_{61.5}Cr_{25}Co_{12}Hf_{1.0}Be_{0.5}$	470	12.1	3.5
	$Fe_{60}Cr_{22}Co_{8.0}Nd_{9.0}B_{1.0}$	500	10.9	3.8
	$Fe_{57}Cr_{22}Co_{8.0}Pr_{12}B_{1.0}$	520	10.5	4.5
	$Fe_{51}Cr_{22}Co_{7.0}Sm_{10}Nd_{10}$	580	8.2	5.5
	$Fe_{51}Cr_{22}Co_{7.0}Y_{10}Sm_{10}$	570	8.5	5.2
Comparative Example	$Fe_{55}Cr_{25}Co_{15}Al_4Zn_1$	360	10.1	2.6
	$Fe_{61.5}Cr_{25}Co_{12}B_1Cu_{0.5}$	350	10.9	2.8
	$Fe_{60}Cr_{22}Co_{8.0}Nd_9B_1$	300	11.8	2.2
	$Fe_{51}Cr_{22}Co_{7.0}Y_{10}Sm_{10}$	280	12.5	1.5

Example 19

An ingot having an alloy composition as shown in the following Table 16 was hot rolled in the usual manner at a final temperature of about 800°C to form a hot rolled sheet of 1 mm in thickness. Then, the resulting sheet was subjected to a solution treatment by annealing at 1250°C for 1 hour and quenching. The thus treated sheet was shaped into a disc and subjected to two-phase separation annealing in a rotating magnetic field of about 3 kOe at 675°C for about 50 minutes. Thereafter, the disc was cooled from 650°C to 500°C over about 50 hours and then cooled in air. The magnetic properties of the thus treated disc were measured to obtain results as shown in Table 16. For the comparison, the magnetic properties of the disc without the solution treatment are also shown in Table 16.

Table 16

	Chemical composition (wt%)	Magnetic properties		
		Hc(Oe)	Br(kG)	(BH)max (MGOe)
Acceptable Example	$Fe_{55}Cr_{30}Co_{15}$	480	10.5	3.2
	$Fe_{55}Cr_{25}Co_{15}Al_{4}Zn_{1}$	500	9.2	3.8
	$Fe_{55}Cr_{25}Co_{15}Al_{3}Sn_{2}$	520	8.5	4.2
	$Fe_{55}Cr_{25}Co_{15}Zr_{3}Ti_{2}$	510	8.6	4.0
	$Fe_{55}Cr_{25}Co_{15}Ta_{3}Mo_{2}$	470	8.9	3.7
	$Fe_{55}Cr_{25}Co_{15}Nb_{3}W_{2}$	460	9.5	3.5
	$Fe_{61.5}Cr_{25}Co_{12}B_{1.0}Cu_{0.5}$	480	9.8	3.5
	$Fe_{61.5}Cr_{25}Co_{12}Hf_{1.0}Be_{0.5}$	470	10.2	3.6
	$Fe_{60}Cr_{22}Co_{8.0}Nd_{9.0}B_{1.0}$	490	9.2	4.0
	$Fe_{57}Cr_{22}Co_{8.0}Pr_{12}B_{1.0}$	500	9.1	4.3
	$Fe_{51}Cr_{22}Co_{7.0}Sm_{10}Nd_{10}$	550	7.8	4.6
	$Fe_{51}Cr_{22}Co_{7.0}Y_{10}Sm_{10}$	550	7.5	4.5
Comparative Example	$Fe_{55}Cr_{25}Co_{15}Al_{4}Zn_{1}$	330	9.7	2.7
	$Fe_{61.5}Cr_{25}Co_{12}B_{1}Cu_{0.5}$	320	9.9	2.3
	$Fe_{60}Cr_{22}Co_{8.0}Nd_{9}B_{1}$	270	10.2	1.9
	$Fe_{51}Cr_{22}Co_{7.0}Y_{10}Sm_{10}$	220	11.1	1.3

As seen from Examples 13-19, according to the invention, there can be obtained permanent magnets having a radial anisotropy in plane, which have hardly be obtained in the conventional technique. Particularly, when the rapidly solidified tape is used as a base plate, the solution treatment may be omitted, resulting in the simplification of steps and the energy-saving.

Example 20

A melt having an alloy composition as shown in the following Table 17 was rapidly solidified by a twin roll process to form a tape of 0.5 mm in thickness and 20 mm in width. Then, the resulting tape was subjected to two-stage rolling at first and second drafts shown in Table 17 through an intermediate annealing in N_2 atmosphere at 830°C for 6 minutes to obtain a rolled tape of 0.1 mm in thickness.

Thereafter, the rolled tape was heated at 1180°C, subjected to two-phase separation annealing under a vacuum of 2×10^{-3} Torr for 3 hours, cooled with water and then subjected to age annealing at 680°C for 90 minutes.

The magnetic properties of the thus treated tape having a highly aligned {100}<001> orientation were measured in only the rolling direction (or longitudinal direction of the tape) to obtain results as shown in Table 17. For the comparison, the magnetic properties of the rapidly solidified tape of 0.1 mm in thickness, which was subjected only to the age annealing without rolling and separation annealing, are also shown in Table 17.

Table 17(a)

	Chemical composition (wt%)	Draft at rolling (%)		Residual magnetic flux density (kG)	Coercive force (Oe)
		first	second		
Comparative Example	$Fe_{47}Cr_{30}Co_{23}$	-	-	11.5	550
	$Fe_{46}Cr_{30}Co_{23}Al_{1}$	-	-	11.5	605
	$Fe_{44}Cr_{30}Co_{23}W_{3}$	-	-	10.3	600
	$Fe_{46.5}Cr_{30}Co_{23}V_{0.5}$	-	-	11.0	580
	$Fe_{45}Cr_{30}Co_{23}Nb_{2}$	-	-	9.5	690
	$Fe_{46}Cr_{30}Co_{23}Zr_{1}$	-	-	9.7	650
Acceptable Example	$Fe_{47}Cr_{30}Co_{23}$	50	60	12.0	610
	$Fe_{46}Cr_{30}Co_{23}Al_{1}$	50	60	12.1	630
	$Fe_{44}Cr_{30}Co_{23}W_{3}$	50	60	11.0	790
	$Fe_{46.5}Cr_{30}Co_{23}V_{0.5}$	50	60	11.5	650
	$Fe_{45}Cr_{30}Co_{23}Nb_{2}$	20	75	10.6	710
	$Fe_{46}Cr_{30}Co_{23}Zr_{1}$	20	75	11.3	740

Table 17(b)

	Chemical composition (wt%)	Draft at rolling (%)		Residual magnetic flux density (kG)	Coercive force (Oe)
		first	second		
Acceptable Example	$Fe_{49}Cr_{28}Co_{22}Mn_{1}$	20	75	9.5	770
	$Fe_{49.5}Cr_{28}Co_{22}Zn_{0.5}$	60	50	10.9	630
	$Fe_{39}Cr_{38}Co_{22}Sn_{1}$	60	50	11.0	650
	$Fe_{49.5}Cr_{28}Co_{22}P_{0.5}$	60	50	12.3	590
	$Fe_{34}Cr_{35}Co_{30}Si_{1}$	10	78	9.0	800
	$Fe_{62}Cr_{22}Co_{15}B_{1}$	10	78	12.6	600
	$Fe_{60}Cr_{22}Co_{15}Mo_{3}$	40	67	14.0	720
	$Fe_{60}Cr_{22}Co_{15}Mo_{2}Ti_{1}$	40	67	14.2	710
	$Fe_{63}Cr_{25}Co_{10}Si_{1}Ti_{1}$	40	67	13.8	660
	$Fe_{65}Cr_{22}Co_{12}C_{1}$	30	71	12.9	690
	$Fe_{63.5}Cr_{24}Co_{10}A\ell_{2}Zr_{0.5}$	30	71	13.4	640

Example 21

A melt having an alloy composition as shown in the following Table 18 was rapidly solidified by a twin roll process to form a tape of 0.2 mm in thickness and 30 mm in width. The resulting tape was rolled to a thickness of 0.15 mm (draft: 25%), annealed in H_2+N_2 atmosphere at 870°C for 3 minutes and further rolled to a thickness of 0.07 mm (draft: about 53%). The thus treated tape was annealed in a hydrogen atmosphere at 1250°C for 2 hours, cooled with water and subjected to two-phase separation annealing at 690°C for 60 minutes while applying a magnetic field of 2 kOe in a direction perpendicular to the longitudinal direction of the tape and further to age annealing at 530°C for 10 hours.

The magnetic properties of the thus obtained tape were measured to obtain results as shown in Table 18. For the comparison, the magnetic properties of the rapidly solidified tape of 0.1 mm in thickness, which was subjected only to the age annealing without rolling and separation annealing, are also shown in Table 18.

Table 18

	Chemical composition (wt%)	Br(kG)	Hc(Oe)
Comparative Example	$Fe_{68}Cr_{22}Co_{10}$	14.0	630
	$Fe_{61}Cr_{26}Co_{11}V_1Nb_1$	13.9	660
	$Fe_{61}Cr_{23}Co_{15}Zr_1$	14.5	770
	$Fe_{52}Cr_{22}Co_{25}Si_1$	15.4	620
	$Fe_{59}Cr_{30}Co_{10}Mo_1$	13.5	650
Acceptable Example	$Fe_{68}Cr_{22}Co_{10}$	15.1	780
	$Fe_{61}Cr_{26}Co_{11}V_1Nb_1$	15.2	800
	$Fe_{61}Cr_{23}Co_{15}Zr_1$	15.6	790
	$Fe_{52}Cr_{22}Co_{25}Si_1$	15.4	770
	$Fe_{59}Cr_{30}Co_{10}Mo_1$	14.9	800
	$Fe_{64.5}Cr_{25}Co_{10}Mn_{0.5}$	14.8	790
	$Fe_{66}Cr_{22}Co_{10}Ti_2$	14.5	820
	$Fe_{66.5}Cr_{22}Co_{10}Si_1B_{0.5}$	13.7	760
	$Fe_{66}Cr_{22}Co_{10}Si_1Al_1$	13.3	730
	$Fe_{66.9}Cr_{22}Co_{10}C_{0.1}Nb_1$	14.1	810
	$Fe_{66.7}Cr_{22}Co_{10}P_{0.8}Zn_{0.5}$	13.9	780
	$Fe_{65.3}Cr_{22}Co_{10}V_{0.7}P_1Mo_1$	14.0	790

Example 22

A melt having an alloy composition as shown in the following Table 19 was rapidly solidified by a twin roll process to form a tape of 0.5 mm in thickness. Then, the resulting tape was subjected to two-stage rolling at first and second drafts shown in Table 19 through an intermediate annealing in N_2 atmosphere at

830°C for 6 minutes to obtain a rolled tape of 0.1 mm in thickness. This rolled tape was subjected to two-phase separation annealing at 690°C for 60 minutes while applying a magnetic field of 2 kOe in a direction perpendicular to the longitudinal direction of the tape and further to age annealing at 530°C for 10 hours.

The magnetic properties of the thus obtained tape were measured to obtain results as shown in Table 19. For the comparison, the magnetic properties of the rapidly solidified tape of 0.1 mm in thickness, which was subjected only to the age annealing without the rolling and separation annealing, are also shown in Table 19.

Table 19(a)

	Chemical composition (wt%)	Draft at rolling (%)		Residual magnetic flux density (kG)	Coercive force (Oe)	(BH)max (MGOe)
		first	second			
Comparative Example	$Fe_{47}Cr_{30}Co_{23}$			10.8	455	4.1
	$Fe_{46}Cr_{30}Co_{23}Al_{1}$			11.3	520	4.2
	$Fe_{44}Cr_{30}Co_{23}W_{3}$			11.9	495	4.5
	$Fe_{46.5}Cr_{30}Co_{23}V_{0.5}$			11.8	490	4.3
	$Fe_{45}Cr_{30}Co_{23}Nb_{2}$			11.7	480	4.1
	$Fe_{46}Cr_{30}Co_{23}Zr_{1}$			11.0	560	4.8
	$Fe_{45}Cr_{25}Co_{10}Sm_{10}$			11.6	540	4.6
	$Fe_{55}Cr_{25}Co_{10}Pr_{10}$			11.4	410	4.7
	$Fe_{50}Cr_{25}Co_{5}Pr_{10}Nd_{10}$			11.9	430	4.9

Table 19(b)

	Chemical composition (wt%)	Draft at rolling (%)		Residual magnetic flux density (kG)	Coercive force (Oe)	(BH)max (MGOe)
		first	second			
Acceptable Example	$Fe_{47}Cr_{30}Co_{23}$	50	60	12.2	620	6.9
	$Fe_{46}Cr_{30}Co_{23}Al_{1}$	50	60	12.8	635	7.5
	$Fe_{44}Cr_{30}Co_{23}W_{3}$	50	60	12.3	610	6.8
	$Fe_{46.5}Cr_{30}Co_{23}V_{0.5}$	50	60	12.9	645	5.9
	$Fe_{45}Cr_{30}Co_{23}Nb_{2}$	20	75	12.5	740	6.1
	$Fe_{46}Cr_{30}Co_{23}Zr_{1}$	20	75	12.4	760	6.4
	$Fe_{49}Cr_{28}C_{22}Mn_{1}$	20	75	11.5	740	5.3
	$Fe_{49.5}Cr_{28}Co_{22}Zn_{0.5}$	60	50	11.8	690	5.4
	$Fe_{49}Cr_{28}Co_{22}Sn_{1}$	60	50	12.3	640	5.2
	$Fe_{49.5}Cr_{28}Co_{22}P_{0.5}$	60	50	12.5	620	5.0
	$Fe_{48}Cr_{28}Co_{22}Ta_{2}$	60	50	12.4	620	4.9

Table 19(c)

	Chemical composition (wt%)	Draft at rolling (%)		Residual magnetic flux density (kG)	Coercive force (Oe)	(BH)max (MGOe)
		first	second			
Acceptable Example	$Fe_{34}Cr_{35}Co_{30}Si_{1}$	10	78	11.8	760	5.6
	$Fe_{33.5}Cr_{35}Co_{30}Cu_{1.5}$	10	78	11.6	750	6.2
	$Fe_{34.5}Cr_{35}Co_{30}Be_{0.5}$	10	78	12.3	780	6.5
	$Fe_{62}Cr_{22}Co_{15}B_{1}$	10	78	13.5	670	6.0
	$Fe_{60}Cr_{22}Co_{15}Mo_{3}$	40	67	14.6	790	7.4
	$Fe_{61}Cr_{22}Co_{15}Hf_{2}$	40	67	14.9	760	7.7
	$Fe_{66}Cr_{22}Co_{15}Mo_{2}Ti_{1}$	40	67	14.6	790	8.1
	$Fe_{63}Cr_{25}Co_{10}Si_{1}Ti_{1}$	40	67	14.5	740	7.2
	$Fe_{55}Cr_{25}Co_{10}Sm_{10}$	40	67	14.2	680	6.9
	$Fe_{55}Cr_{25}Co_{10}Pr_{10}$	40	67	13.9	650	6.0
	$Fe_{50}Cr_{25}Co_{5}Pr_{10}Nd_{10}$	40	67	13.7	685	6.4

As seen from Examples 20-22, according to the invention, there can be provided permanent magnets having excellent magnetic properties in the longitudinal, widthwise and thickness directions.

Example 23

A melt of $Fe_{65}Cr_{22}Co_{12}Mn_1$ alloy composition was rapidly solidified by a twin roll process under conditions that the injection pressure was 1.5 atm, the injection amount was 0.5 kg/sec and the revolution number was 1200 rpm or 700 rpm to obtain a tape A of 0.3 mm in thickness or a tape B of 0.5 mm in thickness.

The rate of columnar grain at as-cast state was about 80% in the tape A or about 28% in the tape B.

Each of these tapes A and B was subjected to recrystallization annealing at 1000°C for 10 minutes, two-phase separation annealing at 660°C for 10 minutes while applying a magnetic field of 2 kOe in a direction perpendicular to the plane of the tape, and multi-stage age annealing at 600°C for 5 hours, at 575°C for 5 hours, at 550°C for 5 hours and at 500°C for 10 hours.

When the magnetomotive force of the thus treated tape was measured by means of a gauss meter, the tape A was 600 G, while the tape B was 350 G. From these results, it is apparent that the easy magnetization axis is aligned in the direction perpendicular to the plane of the tape in the tape A rather than in the tape B.

Example 24

A melt of $Fe_{60}Cr_{23}Co_{15}Si_1$ alloy composition was rapidly solidified by a twin roll process under conditions that the injection pressure was 1.6 atm, the injection amount was 0.6 kg/sec and the revolution number of the roll was 300 rpm, 600 rpm or 1200 rpm to obtain a tape C of 0.20 mm in thickness, a tape D of 0.35 mm in thickness or a tape E of 0.52 mm in thickness.

The columnar grain rates of these tapes C, D and E were 95%, 58% and 28%, respectively.

Each of these tapes C, D and E was subjected to recrystallization annealing at 980°C for 12 minutes, two-phase separation annealing at 665°C for 10 minutes while applying a magnetic field of 2 kOe in a direction perpendicular to the plane of the tape, and multi-stage age annealing at 600°C for 5 hours, at 575°C for 5 hours, at 550°C for 5 hours and at 500°C for 10 hours.

When the magnetomotive force of the thus treated tape was measured by means of a gauss meter, the tapes C and D were 600 G, while the tape E was only 370 G.

Example 25

A melt of $Fe_{65}Cr_{20}Co_{15}$ alloy composition was rapidly solidified by a twin roll process to form a tape of 0.5 mm in thickness. The resulting tape was subjected to two-phase separation annealing at 650°C for 30 minutes while applying a magnetic field of 10 kOe in the thickness direction of the tape without the solution treatment and further to age annealing at 560°C for 50 hours. The maximum energy product (BH)max of the thus treated tape was 3.5 MOe.

Then, the tape was toroidally wound twice to form a ring, which was easily magnetized so as to exhibit S pole in the inside of the ring and N pole in the outside thereof.

Example 26

A melt having an alloy composition as shown in the following Table 20 was injected from an injection nozzle onto a contact portion between two rotating cooled rolls to form a rapidly solidified tape of 0.5 mm in thickness and 10 cm in width. After a disc of 20 mm in diameter was punched out from the tape, a set of 100 discs piled one upon the other was subjected to two-phase separation annealing at 665°C for 30 minutes while applying a magnetic field of 10 kOe in the piled direction of the tape, cooled from 640°C to 500°C over 50 hours and then cooled in air. The magnetic properties of the thus treated tape set were measured to obtain results as shown in Table 20. For the comparison, the magnetic properties of the thin sheets, which were produced from the same melt through ingot making, hot rolling and cold rolling and subjected to the same heat treatment as mentioned above, are also shown in Table 20.

Table 20

	Chemical composition (wt%)	Magnetic properties		
		Hc(Oe)	Br(kG)	(BH)max (MGOe)
Acceptable Example	$Fe_{60}Cr_{24}Co_{16}$	580	13.8	4.0
	$Fe_{60}Cr_{30}Co_{10}$	550	13.6	4.2
	$Fe_{60}Cr_{24}Co_{13}Sn_{3}$	620	13.1	5.2
	$Fe_{60}Cr_{24}Co_{13}A\ell_{3}$	600	13.5	5.3
	$Fe_{60}Cr_{24}Co_{13}Ta_{3}$	630	13.1	5.7
	$Fe_{60}Cr_{24}Co_{13}Hf_{2}Cu_{1.0}$	680	12.8	6.0
	$Fe_{60}Cr_{24}Co_{13}Zr_{2}Zn_{1.0}$	660	13.0	5.9
	$Fe_{61}Cr_{23}Co_{13}A\ell_{2}B_{1.0}$	670	13.2	6.0
	$Fe_{61}Cr_{23}Co_{13}Si_{2}B_{1.0}$	700	13.3	5.9
	$Fe_{59}Cr_{17}Co_{10}Nd_{13}B_{1.0}$	720	11.5	6.6
	$Fe_{53}Cr_{17}Co_{10}Pr_{15}Nd_{5}$	750	10.9	6.7
	$Fe_{57}Cr_{17}Co_{10}Y_{15}B_{1.0}$	720	11.2	6.5
	$Fe_{57}Cr_{17}Co_{10}Pr_{15}B_{1.0}$	710	11.5	6.2
Comparative Example	$Fe_{60}Cr_{24}Co_{13}A\ell_{3}$	300	10.2	2.5
	$Fe_{60}Cr_{24}Co_{13}Hf_{2}Cu_{1}$	310	10.1	2.4
	$Fe_{59}Cr_{17}Co_{10}Nd_{13}B_{1}$	340	9.8	2.1

Example 27

A melt having an alloy composition as shown in the following Table 21 was rapidly solidified by a twin roll process to form a tape of 0.4 mm in thickness and 10 cm in width. In this case, the tape having a columnar grain rate of 0-100% was formed by varying the cooling conditions. After the resulting tape was subjected to recrystallization annealing at 1200°C and quenched, a disc of 20 mm in diameter was punched out from the tape. A set of 100 discs piled one upon the other was subjected to a two-phase separation annealing at 665°C for 30 minutes while applying a magnetic field of 10 kOe in the piled direction of the tape, cooled from 640°C to 500°C over 50 hours and then cooled in air. The maximum energy product (BH)max of the thus treated disc set was measured to obtain a results as shown in Table 21.

Table 21

Chemical composition (wt%)	(BH)max (MGOe)					
	Columnar grain rate (%)					
	0	20	30	50	70	100
$Fe_{51}Cr_{28}Co_{17}Sn_4$	3.5	3.8	4.8	5.0	5.1	5.0
$Fe_{51}Cr_{28}Co_{17}Ta_3Zn_1$	3.6	3.6	5.2	5.5	5.4	5.4
$Fe_{51}Cr_{28}Co_{17}Mo_3B_1$	2.8	3.9	6.2	6.0	6.1	6.0
$Fe_{51}Cr_{28}Co_{17}W_3B_1$	2.8	3.5	6.2	6.3	6.4	6.4
$Fe_{51}Cr_{28}Co_{17}Zr_3B_1$	3.0	3.2	5.5	5.7	5.8	5.9
$Fe_{55}Cr_{22}Co_{12}Sm_{10}B_1$	3.6	3.4	5.0	5.3	5.3	5.1
$Fe_{55}Cr_{22}Co_{12}Nd_{10}B_1$	3.5	3.5	5.0	5.0	5.0	5.2
$Fe_{55}Cr_{22}Co_{12}Pr_{10}B_1$	3.5	3.8	5.1	5.0	5.1	5.1
$Fe_{55}Cr_{22}Co_{12}Hf_{10}B_1$	3.4	3.7	5.2	5.2	5.3	5.3
$Fe_{62}Cr_{22}Co_{12}Ti_3B_1$	3.4	3.7	5.8	5.7	5.9	5.8
$Fe_{58}Cr_{28}Co_{12}Mn_1Ti_1$	3.2	3.6	4.8	5.1	5.3	5.3
$Fe_{56}Cr_{28}Co_{12}Mn_3A\ell_1$	2.8	2.9	4.2	5.0	4.8	4.8
$Fe_{59.5}Cr_{23}Co_{17.5}$	3.0	3.0	4.5	4.4	4.5	4.6
$Fe_{54.5}Cr_{28}Co_{17.5}$	2.9	3.2	4.8	4.9	5.2	5.2

As seen from Examples 23 to 27, in the Fe-Cr-Co series permanent magnet, the easy magnetization axis can be aligned in a direction perpendicular to plane by positively utilizing the arrangement of crystal texture inherent to the rapid solidification process. Further, since the direction of magnetic field applied in the two-phase separation annealing is coincident with the direction perpendicular to the plane, plate-like permanent magnets having improved magnetic properties in the direction perpendicular to the plane can easily be produced in an industrial scale. Moreover, when the plate-like magnet material is wound into a toroidal ring having optional width, thickness and diameter, such a ring exhibits a radial anisotropy, so that the magnetization in radial direction of ring is easy.

Claims

1. A method of producing a two-phase separation type Fe-Cr-Co series permanent magnet, which comprises melting a two-phase separation type alloy of the following formula:

$$Fe_{100-x-y}Cr_xCo_y \quad \text{or}$$

$$Fe_{100-x-y-z}Cr_xCo_yM_z$$

, wherein M is at least one element selected from the group consisting of Ti, Zr, V, Nb, Ta, Mo, B, W, Aℓ, Cu, Si, Sn, P, Mn, Zn, Be, Hf and rare earth elements, x is 3 to 40 wt%, y is 2 to 40 wt% and z is 0.01 to 35 wt% in total, subjecting the resulting melt to a rapid solidification process to form a metallic tape, and then subjecting the resulting tape to a heat treatment within a given temperature range.

2. A method of producing a two-phase separation type Fe-Cr-Co series permanent magnet, which comprises melting a two-phase separation type alloy of the following formula:

$$Fe_{100-x-y}Cr_xCo_y \quad \text{or}$$

$$Fe_{100-x-y-z}Cr_xCo_yM_z$$

, wherein M is at least one element selected from the group consisting of Ti, Zr, V, Nb, Ta, Mo, B, W, Aℓ, Cu, Si, Sn, P, Mn, Zn, Be, Hf and rare earth elements, x is 3 to 40 wt%, y is 2 to 40 wt% and z is 0.01 to 35 wt% in total, subjecting the resulting melt to usual ingot making-slabbing or continuous casting, hot rolling and cold rolling process to form a thin sheet, and then subjecting the resulting sheet to a heat treatment within a given temperature range.

3. The method according to claim 1 or 2, wherein said tape or sheet made from said melt of the given alloy composition is rolled at a draft of 30-95% prior to the heat treatment and then subjected to a recrystallization annealing at a temperature of 800-1300°C, a two-phase separation annealing in a magnetic field at a temperature of 600-750°C and an age annealing at a temperature below the separation annealing temperature in this order as the heat treatment to highly align {100}<001> orientation.

4. The method according to claim 3, wherein said melt further contains 0.005-0.06 wt% of C and 0.01-0.15 wt% in total of at least one of S, Se and Te, and said tape or sheet is subjected to a decarburization annealing at 800-1300°C after the rolling and before the heat treatment.

5. The method according to claim 3, wherein said melt further contains 0.005-0.06 wt% of C and 0.003-0.30 wt% in total of at least one of Bi, Sb and As, and said tape or sheet is subjected to a decarburization annealing at 800-1300°C after the rolling and before the heat treatment.

6. The method according to claim 3, wherein said melt further contains 0.005-0.06 wt% of C, 0.005-0.10 wt% in total of at least one of S, Se and Ti and 0.003-0.30 wt% in total of at least one of Bi, Sb and As, and said tape or sheet is subjected to a decarburization annealing at 800-1300°C after the rolling and before the heat treatment.

7. The method according to claim 1 or 2, wherein said tape or sheet made from said melt of the given alloy composition is rolled at a draft of not less than 40% prior to the heat treatment and then subjected to a two-phase separation annealing at a temperature of 500-750°C as the heat treatment to highly align {100}<011> orientation.

8. The method according to claim 1 or 2, wherein said tape or sheet made from said melt of the given alloy composition is subjected to a two-phase separation annealing in a magnetic field at a temperature of 600-750°C while rotating a direction of the magnetic field applied to the tape or sheet in a plane parallel thereto and an age annealing at a temperature below the separation annealing temperature in this order as the heat treatment to align an easy magnetization axis in radial direction of the plane.

9. The method according to claim 8, wherein said tape or sheet is subjected to a solution treatment at a temperature of 900-1300°C prior to the heat treatment.

10. The method according to claim 1 or 2, wherein said tape or sheet after the hot rolling made from said melt of the given alloy composition is subjected to two-stage cold rolling at a first draft of not less than 10% and a second draft of 50-80% through an intermediate annealing prior to the heat treatment and then subjected to a recrystallization annealing at a temperature of 800-1300°C and an age annealing at a temperature of 500-750°C as the heat treatment to highly align {100}<001> orientation.

11. The method according to claim 1 or 2, wherein said tape made from said melt of the given alloy composition is subjected to a two-phase separation annealing in a magnetic field at a tmperature of 600-750°C while applying the magnetic field in a direction perpendicular to the plane of the tape and an age annealing at a temperature below the separation annealing temperatue as the heat treatment to align an easy magnetization axis in the direction perpendicular to the plane of the tape.

12. The method according to claim 11, wherein said tape contains at least 30% of columnar grain by adjustment of cooling conditions in the tape formation and is subjected to a recrystallization annealing at a temperature of 800-1300°C prior to the heat treatment.

FIG_1

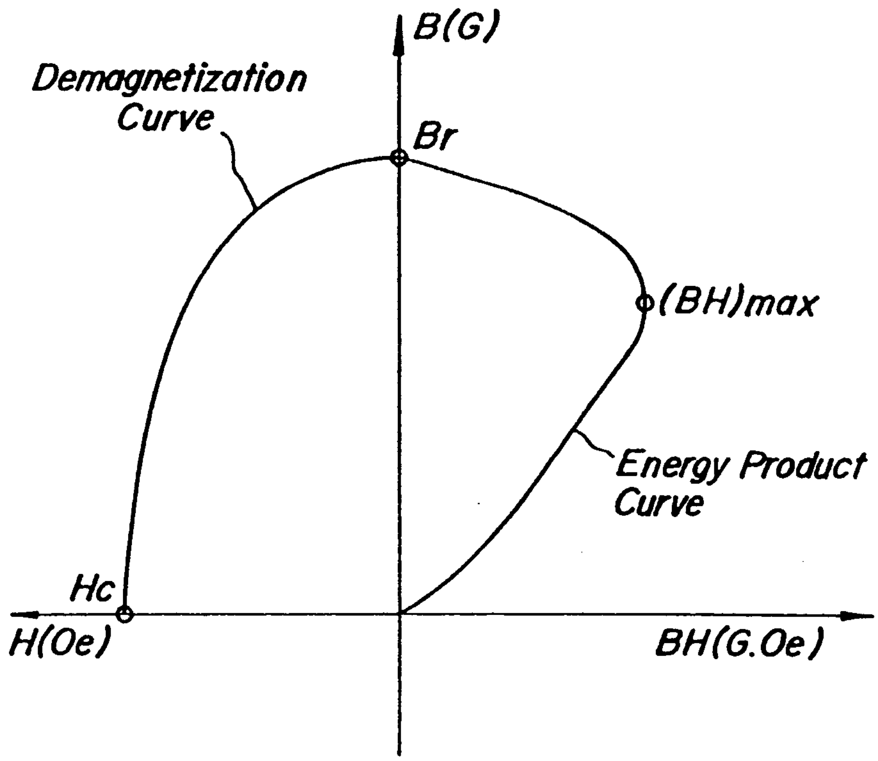

B(G)
Demagnetization Curve
Br
(BH)max
Energy Product Curve
Hc
H(Oe)
BH(G.Oe)

FIG.2

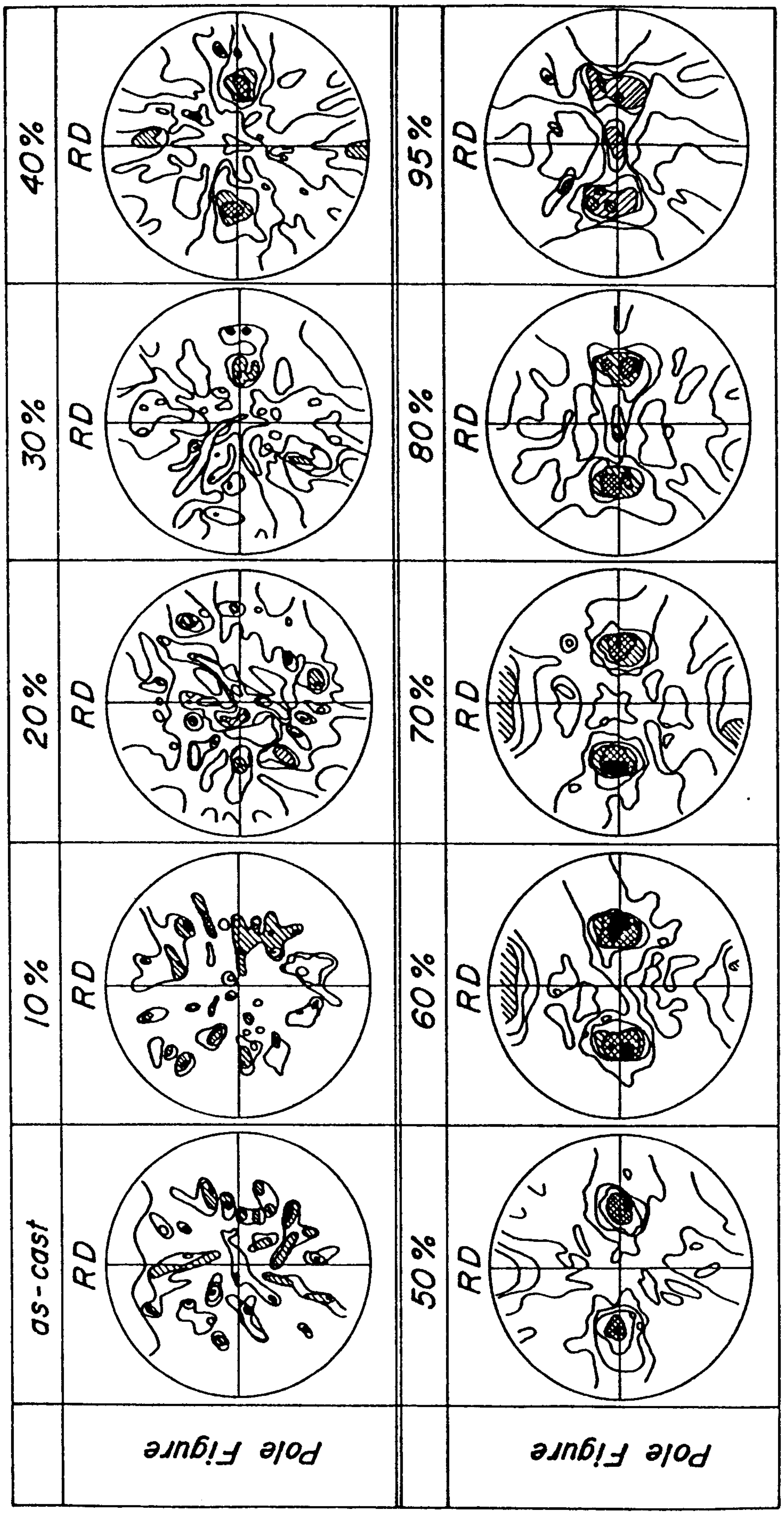
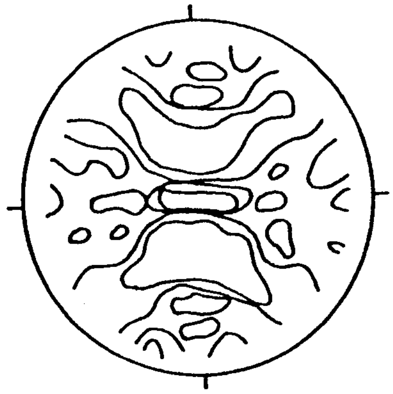
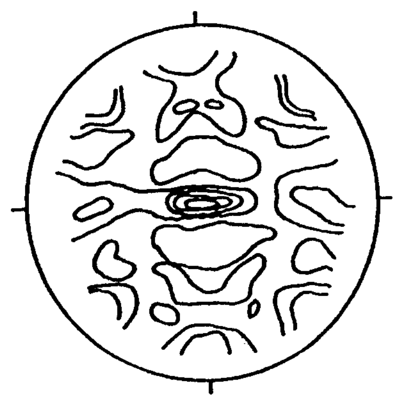


FIG_3a



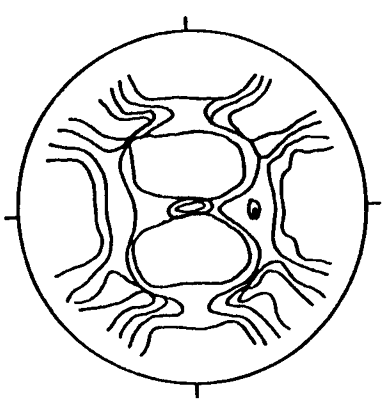
Draft: 0 %

FIG_3b



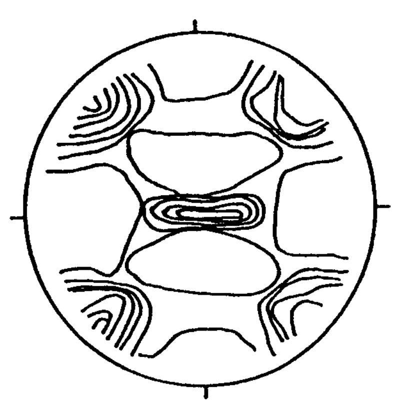
Draft: 40 %

FIG_3c



Draft: 85 %

FIG_3d



Draft: 95 %

FIG_4

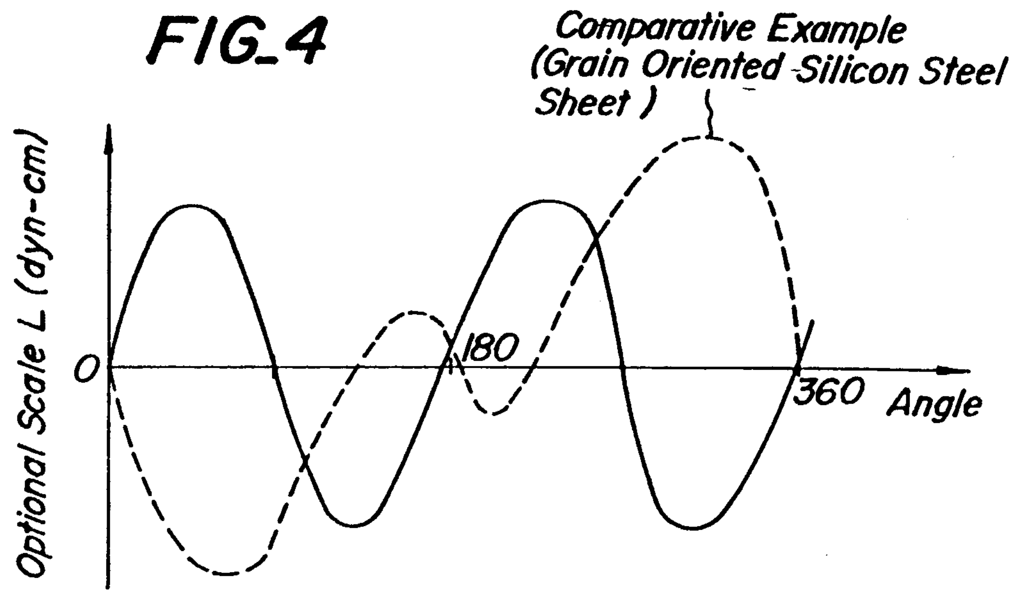


FIG_5a

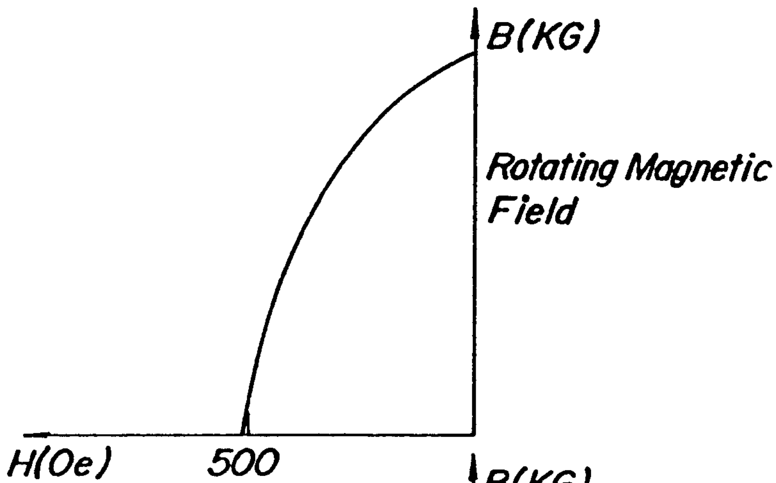


FIG_5b

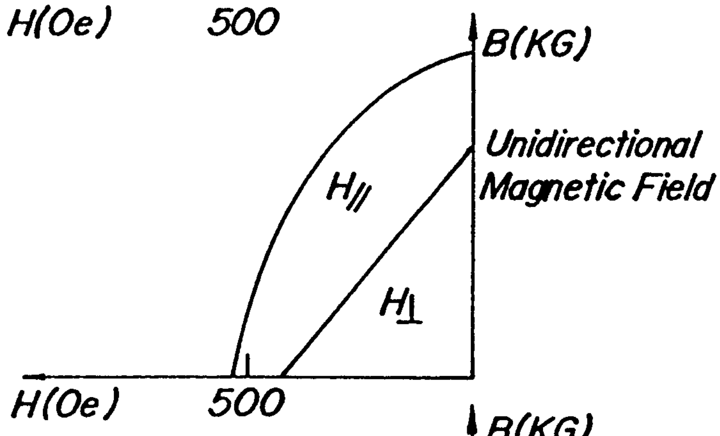


FIG_5c

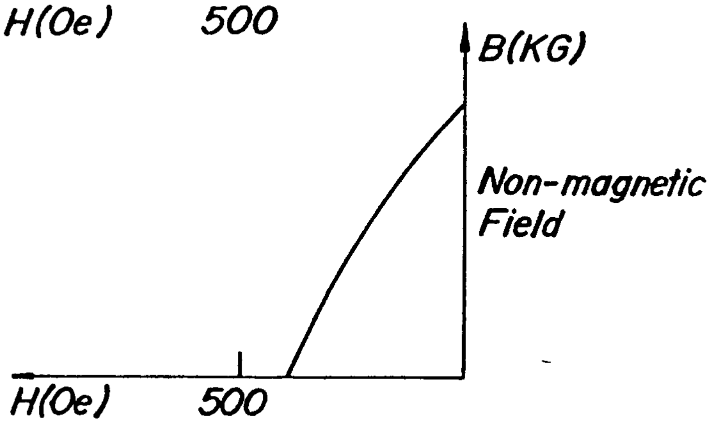


FIG_6a

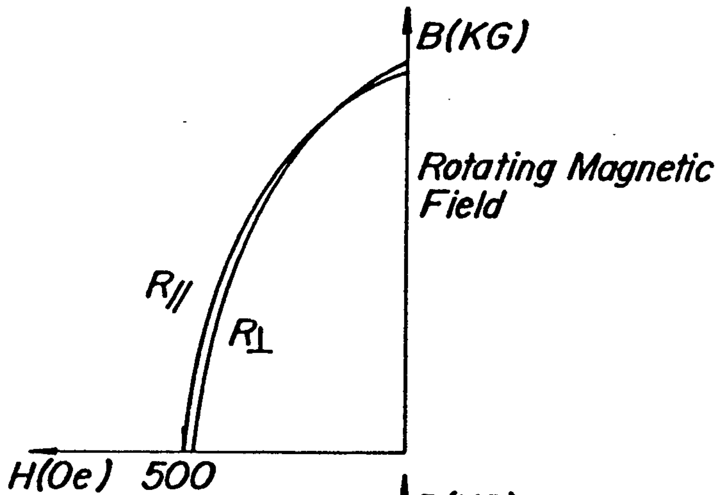


FIG_6b

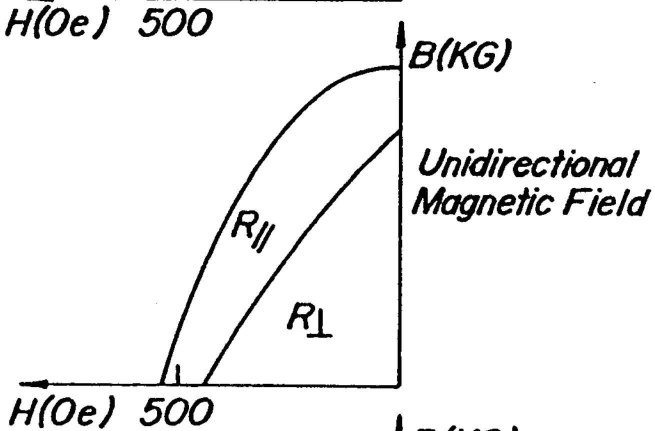


FIG_6c

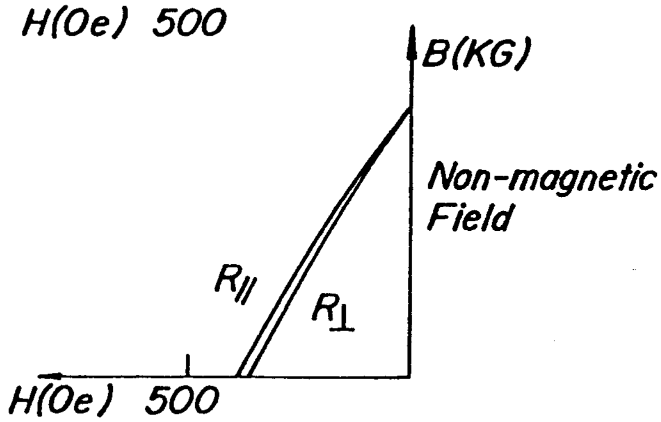


FIG_7

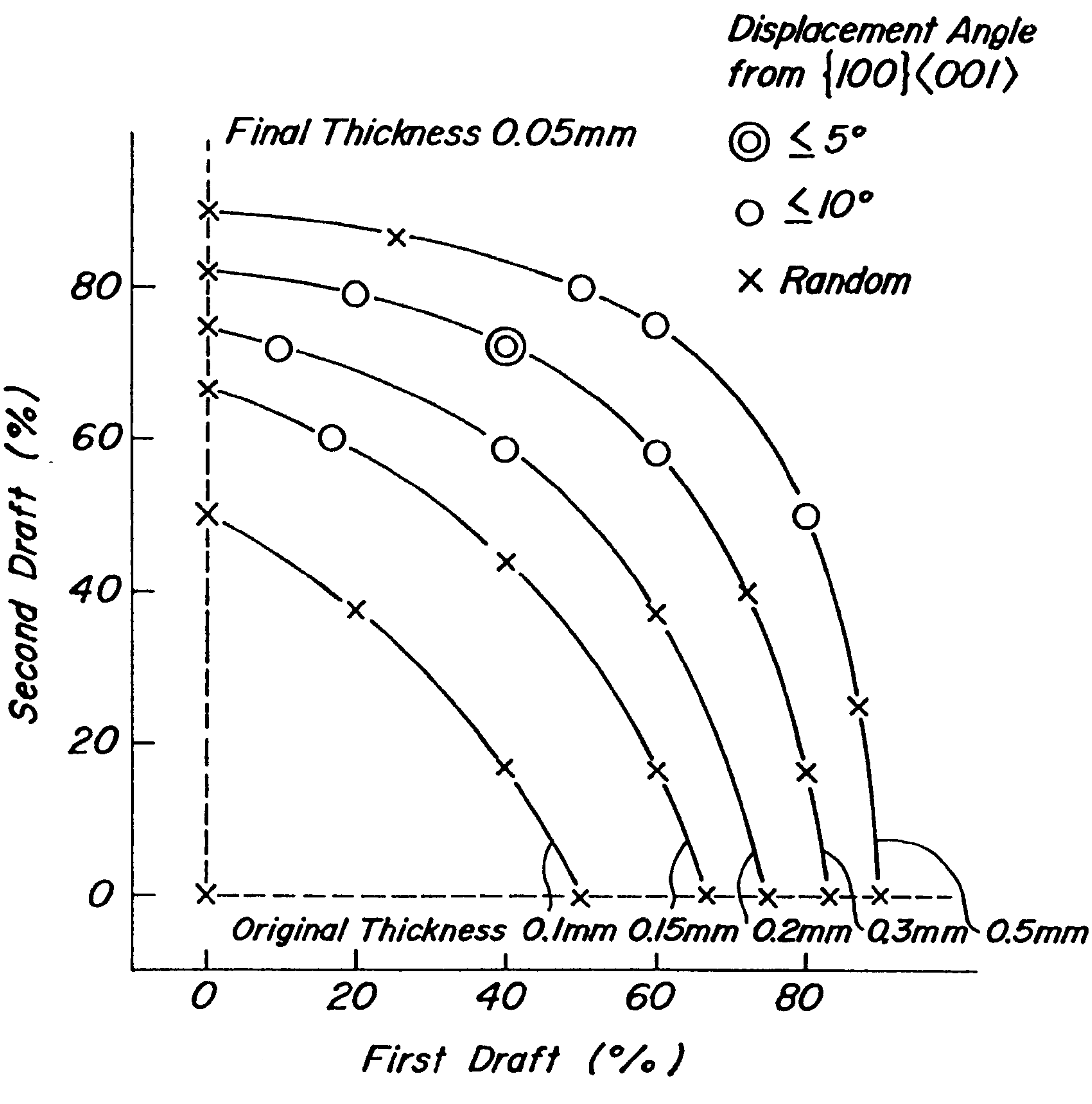

Displacement Angle from {100}⟨001⟩
◎ ≤5°
○ ≤10°
× Random
Final Thickness 0.05mm
Original Thickness 0.1mm 0.15mm 0.2mm 0.3mm 0.5mm
Second Draft (%)
First Draft (%)
0
20
40
60
80

FIG_8

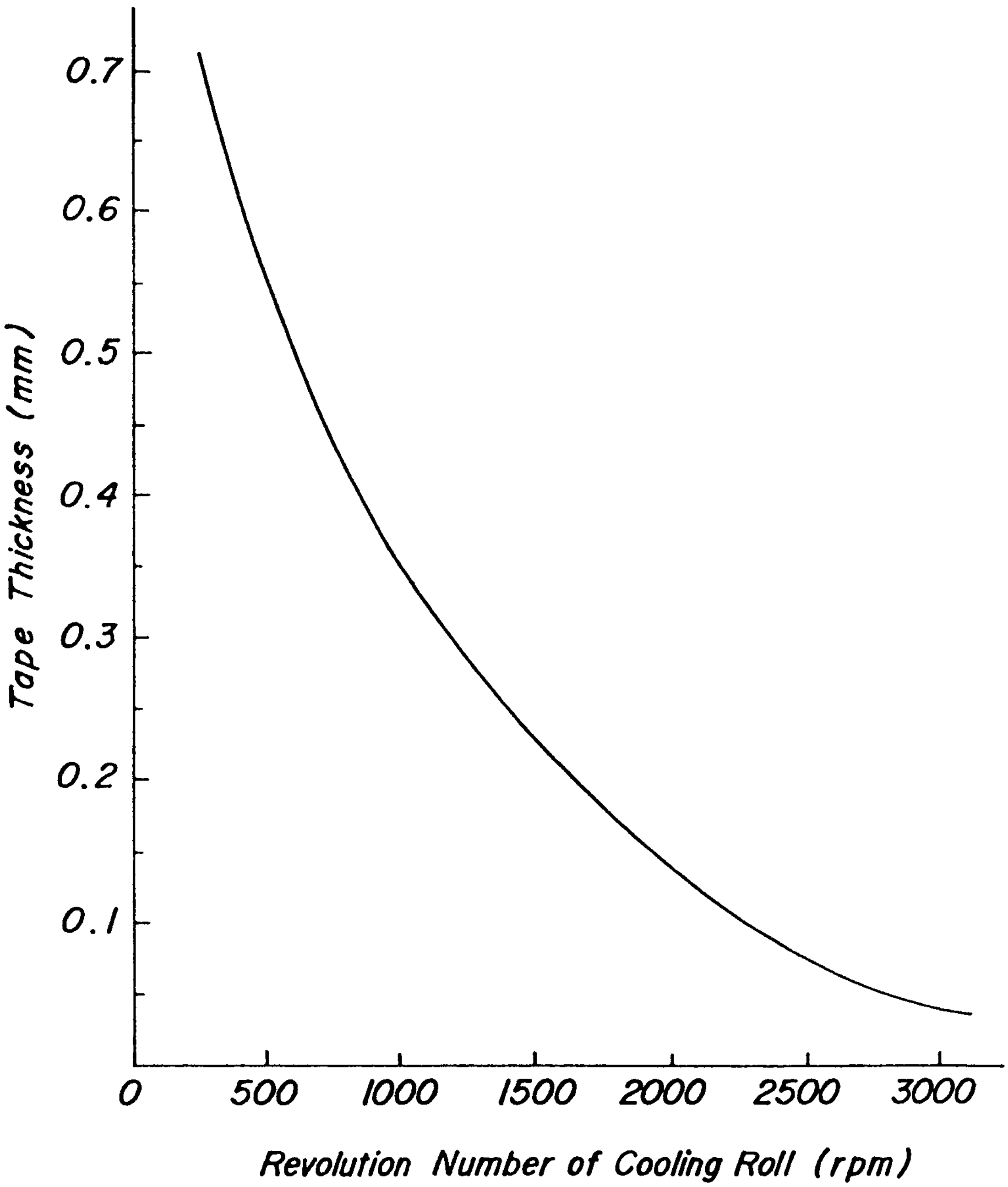

Tape Thickness (mm)
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
500
1000
1500
2000
2500
3000
Revolution Number of Cooling Roll (rpm)

FIG_9

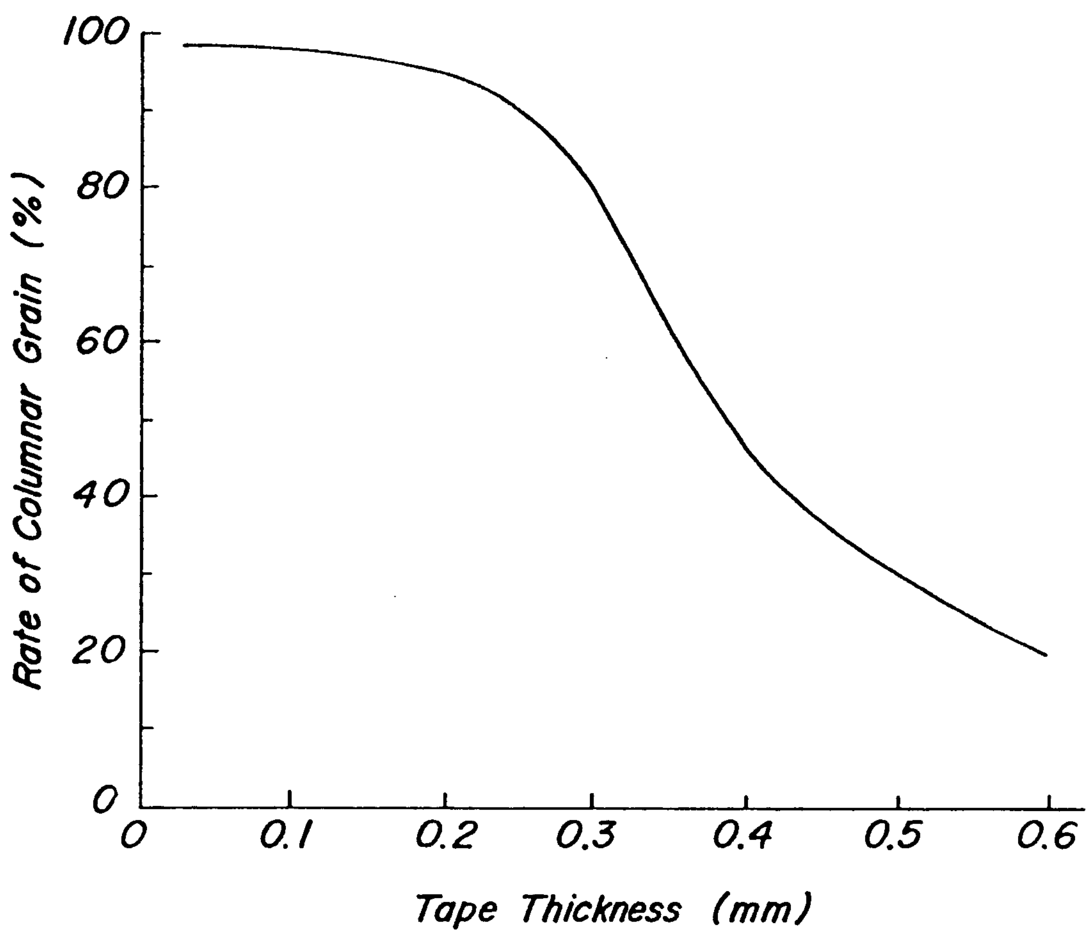

100
80
60
40
20
0
Rate of Columnar Grain (%)
0
0.1
0.2
0.3
0.4
0.5
0.6
Tape Thickness (mm)

FIG_10a

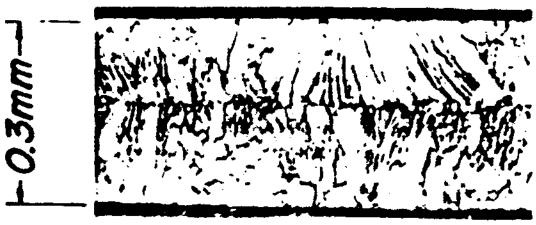


FIG_11a

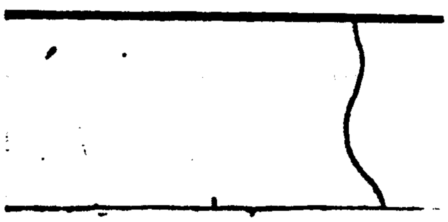


FIG_12a

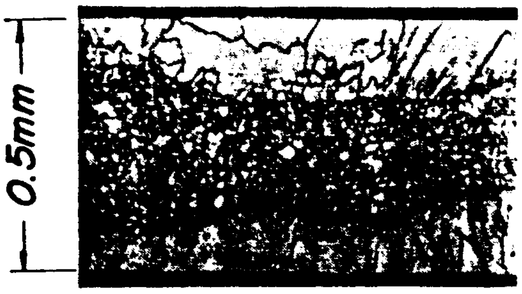
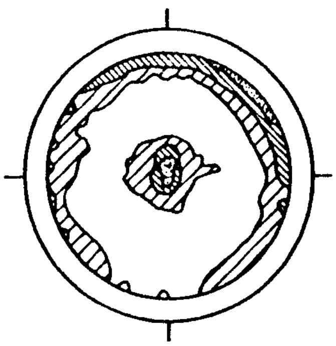


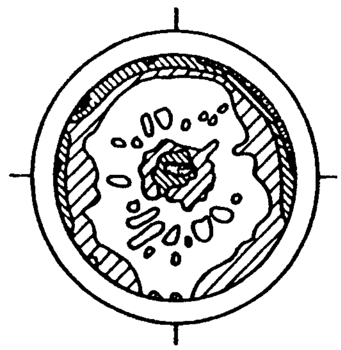
FIG_13a

FIG_10b



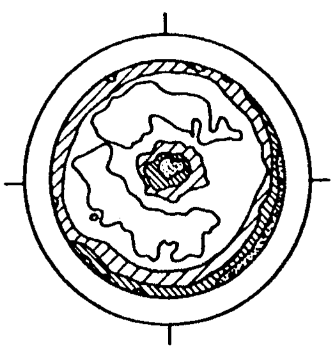
(200) Pole Figure
as-cast state

FIG_11b



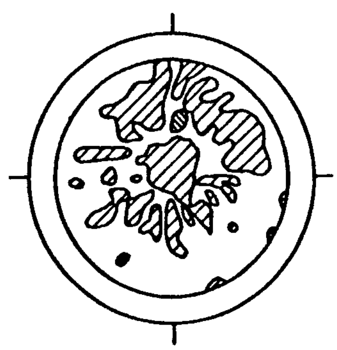
(200) Pole Figure
Recrystallization
Annealing, 1100°C x 10min

FIG_12b



(200) Pole Figure
as-cast state

FIG_13b



(200) Pole Figure
Recrystallization
Annealing, 1100°C x 10min

0216457

European Patent Office

EUROPEAN SEARCH REPORT

Application number

EP 86305484.7

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int Cl 4)
A	US - A - 4 366 007 (INOUE) * Abstract * --	1	H 01 F 1/04 C 21 D 6/00 C 22 C 38/30
A	US - A - 4 324 597 (KAMINO et al.) * Abstract * --	1	
A	US - A - 4 305 764 (IWATA) * Abstract * --	1	
A	US - A - 4 284 440 (TOKUNAGA et al.) * Abstract * --	1	
A	US - A - 4 194 932 (IWATA) * Claim 1 * ----	1	

TECHNICAL FIELDS SEARCHED (Int Cl 4)

H 01 F
C 21 D
C 22 C

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
VIENNA	16-12-1986	LUX

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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L : document cited for other reasons

& : member of the same patent family, corresponding document