(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) **EP 3 522 178 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
07.08.2019 Bulletin 2019/32

(51) Int Cl.:
H01F 1/057 *(2006.01)* ***H01F 41/02*** *(2006.01)*

(21) Application number: **18215888.1**

(22) Date of filing: **24.12.2018**

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR
Designated Extension States:
BA ME
Designated Validation States:
KH MA MD TN

(30) Priority: **28.12.2017 JP 2017254475**
10.08.2018 JP 2018151433
27.11.2018 JP 2018221584

(71) Applicant: **TOYOTA JIDOSHA KABUSHIKI KAISHA**
Toyota-shi, Aichi-ken, 471-8571 (JP)

(72) Inventors:
- **Ito, Masaaki**
  Aichi-ken, Aichi 471-8571 (JP)
- **Shoji, Tetsuya**
  Aichi-ken, Aichi 471-8571 (JP)
- **Sakuma, Noritsugu**
  Aichi-ken, Aichi 471-8571 (JP)
- **Ichigozaki, Daisuke**
  Aichi-ken, Aichi 471-8571 (JP)

(74) Representative: **J A Kemp**
14 South Square
Gray's Inn
London WC1R 5JJ (GB)

(54) RARE EARTH MAGNET AND PRODUCTION METHOD THEREOF

(57) [SUMMARY]

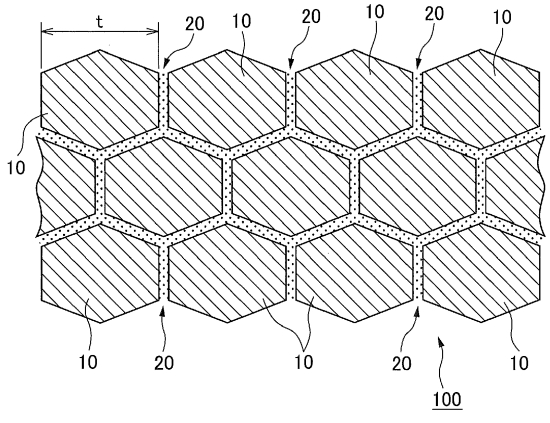
[PROBLEM TO BE SOLVED]

To provide a rare earth magnet protected from reduction in the coercive force at high temperatures and a production method thereof.

[MEANS TO SOLVE THE PROBLEM]

A rare earth magnet comprising a main phase and a grain boundary phase present around the main phase, wherein: the overall composition is represented by the formula: $(Nd_x(Ce, La)_{(1-x-y)}R^1y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1s\cdot(R^2{}_zR^3{}_wM^2{}_{1-z-w})_t$, wherein R^1 is one or more members selected from rare earth elements other than N_d, Ce and La, R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd, R^3 is one or more members selected from rare earth elements other than R^2, M^1 and M^2 are a predetermined element, $5.0\leq p\leq 20.0$, $0\leq q\leq 8.0$, $4.0\leq r\leq 6.5$, $0\leq s\leq 2.0$, $0\leq t\leq 10.0$, $0.4\leq x\leq 0.8$, $0\leq y\leq 0.1$, $0.5\leq z\leq 0.8$, and $0\leq w\leq 0.1$ and La is contained in an amount of 1/9 to 3 times by molar ratio relative to Ce.

FIG. 2



EP 3 522 178 A1

Description

[TECHNICAL FIELD]

[0001] The present disclosure relates to an R-Fe-B-based rare earth magnet, wherein R is a rare earth element, and a production method thereof. More specifically, the present disclosure relates to an R-Fe-B-based rare earth magnet protected from reduction in the coercive force at high temperatures, and a production method thereof.

[BACKGROUND ART]

[0002] An R-Fe-B-based rare earth magnet has a main phase and a grain boundary phase present around the main phase. The main phase has a composition represented by $R_2Fe_{14}B$ and is a magnetic phase. Due to this main phase, strong magnetism is exhibited. On the other hand, the grain boundary phase is present around the main phase and magnetically isolates the main phases from one another. The coercive force of the R-Fe-B-based rare earth magnet is enhanced by this magnetic isolation.

[0003] In order to enhance the magnetic isolation effect, various attempts are being made. For example, Patent Document 1 discloses a rare earth magnet using, as a precursor, a rare earth magnet having a main phase and a grain boundary phase, in which a modifier is infiltrated into the inside of the precursor.

[0004] In the rare earth magnet disclosed in Patent Document 1, the coercive force of the entire rare earth magnet is enhanced by having an intermediate phase between the main phase and the grain boundary phase.

[RELATED ART]

[Patent Document]

[0005] [Patent Document 1] International Publication No. 2014/196605A1

[SUMMARY OF THE INVENTION]

[Problems to be Solved by the Invention]

[0006] The R-Fe-B-based rare earth magnet is of high performance, and therefore its use is expanding to a variety of fields. Consequently, the opportunity of using the R-Fe-B-based rare earth magnet under a high-temperature environment is increased. In addition, when the R-Fe-B-based rare earth magnet is used in a high-power motor and high output was maintained for a long time, the R-Fe-B-based rare earth magnet is sometimes subjected to high temperatures due to self-heating of the motor.

[0007] It is known that when the R-Fe-B-based rare earth magnet is subjected to high temperatures, the coercive force may decrease.

[0008] Accordingly, the present inventors have found a problem that an R-Fe-B-based rare earth magnet protected from reduction in the coercive force even at high temperatures is demanded. Incidentally, in the present description, the high temperature indicates a range from 130 to 170°C, particularly from 140 to 160°C, the room temperature indicates a range from 20 to 25°C, and the R-Fe-B-based rare earth magnet indicates a magnet having a main phase and a grain boundary phase present around the main phase, the main phase containing a phase having a composition represented by $R_2Fe_{14}B$.

[0009] The present disclosure have been made to solve the problem above. An object of the present disclosure is to provide an R-Fe-B-based rare earth magnet protected from reduction in the coercive force even at high temperatures and a production method thereof.

[Means to Solve the Problems]

[0010] As a result of many intensive studies to attain the object above, the present inventors have accomplished the rare earth magnet of the present disclosure and the production method thereof. The rare earth magnet of the present disclosure and the production method thereof include the following embodiments.

<1> A rare earth magnet including:

a main phase, and
a grain boundary phase present around the main phase,

wherein the overall composition is represented by the formula,
wherein $Nd_x(Ce, La)_{(1-x-y)}R^1{}_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1{}_s\cdot(R^2{}_zR^3{}_wM^2{}_{1-z-w})_t$,
wherein R^1 is one or more members selected from rare earth elements other than Nd, Ce and La, R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd, R^3 is one or more members selected from rare earth elements other than R^2, M^1 represents one or more members selected from Ga, Al, Cu, Au, Ag, Zn, In and Mn, and an unavoidable impurity element, M^2 represents an alloy element for decreasing the melting point of $R^2{}_zR^3{}_wM^2{}_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element,
wherein p, q, r, s, and t are, in at%,

$5.0 \leq p \leq 20.0$,
$0 \leq q \leq 8.0$,
$4.0 \leq r \leq 6.5$,
$0 \leq s \leq 2.0$, and
$0 \leq t \leq 10.0$, and

wherein x, y, z, and w are, by molar ratio,

$0.4 \leq x \leq 0.8$,
$0 \leq y \leq 0.1$,
$0.5 \leq z \leq 0.8$, and
$0 \leq w \leq 0.1$, and

wherein La is contained in an amount of 1/9 to 3 times by molar ratio relative to Ce.

<2> The rare earth magnet according to item <1>, wherein La is contained in an amount of 1/9 to 2 times by molar ratio relative to Ce.
<3> The rare earth magnet according to item <1> or <2>,

wherein: an intermediate phase is further provided between the main phase and the grain boundary phase,
wherein t is $0.1 \leq t \leq 10.0$, and
wherein the concentration of R^2 is higher in the intermediate phase than in the main phase.

<4> The rare earth magnet according to any one of items <1> to <3>, wherein R^2 is Nd.
<5> The rare earth magnet according to item <3> or <4>, wherein the concentration of R^2 is higher by 1.5 to 8.0 times in the main phase than in the intermediate phase.
<6> The rare earth magnet according to any one of items <3> to <5>, wherein the thickness of the intermediate phase is from 2 to 100 nm.
<7> A method for producing a rare earth magnet, including:

preparing a molten metal having a composition represented by the formula: $Nd_x(Ce, La)_{(1-x-y)}R^1{}_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1{}_s$,

wherein R^1 is one or more members selected from rare earth elements other than Nd, Ce and La, M^1 represents one or more members selected from Ga, Al, Cu, Au, Ag, Zn, In and Mn, and an unavoidable impurity element,
wherein p, q, r, and s are, in at%,

$5.0 \leq p \leq 20.0$,
$0 \leq q \leq 8.0$,
$4.0 \leq r \leq 6.5$, and
$0 \leq s \leq 2.0$, and

wherein x and y are, by molar ratio,

$0.4 \leq x \leq 0.8$, and
$0 \leq y \leq 0.1$, and

wherein La is contained in an amount of 1/9 to 3 times by molar ratio relative to Ce,

quenching the molten metal to obtain a ribbon,
compressing a plurality of ribbons by hot working to obtain a molded body, and
compressing the molded body by hot working to obtain a compressed body.

<8> The method according to item <7>, wherein the molten metal contains La in an amount of 1/9 to 2 times by molar ratio relative to Ce.
<9> The method according to item <7> or <8>, including:

preparing a modifier containing an alloy represented by the formula: $R^2_zR^3_wM^9_{1-z-w}$,

wherein R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd, R^3 is one or more members selected from rare earth elements other than R^2, M^2 represents an alloy element for decreasing the melting point of $R^2_zR^3_wM^2_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element,
wherein z and w are, by molar ratio, $0.5 \leq z \leq 0.8$ and $0 \leq w \leq 0.1$,

contacting the compressed body and the modifier with each other to obtain a contact body, and
heat-treating the contact body to infiltrate a melt of the modifier into the inside of the compressed body.

<10> The method according to item <9>, wherein R^2 is Nd.
<11> The method according to any one of items <7> to <10>, wherein the molded body is compressed at a strain rate of 0.001/s or more and less than 0.1/s, a reduction ratio of 50 to 70%, and a temperature of 700 to 800°C to obtain a compressed body.

[Effects of the Invention]

[0011] According to the present disclosure, a rare earth magnet protected from reduction in the coercive force at high temperatures by causing Nd, Ce and La to be present together and setting the content ratio between Ce and La to a predetermined range, and a production method thereof can be provided.

[BRIEF DESCRIPTION OF THE DRAWINGS]

[0012]

Fig. 1 is a diagram illustrating the content ratio of Nd, Ce and La.
Fig. 2 is a diagram schematically illustrating one embodiment of the texture of the rare earth magnet according to the present disclosure.
Fig. 3 is a diagram illustrating another embodiment of the texture of the rare earth magnet according to the present disclosure.
Fig. 4 is a graph illustrating the relationship between the temperature and the cohesive force with respect to the samples of Example 15 and Comparative Example 1.
Fig. 5 is a diagram illustrating the relationship between the temperature and the residual magnetization with respect to the samples of Example 15 and Comparative Example 1.
Fig. 6 is a diagram illustrating the positions for texture observation and component analysis with respect to the sample of Example 6.
Fig. 7 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 6 (first visual field).
Fig. 8 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 6 (second visual field).
Fig. 9 is a diagram illustrating the positions for texture observation and composition analysis with respect to the sample of Example 12.
Fig. 10 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 12 (first visual field).
Fig. 11 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 12 (second visual field).
Fig. 12 is a diagram illustrating the positions for texture observation and composition analysis with respect to the

sample of Example 17.

Fig. 13 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 17 (first visual field).

Fig. 14 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 17 (second visual field).

Fig. 15 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 39.

Fig. 16 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 40.

Fig. 17 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 6.

Fig. 18 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 12.

Fig. 19 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 39.

Fig. 20 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 19.

Fig. 21 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 40.

Fig. 22 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 21.

Fig. 23 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 6.

Fig. 24 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 23.

Fig. 25 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 12.

Fig. 26 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 25.

[Mode for Carrying Out the Invention]

[0013] The embodiments of the rare earth magnet according to the present disclosure and the production method thereof are described in detail below. Incidentally, the embodiments set forth below should not be construed to limit the rare earth magnet according to the present disclosure and the production method thereof.

[0014] In the R-Fe-B-based rare earth magnet, when 1) the grain size of the main phase is reduced, 2) the anisotropic magnetic field of the main phase is increased, and 3) main phases are magnetically isolated from one another, the coercive force is enhanced.

[0015] In order to reduce the grain size of the main phase, in the R-Fe-B-based rare earth magnet, the main phase is nanocrystallized. Consequently, in the R-Fe-B-based rare earth magnet, a large amount of $R_2Fe_{14}B$ phase is present as the main phase, and a grain boundary phase is present around the main phase. In the grain boundary phase, an R-rich phase containing excess R, and a small amount of magnetic phase containing Fe (for example, RFe_2 phase) are present.

[0016] In the $Nd_2Fe_{14}B$ phase, the anisotropic magnetic field at room temperature is high, but the Curie point is 320°C and is not so high. Accordingly, even if the Curie point is not reached, at high temperatures, the anisotropic magnetic field of the $Nd_2Fe_{14}B$ phase is reduced. On the other hand, the Fe-containing magnetic phase (for example, RFe_2 phase) is paramagnetic at a temperature higher than the normal temperature but has a possibility of propagating the interaction of magnetic spins between $Nd_2Fe_{14}B$ phases (between crystal grains). When a large amount of $Nd_2Fe_{14}B$ phase is present as the main phase, the coercive force is high at room temperature, because the Fe-containing magnetic phase in the grain boundary phase has a small effect. However, at high temperature, the Fe-containing magnetic phase in the grain boundary phase has the effect of propagating the interaction of magnetic spins between $Nd_2Fe_{14}B$ phases (between crystal grains), and the grain size of the main phase is thereby apparently increased, presenting the possibility of reducing the effect of nanocrystallization of the main phase. As a result, the coercive force rapidly decreases.

[0017] When R of the R-Fe-B-based rare earth magnet contains Nd, Ce and La, the anisotropic magnetic field of $(Nd, Ce, La)_2Fe_{14}B$ is lower than the anisotropic magnetic field of $Nd_2Fe_{14}B$ at both room temperature and high temperature. Hereinafter, the R-Fe-B-based rare earth magnet containing Nd, Ce and La is sometimes referred to as "(Nd, Ce, La)-Fe-B-based rare earth magnet".

[0018] Although not bound by theory, in the (Nd, Ce, La)-Fe-B-based rare earth magnet, when the content ratio between Ce and La is in a predetermined range, the stability of the Fe-containing magnetic phase (e.g., RFe_2 phase) in the grain boundary phase decreases, compared with the Nd-Fe-B-based rare earth magnet. Consequently, in the (Nd, Ce, La)-Fe-B-based rare earth magnet, Fe in the grain boundary phase is likely to contribute to the production of a phase other than the Fe-containing magnetic phase. The phase other than the Fe-containing magnetic phase includes $CeFe_2$ phase, etc.

[0019] Formation of the $(Nd, Ce, La)_2Fe_{14}B$ phase brings about an increase in the total number of main phases, and

consequent replacement of Nd by Ce and La compensates for the reduction in the anisotropic magnetic field and suppresses the reduction in the coercive force of the entire (Nd, Ce, La)-Fe-B-based rare earth magnet. This enhancement of coercive force is prominent at high temperatures. Incidentally, in the present description, although not bound by theory, with respect to the $(Nd, Ce, La)_2Fe_{14}B$ phase, Ce or La is present at the position of Nd of the $Nd_2Fe_{14}B$ phase.

[0020] In addition, when the (Nd, Ce, La)-Fe-B-based rare earth magnet is used as a precursor and a modifier containing R^2 is infiltrated into the inside of the precursor, depending on the infiltration amount of the alloy from the modifier, an intermediate phase is formed between the main phase and the grain boundary phase.

[0021] Although not bound by theory, it is considered that part of Ce and/or La present in the main phase of the precursor is replaced by R^2 and an intermediate phase is thereby formed. Accordingly, in the intermediate phase, the concentration of R^2 is higher than in the main phase of the precursor and in turn, the anisotropic magnetic field of the intermediate phase is higher than the anisotropic magnetic field of the main phase of the precursor. At high temperature, the anisotropic magnetic field of the intermediate phase is reduced. However, even at high temperature, the anisotropic magnetic field of the intermediate phase is higher than the anisotropic magnetic field of the main phase of the precursor by the amount corresponding to the R^2 concentration that is increased compared with the main phase of the precursor. This contributes to the protection from reduction in the coercive force.

[0022] From the matters described hereinbefore, the present inventors have found that with respect to the R-Fe-B-based rare earth magnet, the reduction in the coercive force at high temperatures can be suppressed.

[0023] The configuration requirements of the rare earth magnet according to the present disclosure and the production method thereof, based on the finding above, are described below.

<<Rare Earth Magnet>>

[0024] First, the configuration requirements of the rare earth magnet of the present disclosure are described.

<Overall Composition>

[0025] The overall composition of the rare earth magnet of the present invention is represented by the formula: $(Nd_x(Ce, La)_{(1-x-y)}R^1{}_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1{}_s\cdot(R^2{}_zR^3{}_wM^2{}_{1-z-w})_t$.

[0026] In the formula above, $(R^2{}_zR^3{}_wM^2{}_{1-z-w})_t$ represents a composition derived from the later-described modifier. In the case of not infiltrating a modifier, t=0, and the overall composition of the rare earth magnet of the present disclosure is represented by $(Nd_x(Ce, La)_{(1-x-y)}R^1{}_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1{}_s$.

[0027] On the other hand, in the case of infiltrating a modifier, t is a positive value and is not 0, and $(Nd_x(Ce, La)_{(1-x-y)}R^1{}_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1{}_s$ represents a composition of the rare earth magnet precursor.

[0028] In the formula above, Nd stands for neodymium, Ce stands for cerium, La stands for lanthanum, R^1 is one or more members selected from rare earth elements other than Nd, Ce and La, Fe stands for iron, Co stands for cobalt, and B stands for boron. M^1 represents one or more members selected from Ga, Al, Cu, Au, Ag, Zn, In and Mn, and an unavoidable impurity element. Ga stands for gallium, Al stands for aluminum, Cu stands for copper, Au stands for gold, Ag stands for silver, Zn stands for zinc, In stands for indium, and Mn stands for manganese. R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd. Pr stands for praseodymium, Nd stands for neodymium, Pm stands for promethium, Sm stands for samarium, Eu stands for europium, and Gd stands for gadolinium. M^2 represents an alloy element for decreasing the melting point of $R^2{}_zR^3{}_wM^2{}_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element.

[0029] In the present description, the rare earth element includes 17 elements of Sc, Y, La, Ce, Pr, Nd, Pm, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, and Lu. Of these, Sc, Y, La, and Ce are a light rare earth element, Pr, Nd, Pm, Sm, Eu, and Gd are a medium rare earth element, and Tb, Dy, Ho, Er, Tm, Yb, and Lu are a heavy rare earth element. Incidentally, in general, the rarity of the heavy rare earth element is high, and the rarity of the light rare earth element is low. The rarity of the medium rare earth element is between the heavy rare earth element and the light rare earth element.

[0030] Next, p, q, r, s and t, and x, y, z and w are described. In the following description, the case of infiltrating a modifier is explained. As for the case of not infiltrating a modifier, the "rare earth magnet precursor" is read as "rare earth magnet", and the description of items derived from a modifier is treated as non-existing.

[0031] In the rare earth magnet precursor, p is the total content of Nd, Ce, La and R^1, q is the content of Co, r is the content of B (boron), and s is the content of M^1. With respect to the items derived from a modifier, t is the infiltration amount of an alloy from the modifier, relative to the rare earth magnet precursor, and is the total content of R^2, R^3 and M^2. Each of the values of p, q, r, s and t is at%.

[0032] In the rare earth magnet precursor, each of the values of x and y is the following content ratio (molar ratio). x represents the content ratio of Nd relative to the total content of Nd, Ce, La and R^1, and y represents the content ratio of R^1 relative to the total content of Nd, Ce, La and R^1. With respect to the items derived from a modifier, each of the values of z and w is the following content ratio (molar ratio). z is the content ratio of R^2 relative to the total content of R^2,

R^3 and M^2, and w represents the content ratio of R^3 relative to the total content of R^2, R^3 and M^2.

[0033] The constituent elements of the rare earth magnet precursor represented by the formula above are described below.

<Nd>

[0034] Nd is an element essential for the rare earth magnet precursor of the present disclosure. By containing Nd, high magnetization can be exhibited at room temperature and high temperature. In addition, at room temperature, the $Nd_2Fe_{14}B$ phase has a high anisotropic magnetic field.

<Ce>

[0035] Ce is an element essential for the rare earth magnet precursor of the present disclosure. When Nd in the main phase ($Nd_2Fe_{14}B$ phase) is replaced by Ce, an Fe-containing magnetic phase, i.e., a $CeFe_2$ phase, in the grain boundary phase is readily formed. The $CeFe_2$ phase is paramagnetic and is expected to have an effect of propagating the interaction of magnetic spins between main phases to reduce the coercive force. In order to suppress the reduction in the coercive force, it is necessary to reduce the stability of the Fe-containing magnetic phase in the grain boundary phase.

[0036] In addition, Ce can have an atomic valence of trivalence or tetravalence. Although not bound by theory, a lot of Ce becomes trivalent due to an action of La. In the trivalent Ce, 4f electrons are localized, and therefore magnetization is advantageously enhanced.

<La>

[0037] La is an element essential for the rare earth magnet precursor of the present disclosure. Nd in the main phase ($Nd_2Fe_{14}B$ phase) is replaced by La, and the stability of the Fe-containing magnetic phase in the grain boundary phase is reduced, because compounds of a transition metal such as La and Fe are thermodynamically unstable as a whole and are not mixed with one another. That is, the addition of La is expected to provide an effect of forming an RFe_2 phase. Accordingly, La greatly contributes to protection from reduction in the coercive force. Moreover, La is advantageously inexpensive compared with Nd. In addition, when Ce is added, a $CeFe_2$ phase is likely to be formed, and the coercive force is reduced. However, when La is added together with Ce, the formation of $CeFe_2$ phase is suppressed, and the propagation of interaction of magnetic spins between grains in the main phase is restricted.

<Content Ratio of Nd, Ce and La>

[0038] As described above, x is the content ratio of Nd. The saturation magnetization and anisotropic magnetic field are higher in the $Nd_2Fe_{14}B$ phase than in $Ce_2Fe_{14}B$ phase and $La_2Fe_{14}B$ phase. Accordingly, when x is 0.40 or more, desired magnetization and coercive force are readily obtained in the rare earth magnet of the present disclosure. From this viewpoint, x may be 0.45 or more, 0.50 or more, or 0.55 or more. On the other hand, when x is 0.80 or less, it is unlikely that the content ratio of Ce and La is too small and the actions and effects of Ce and La are hardly obtained. From this viewpoint, x may be 0.75 or less, 0.70 or less, or 0.65 or less.

[0039] In the rare earth magnet precursor, the content of La is, by molar ratio, from 1/9 to 3 times relative to the content of Ce. Fig. 1 is a diagram illustrating the content ratio of Nd, Ce and La. In Fig. 1, the straight line denoted by (1) indicates a composition in which the content of La is, by molar ratio, 1/9 times relative to the content of Ce; the straight line denoted by (2) indicates a composition in which the content of La is, by molar ratio, 1/3 times relative to the content of Ce; the straight line denoted by (3) indicates a composition in which the content of La is, by molar ratio, 2/3 times relative to the content of Ce; and the straight line denoted by (4) indicates a composition in which the content of La is, by molar ratio, 3 times relative to the content of Ce.

[0040] More specifically, these are rephrased as follows. The straight line of (1) indicates a composition at Ce:La=1:1/9; the straight line of (2) indicates a composition at Ce:La=1:1/3; the straight line of (3) indicates a composition at Ce:La=1:2/3; and the straight line of (4) indicates a composition at Ce:La=1:3.

[0041] As described above, the content ratio x of Nd is from 0.4 to 0.8, and therefore in Fig. 1, the composition of the rare earth magnet precursor of the present disclosure is denoted by a portion in which the region sandwiched by "Nd80" and "Nd40" and the region sandwiched by straight line (1) and straight line (4) are overlapped.

[0042] When the content of La is, by molar ratio, 1/9 times or more relative to the content of Ce, desired magnetization can be obtained at room temperature and high temperature. From this viewpoint, the content is preferably 1/8 times or more, more preferably 1/7 times or more. On the other hand, when the content of La is by molar ratio, 3 times or less relative to the content of Ce, Nd of the grain boundary phase is replaced by Ce and/or La, thereby reducing the stability of the Fe-containing magnetic phase (e.g., RFe_2 phase), and the content (volume ratio) of the Fe-containing magnetic

phase decreases. As a result, the grain boundary phase restricts the effect of propagating the interaction of magnetic spins between main phases and suppresses the reduction in the coercive force at high temperature. From this viewpoint, the content is preferably 5/2 times or less, more preferably 2 times or less.

<R^1>

[0043] R^1 is one or more members selected from rare earth elements other than Nd, Ce and La. The rare earth magnet of the present disclosure contains Nd, Ce and La as essential components. It is difficult for raw materials of these essential components not to contain the rare earth element R^1 other than Nd, Ce and La at all. However, when the value of the content ratio y of R^1 is from 0 to 0.1, the properties of the rare earth magnet of the present disclosure can be regarded as substantially the same as those when y is 0.

[0044] Excessively increasing the purity of raw materials of essential components entails a rise in the production cost, and therefore the value of y may be 0.01 or more, 0.02 or more, 0.03 or more, 0.04 or more, or 0.05 or more. On the other hand, the value of y is preferably lower as long as a rise in the production cost is not caused, and the value may be 0.09 or less, 0.08 or less, 0.07 or less, or 0.06 or less.

[0045] When the total content p of Nd, Ce, La and R^1 is 5.0 at% or more, the main phase represented by (Nd, Ce, La)$_2$Fe$_{14}$B is not difficult to be formed. From the viewpoint that the main phase represented by (Nd, Ce, La)$_2$Fe$_{14}$B is readily formed, p may be 7.0 at% or more, 9.0 at% or more, 11.0 at% or more, or 13.0 at% or more. On the other hand, when p is 20.0 at% or less, the existence ratio (volume ratio) of the grain boundary phase does not become excessive. From the viewpoint that the exsistence ratio of the grain boundary phase does not become excessive, the total content may be 19.0 at% or less, 18.0 at% or less, or 17.0 at% or less.

<B>

[0046] B affects the content of the main phase and the content of the Fe-containing magnetic phase in the grain boundary phase. If the content of B is too small, the main phase represented by (Nd, Ce, La)$_2$Fe$_{14}$B is difficult to be formed. When the content r of B is 4.0 at% or more, it is unlikely that the main phase represented by (Nd, Ce, La)$_2$Fe$_{14}$B is difficult to be formed. From this viewpoint, r may be 4.5 at% or more, 5.0 at% or more, or 5.5 at% or more. On the other hand, if the content r of B is excessive, an Fe-containing magnetic phase such as RFe_4B_4 phase is readily formed in the grain boundary phase. When r is 6.5 at% or les, an α-Fe phase is less likely to be formed in a large amount. From this viewpoint, r may be 6.3 at% or less, or 6.0 at% or less.

<Co>

[0047] Co can substitute for iron in the main phase, grain boundary phase and intermediate phase. When Fe is referred to in the present description, part of Fe can be replaced by Co. For example, part of Fe of the (Nd, Ce, La)$_2$Fe$_{14}$B phase is replaced by Co to form the (Nd, Ce, La)$_2$(Fe, Co)$_{14}$B phase. In addition, the Fe-containing magnetic phase (e.g., R_2Fe_{17} phase) in the grain boundary phase allows part of Fe thereof to be replaced by Co and becomes a magnetic phase (e.g., R_2(Fe, Co)$_{17}$ phase).

[0048] In this way, part of Fe is replaced by Co, and the Curie point in each phase is thereby enhanced. In the case of preferring not to enhance the Curie point, Co may not be contained. It is not essential to contain Co. When the content q of Co is 0.5 at% or more, enhancement of the Curie point is substantially recognized. From the viewpoint of enhancing the Curie point, the content may be 1.0 at% or more, 2.0 at% or more, 3.0 at% or more, or 4.0 at% or more. On the other hand, Co is expensive, and therefore, in economic terms, the content q of Co may be 8.0 at% or less, 7.0 at% or less, or 0.6 at% or less.

<M^1>

[0049] M^1 may be contained within the range not compromising the properties of the rare earth magnet of the present disclosure. M^1 may contain an unavoidable impurity element. The unavoidable impurity element indicates an impurity element that is unavoidably contained or causes a significant rise in the production cost for avoiding its inclusion, such as impurity element contained in raw materials of the rare earth magnet or impurity element mixed in the production step. The impurity element, etc. mixed in the production step encompass an element incorporated due to manufacturing reasons within a range not affecting the magnetic properties.

[0050] The element that can be incorporated within a range not affecting the properties of the rare earth magnet of the present disclosure includes Ga, Al, Cu, Au, Ag, Zn, In, and Mn.

[0051] Ga, Al, Zn, In, Au, Ag and Cu decrease the melting point of the grain boundary phase present inside of a ribbon, etc. obtained, for example, by a liquid quenching method. For this reason, in the case of obtaining a molded body from

a plurality of ribbons and/or obtaining a compressed body from the molded body, such elements may be incorporated so as to, for example, enhance the mold life but are not essential. When the content of M^1 is not more than the upper limit, the elements exert substantially no effect on the magnetic properties. In view of magnetic properties, these elements may be regarded as an unavoidable impurity element.

[0052] Mn contributes to the stabilization of $(Nd, Ce, La)_2Fe_{14}B$ phase by replacing part of Fe in the $(Nd, Ce, La)_2Fe_{14}B$ phase.

[0053] When the content s of M^1 is 2.0 at% or less, the magnetic properties of the present disclosure are not compromised. From this viewpoint, the content s of M^1 may be 1.5 at% or less, 1.0 at% or less, or 0.5 at% or less.

[0054] In the case of not containing Ga, Al, Cu, Au, Ag, Zn, In, and Mn as M^1, since it is impossible not to contain an unavoidable impurity element at all, the lower limit of the content s of M^1 may be 0.05 at%, 0.1 at%, or 0.2 at%, and this poses no practical problem.

[0055] Each of the values of p, q, r and s described hereinbefore is the same as that in the case of a normal R-Fe-B-based rare earth magnet.

<Fe>

[0056] Fe is the remainder after removing Nd, Ce, La, R^1, Co, B, and M^1 described hereinbefore, and the content (at%) of Fe is represented by (100-p-q-r-s). When p, q, r and s are in the ranges above, a main phase and a grain boundary phase are obtained. In addition, when the rare earth magnet having a main phase and a grain boundary phase is used as a precursor and a modifier is sufficiently infiltrated into the precursor, an intermediate phase is obtained. The main phase, grain boundary phase and intermediate phase are described below.

<Main Phase, Grain Boundary Phase, and Intermediate Phase>

[0057] Fig. 2 is a diagram schematically illustrating one embodiment of the texture of the rare earth magnet according to the present disclosure. Fig. 3 is a diagram illustrating another embodiment of the texture of the rare earth magnet according to the present disclosure.

[0058] In the embodiment illustrated in Fig. 2, the rare earth magnet 100 of the present disclosure has a main phase 10 and a grain boundary phase 20. In the embodiment illustrated in Fig. 3, the rare earth magnet 100 of the present disclosure further has an intermediate phase 30, in addition to a main phase 10 and a grain boundary phase 20.

[0059] The embodiment illustrated in Fig. 2 is recognized when a modifier is not infiltrated or a very small amount of a modifier is infiltrated. The rare earth magnet 100 of the embodiment illustrated in Fig. 2 is used as a rare earth magnet precursor into which a modifier is infiltrated. The embodiment illustrated in Fig. 3 is recognized when a sufficient amount of a modifier is infiltrated.

[0060] The rare earth magnet 100 may have a phase (not shown) other than the main phase 10, the grain bounder phase 20, and the intermediate phase 30. The phase other than the main phase 10, the grain bounder phase 20, and the intermediate phase 30 includes an oxide, a nitride, an intermetallic compound, etc.

[0061] The properties of the rare earth magnet 100 are exerted mainly by the main phase 10, the grain boundary phase 20, and the intermediate phase 30. Most of the phases other than the main phase 10, the grain boundary phase 20, and the intermediate phase 30 are an impurity. Accordingly, the total content of the main phase 10, the grain boundary phase 20, and the intermediate phase 30 is preferably 95 vol% or more, more preferably 97 vol% or more, still more preferably 99 vol% or more, relative to the rare earth magnet 100.

[0062] The main phase 10 is nanocrystallized. Being nanocrystallized means that the average grain size of the main phase 10 is from 1 to 1,000 nm. The average grain size may be 10 nm or more, 50 nm or more, or 100 nm or more, and may be 900 nm or less, 700 nm or less, 500 nm or less, or 300 nm or less.

[0063] The "average grain size" indicates an average value of longitudinal lengths t of main phases 10, for example, illustrated in Fig. 2. For example, a given region is specified in a scanning electron microscope image or a transmission electron microscope image of the rare earth magnet 100, and the average value of respective lengths t of main phases 10 present in the given region is calculated and defined as the "average grain size". In the case where the cross-sectional shape of the main phase 10 is elliptic, t is denoted as the length of the long axis, and in the case where the cross-section of the main phase is quadrilateral, t is denoted as the length of a longer diagonal. In the case of the embodiment illustrated in Fig. 3, t is set including the intermediate phase 30, because, as described later, the intermediate phase 30 is derived from the main phase 10.

[0064] When the rare earth magnet 100 illustrated in Fig. 2 is used as a rare earth magnet precursor (hereinafter, sometimes referred to as "precursor 100") and a modifier is infiltrated thereinto, the modifier reaches the interface of the main phase 10 and the grain boundary 20 via the grain bounder phase 20. Then, R^2 in the modifier infiltrates the inside of the main phase 10 from the grain boundary phase 20 and, as illustrated in Fig. 3, an intermediate phase 30 is formed.

[0065] The grain boundary phase 20 is present around the main phase 10. The intermediate phase 30 is sandwiched

between the main phase 10 and the grain boundary phase 20. Formation of the intermediate phase 30 is described by referring to the composition of the modifier.

<R^2, R^3, and M^2>

[0066] The modifier contains an alloy having a composition represented by $R^2_zR^3_wM^2_{1-z-w}$. On the other hand, the precursor 100 has a composition represented by $(Nd_x(Ce, La)_{(1-x-y)}R^1_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1_s$.

[0067] R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd, and R^3 is one or more members selected from rare earth elements other than R^2. In addition, M^2 represents an alloy element for decreasing the melting point of $R^2_zR^3_wM^2_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element.

[0068] The precursor 100 contains mainly Nd, Ce and La as the rare earth element. On the other hand, the alloy in the modifier contains mainly R^2 that is one or more members selected from Pr, Nd, Pm, Sm, Eu, and Gd.

[0069] R^2 of the modifier differs in the kind of one or more rare earth elements from Nd, Ce and La of the precursor 100, and therefore, although not bound by theory, R^2 infiltrates into the main phase 10 and forms the intermediate phase 30. Accordingly, the concentration of R^2 is higher in the intermediate phase 30 than in the main phase 10. Although not bound by theory, the reason for infiltration of R^2 into the main phase 10 is considered as follows.

[0070] At the time of infiltrating the modifier into the precursor 100, when the alloy in the modifier contains mainly the same rare earth element of the main phase 10, the rare earth element in the modifier is not easily infiltrated into the main phase 10. For example, at the time of infiltrating a modifier containing an Nd-Cu alloy into the Nd-Fe-B-based rare earth magnet precursor, Nd in the modifier is likely to stay in the grain boundary phase 20 and hardly infiltrates into the main phase ($Nd_2Fe_{14}B$ phase).

[0071] On the other hand, when the alloy in the modifier contains mainly a rare earth element different from the main phase 10, the rare earth element in the modifier readily infiltrates into the main phase 10. For example, at the time of infiltrating a modifier containing an Nd-Cu alloy into the (Nd, Ce, La)-Fe-B-based rare earth magnet, Nd in the modifier readily infiltrates into the main phase 10 due to the presence of Ce and La. From the viewpoint of enhancing the saturation magnetization and anisotropic magnetic field of the intermediate phase 30 in a balanced manner, R^2 is preferably Nd.

[0072] The composition of the alloy in the modifier is represented by $R^2_zR^3_wM^2_{1-z-w}$. R^3 is one or more members selected from rare earth elements other than R^2. The rare earth element contained in the alloy in the modifier is R^2, and it is difficult not to contain the rare earth element R^3 other than R^2 at all. However, when the value of the content ratio w of R^3 is from 0 to 0.1, the properties as the modifier can be regarded as substantially the same as those when w is 0.

[0073] The value of w is ideally close to 0, but the value of w may be 0.01 or more, 0.02 or more, 0.03 or more, 0.04 or more, or 0.05 or more. On the other hand, the value of w is preferably lower as long as a rise in the production cost is not caused, and the value may be 0.09 or less, 0.08 or less, 0.07 or less, or 0.06 or less.

[0074] In the formula: $(Nd_x(Ce, La)_{(1-x-y)}R^1_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1_s\cdot(R^2_zR^3_wM^2_{1-z-w})_t$ of the overall composition, the value of t corresponds to the infiltration amount (at%) of the alloy from the modifier relative to the precursor 100. The concentration of R^2 in the intermediate phase 30 and the thickness of the intermediate phase 30 are changed according to the value of t.

[0075] In Fig. 3, when the concentration of R^2 is higher by 1.5 times or more in the intermediate phase 30 than in the main phase 10, the magnetic isolation can be clearly recognized. On the other hand, even when the concentration of R^2 is higher by 8.0 times in the intermediate phase 30 than in the main phase 10, the effect of magnetic isolation is not saturated. Accordingly, the concentration of R^2 is preferably higher by 1.5 to 8.0 times in the intermediate phase 30 than in the main phase 10. The concentration of R^2 may be higher by 1.5 to 5.0 times, or by 1.5 to 3.0 times.

[0076] In order to clearly recognize the function as the intermediate phase 30, the thickness of the intermediate phase 30 is preferably 2 nm or more, more preferably 10 nm or more, still more preferably 20 nm or more. On the other hand, the thickness of the intermediate phase 30 depends on the infiltration amount of the modifier. The modifier contains M^2 not contributing to magnetization, and therefore, if the infiltration amount of M^2 is too large, the volume fraction of the grain boundary phase is increased, and magnetization of the rare earth magnet 100 decreases. From this viewpoint, the thickness of the intermediate phase 30 is preferably 100 nm or less, more preferably 70 nm or less, still more preferably 40 nm or less.

<<Production Method>>

[0077] The production method of the rare earth magnet of the present disclosure is described below.

<Preparation of Molten Metal>

[0078] A molten metal having a composition represented by the formula: $(Nd_x(Ce, La)_{(1-x-y)}R^1_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1_s$ and containing La in an amount of 1/9 to 3 times by molar ratio relative to Ce is prepared. Alternatively, a molten metal

containing La in an amount of 1/9 to 2 times by molar ratio relative to Ce may be prepared. Descriptions regarding Nd, Ce, La, R^1, Fe, Co, B, and M^1 and regarding x, y, p, q, r, and s are the same as those in the rare earth magnet. Incidentally, in the case where a specific component is consumed during preparation of the molten metal or in the subsequent step, the component may be blended by taking into account the consumption.

[0079] The method for preparing a molten metal is not limited and includes, for example, induction heating of raw materials by using high frequency current. The preparation of a molten metal is preferably performed in an inert gas atmosphere so as to prevent oxidation of the raw materials during melting or the molten metal during storage.

<Preparation of Ribbon>

[0080] The molten metal above is quenched to obtain a ribbon. As long as the main phase in the ribbon can be nanocrystallized, the quenching method is not particularly limited and includes, for example, a liquid quenching method. In order to nanocrystallize the main phase in the ribbon, the molten metal-cooling rate may be, typically, 1×10^2 K/sec or more, 1×10^3 K/sec or more, or 1×10^4 K/sec or more, and may be 1×10^7 K/sec or less, 1×10^6 K/sec or less, or 1×10^5 K/sec or less.

[0081] As to the conditions in the liquid quenching method, for example, a molten metal is discharged toward a copper-made single roll in an inert gas atmosphere under reduced pressure of 50 kPa or less to obtain a ribbon, but the conditions are not limited thereto.

[0082] The molten metal discharging temperature may be, typically, 1,300°C or more, 1,350°C or more, or 1,400°C or more, and may be 1,600°C or less, 1,550°C or less, or 1500°C or less.

[0083] The peripheral velocity of the single roll may be, typically, 20 m/s or more, 24 m/s or more, or 28 m/s or more, and may be 40 m/s or less, 36 m/s or less, or 32 m/s or less.

<Preparation of Molded Body>

[0084] The ribbon obtained by liquid quenching is compressed by hot working to obtain a molded body. The molded body is obtained from a plurality of ribbons. The method for compression is not particularly limited but includes, for example, a method where ribbons are charged into a die and hot-pressed. Before hot pressing, the ribbon may be pulverized to 10 μm or less. The temperature at the time of hot pressing may be a temperature at which a molded body is obtained, but may also be a temperature at which part of the grain boundary phase in the ribbon melts, that is, the ribbon may be liquid phase sintered. The atmosphere during hot pressing is preferably an inert gas atmosphere so as to prevent oxidation of the ribbon and molded body. In addition, as for the hot pressing, a powder obtained by pulverizing the ribbon may be compacted to obtain a compact, and the compact may then be sintered (including liquid phase sintering).

[0085] The pressure at the time of hot pressing may be, typically, 200 MPa or more, 300 MPa or more, or 350 MPa or more, and may be 600 MPa or less, 500 MPa or less, or 450 MPa or less.

[0086] The temperature at the time of hot pressing may be, typically, 550°C or more, 600°C or more, or 630°C or more, and may be 750°C or less, 700°C or less, or 670°C or less.

[0087] The pressing time at the time of hot pressing may be, typically, 5 seconds or more, 20 seconds or more, or 40 seconds or more, an may be 120 seconds or less, 100 seconds or less, or 80 seconds or less.

<Preparation of Compressed Body>

[0088] The above-described molded body is further plastically worked by hot working to obtain a compressed body (plastically deformed body). The method for hot-plastic working (hereinafter, sometimes simply referred to as "plastic working") is not particularly limited as long as a compressed body having anisotropy is obtained. The method includes, for example, a method where the molded body is charged into a cemented carbide-made mold and plastically worked at a reduction ratio of 10 to 75%. The method for plastic working includes upsetting, backward extrusion, etc. The reduction ratio may be set to obtain desired anisotropy. The temperature at the time of plastic working may be set such that the compressed body is not broken and the crystal grain in the compressed body is not coarsened.

[0089] The reduction ratio at the time of plastic working may be, typically, 10% or more, 30% or more, 50% or more, or 60% or more, and may be 75% or less, 70% or less, or 65% or less.

[0090] The temperature at the time of plastic working may be 650°C or more, 700°C or more, or 720°C or more, and may be 850°C or less, 800°C or less, or 770°C or less.

[0091] The strain rate at the time of plastic working may be 0.001/s or more, 0.01/s or more, 0.1/s or more, or 1.0/s or more, and may be 10.0/s or less, 5.0/s or less, or 3.0/s or less.

[0092] Although not bound by theory, it is considered that the followings are generated inside the molded body during plastic working. The molded body has a main phase 10 and a grain boundary phase 20 present around the main phase 10 (see, Fig. 2). When the molded body is plastically worked, the main phase 10 is deformed. At this time, in at least

part of the main phase 10, a portion allowing for direct contact between main phases 10 is likely to be produced due to the deformation. This contact part may work out to origin of the grain growth of the main phase 10. If the strain rate at the time of plastic working is low, the main phase 10 readily undergoes grain growth from the contact part as a starting point. The plastic working is performed as hot working, and therefore, when the strain rate is low, this means that the contact part above is subjected to a high temperature over a long period of time. Consequently, atomic diffusion occurs via the contact part, and the main phase 10 undergoes grain growth. On the other hand, in the initial stage of plastic working, Ce and La, particularly, La, are expelled to the grain boundary phase 20 from the main phase 10. At the time of deformation of the main phase 10 resulting from expelling of Ce and La, Ce and La enter between main phases 10, and formation of the contact part above is suppressed. In addition, due to expelling of Ce and La, the melting point of the grain boundary phase 20 lowers. The plastic working is performed at a temperature allowing at least one grain boundary phase 20 to melt. Lowering of the melting point of the grain boundary phase 20 causes reduction in the viscosity of the melt of the grain boundary phase 20 during plastic working. As a result, the main phase 10 undergoing deformation is readily rotated in the melt to facilitate orientation of the main phase 10 in a specific direction. For this reason, when the strain rate is low, typically, even when the strain rate is 0.001/s or more and less than 0.01/s, the grain growth of the main phase 10 is restricted to suppress reduction in the coercive force and at the same time, orientation of the main phase 10 is promoted to enhance the magnetization. From this viewpoint, the strain rate may be from 0.001/s to 0.008/s, or from 0.001/s to 0.005/s.

[0093] The compressed body obtained in this way may be directly used as a rare earth magnet, or by using the compressed body as a rare earth magnet precursor, subsequent steps may be performed.

<Preparation of Modifier>

[0094] A modifier containing an alloy having a composition represented by the formula: $R^2_zR^3_wM^2_{1-z-w}$ is prepared. Descriptions regarding R^2 and R^3 and regarding w are the same as those for the rare earth magnet.

[0095] M^2 represents an alloy element for decreasing the melting point of $R^2_zR^3_wM^2_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element. Due to this element, even when the temperature of the later-described heat treatment is not raised excessively, the alloy in the modifier can be melted. As a result, the alloy in the modifier can be infiltrated into the rare earth magnet precursor without coarsening the texture of the rare earth magnet precursor. M^2 may contain an unavoidable impurity element. The unavoidable impurity element indicates an impurity element that is unavoidably contained or causes a significant rise in the production cost for avoiding its inclusion, such as impurity element contained in raw materials.

[0096] As M^2, one or more members selected from Cu, Al, and Co, and an unavoidable element are preferred, because Cu, Al, and Co have little adverse effect on the magnetic properties, etc. of the rare earth magnet.

[0097] The alloy having a composition represented by the formula: $R^2_zR^3_wM^2_{1-z-w}$ includes an Nd-Cu alloy, a Pr-Cu alloy, an Nd-Pr-Cu alloy, an Nd-Al alloy, a Pr-Al alloy, an Nd-Pr-Al alloy, an Nd-Co alloy, a Pr-Co alloy, and an Nd-Pr-Co alloy.

[0098] The content ratio z of R^2 is described. When z is 0.50 or more, the content of R^2 in the alloy is large, and therefore R^2 is easily infiltrated into the main phase 10 and the intermediate phase 30. From this viewpoint, z is preferably 0.55 or more, more preferably 0.60 or more. On the other hand, when z is 0.80 or less, the melting point of the alloy in the modifier appropriately lowers and in turn, the temperature of the later-described heat treatment is made appropriate. As a result, the texture of the rare earth magnet precursor can be prevented from coarsening. From the viewpoint of making the melting point of the alloy appropriate, z is preferably 0.75 or less, more preferably 0.70 or less. When R^2 is two or more elements, z is the total thereof. The same applies to M^2.

[0099] The production method of the modifier is not particularly limited. The production method of the modifier includes a casting method, a liquid quenching method, etc. From the viewpoint that the alloy composition less varies depending on the region of the modifier and the content of an impurity such as oxide is small, a liquid quenching method is preferred.

[0100] The infiltration amount of the alloy in the modifier is denoted by t (at%) in the formula of the overall composition. When t is 0.05 at% or more, the effect due to infiltration of the modifier is seen, for example, on the enhancement of magnetic properties. In order to clearly recognize the intermediate phase 30 as illustrated in Fig. 3, t is preferably 0.1 at% or more, more preferably 1.0 at% or more, still more preferably 1.5 at% or more. On the other hand, the modifier contains M^2, and therefore, if the infiltration amount of the modifier is excessive, the magnetization of the rare earth magnet after infiltration of the modifier decreases. When t is 10.0 at% or less, the decrease of magnetization poses no problem in practice. From this viewpoint, t is preferably 9.0 at% or less, more preferably 8.0 at% or less, still more preferably 7.0 at% or less.

<Preparation of Contact Body>

[0101] The rare earth magnet precursor and the modifier are contacted with each other to obtain a contact body. The

rare earth magnet precursor is the above-described compressed body. At this time, at least one surface of the rare earth magnet precursor and at least one surface of the modifier are put into contact with each other.

<Heat Treatment>

[0102] The contact body above is heat-treated to infiltrate the melt of the modifier into the inside of the rare earth magnet precursor. The melt of the modifier thereby reaches the surface part of the main phase via the grain boundary phase of the rare earth magnet precursor, and R^2 in the modifier is infiltrated into the main phase to form an intermediate phase.

[0103] The heat treatment temperature is not particularly limited as long as the modifier is melted and the melt of the modifier can be infiltrated into the main phase of the rare earth magnet precursor.

[0104] As the heat treatment temperature is higher, the melt of the modifier, particularly, R^2, is more easily infiltrated into the main phase of the rare earth magnet precursor. From this viewpoint, the heat treatment temperature is preferably 580°C or more, more preferably 600°C or more, still more preferably 620°C or more. On the other hand, as the heat treatment temperature is lower, the texture of the rare earth magnet precursor, particularly, the main phase, is more likely to be restricted from coarsening. From this viewpoint, the heat treatment temperature is preferably 800°C or less, more preferably 775°C or less, still more preferably 725°C or less.

[0105] The heat treatment atmosphere is not particularly limited, but from the viewpoint of preventing oxidation of the rare earth magnet precursor and the modifier, an inter gas atmosphere is preferred.

[Examples]

[0106] The rare earth magnet of the present disclosure and the production method thereof are described more specifically below by referring to Examples. Incidentally, the rare earth magnet of the present disclosure and the production method thereof are not limited to the conditions employed in the following Examples.

<Preparation of Samples of Examples 1 to 26>

[0107] First, a rare earth magnet precursor is prepared. A molten alloy having a composition represented by $R_{13.11}Fe_{80.43}Cu_{0.10}B_{5.99}Ga_{0.37}$ was liquid-quenched by a single roll method to obtain a ribbon. R is as in Table 1-1 later. As for the conditions of liquid quenching, the molten alloy temperature (discharge temperature) was 1,420°C, and the peripheral velocity of the roll was 30 m/s. At this time, the cooling rate of the molten alloy was 10^6 K/sec. The liquid quenching was performed in an argon gas reduced-pressure atmosphere. It was confirmed by transmission electron microscope (TEM) observation that the ribbon is nanocrystallized.

[0108] The ribbon was roughly pulverized into a powder, and the powder was charged into die, pressurized and heated to obtain a molded body. As for the pressurizing and heating conditions, the applied pressure was 400 MPa, the heating temperature was 650°C, and the holding time for pressurization and heating was 60 seconds.

[0109] The molded body was subjected to hot upsetting (hot-plastic working) to obtain a compressed body (plastically deformed body). In the hot-plastic working, a sample of 15 mm in height was compressed to 4.5 mm. As for the hot upsetting conditions, the working temperature was 780°C, the strain rate was 0.01/s, and the reduction ratio was 70%. It was confirmed by scanning electron microscope (SEM) that the compressed body has oriented nanocrystals. This compressed body was used as a rare earth magnet precursor.

[0110] An $Nd_{70}Cu_{30}$ alloy was prepared as the modifier. Nd powder and Cu powder, manufactured by Kojundo Chemical Lab. Co., Ltd., were weighed, arc-melted, and liquid-quenched to obtain a ribbon.

[0111] The rare earth magnet precursor and the modifier were put into contact with each other and heat-treated in a heating furnace. The amount of the modifier was 1.59 at%, 3.72 at%, and 5.32 at%, relative to the rare earth magnet precursor (see, Table 1-1). As for the heat treatment conditions, the heat treatment temperature was 625°C, and the heat treatment time was 165 minutes.

<Preparation of Sample of Comparative Example 1>

[0112] The sample was prepared in the same manner as in Examples 1 to 26 other than the composition of the alloy for preparing the rare earth magnet precursor was $Nd_{13.11}Fe_{80.43}Cu_{0.10}B_{5.99}Ga_{0.37}$ and the modifier was not infiltrated into the rare earth magnet precursor.

<Preparation of Samples of Examples 27 to 32>

[0113] The samples were prepared in the same manner as in Examples 1 to 26 except that R of the rare earth magnet

precursor was changed as in Table 1-3.

<Preparation of Samples of Examples 33 to 36>

[0114] The samples were prepared in the same manner as in Examples 1 to 26 other than R of the rare earth magnet precursor was changed as in Table 1-3 and the modifier was not infiltrated into the rare earth magnet precursor.

<Preparation of Samples of Examples 37 and 38>

[0115] The samples were prepared in the same manner as in Examples 1 to 26 other than the composition of the alloy for preparing the rare earth magnet precursor was $R_{13.11}Fe_{80.80}Cu_{0.10}B_{5.99}$ and R of the rare earth magnet precursor was changed as in Table 1-3.

<Preparation of Sample of Example 39>

[0116] The sample was prepared in the same manner as in Example 6 other than the strain rate at the time of hot upsetting of the molded body was changed to 0.001/s.

<Preparation of Sample of Example 40>

[0117] The sample was prepared in the same manner as in Example 12 except that the strain rate at the time of hot upsetting of the molded body was changed to 0.001/s.

<Preparation of Sample of Comparative Example 2>

[0118] The sample was prepared in the same manner as in Examples 1 to 26 other than the composition of the alloy for manufacturing the rare earth magnet precursor was $Nd_{13.11}Fe_{80.43}Cu_{0.10}B_{5.99}Ga_{0.37}$.

<Preparation of Samples of Comparative Examples 3 to 7>

[0119] The samples were prepared in the same manner as in Examples 1 to 26 other than R of the rare earth magnet precursor was changed as in Table 1-3.

<Preparation of Samples of Comparative Examples 8>

[0120] The sample of Comparative Example 8 was prepared in the same manner as in Comparative Example 1 other than R of the rare earth magnet precursor was changed as in Table 1-3.

<Preparation of Samples of Comparative Examples 9>

[0121] The sample of Comparative Example 9 was prepared in the same manner as in Comparative Example 2 other than R of the rare earth magnet precursor was changed as in Table 1-3 and the infiltrating amount of the modifier was 3.72 at% relative to the rare earth magnet precursor. The sample of Comparative Example 9 is the same as the sample in which the modifier of 3.72 at% is infiltrated into Sample of Comparative Example 8.

<Preparation of Samples of Comparative Examples 10>

[0122] The sample of Comparative Example 10 was prepared in the same manner as in Comparative Example 1 other than R of the rare earth magnet precursor was changed as in Table 1-3.

<Preparation of Samples of Comparative Examples 11>

[0123] The sample of Comparative Example 11 was prepared in the same manner as in Comparative Example 2 other than R of the rare earth magnet precursor was changed as in Table 1-3 and the infiltrating amount of the modifier was 3.72 at% relative to the rare earth magnet precursor. The sample of Comparative Example 11 is the same as the sample in which the modifier of 3.72 at% is infiltrated into Sample of Comparative Example 10.

<Preparation of Samples of Comparative Examples 12>

[0124] The sample of Comparative Example 12 was prepared in the same manner as in Comparative Example 2 other than R of the rare earth magnet precursor was changed as in Table 1-3 and the infiltrating amount of the modifier was 3.72 at% relative to the rare earth magnet precursor.

<Evaluation>

[0125] With respect to the samples of Examples 1 to 40 and Comparative Examples 1 to 12, the coercive force and residual magnetization were measured. In the measurement, a pulse excitation-type magnetic properties measuring apparatus (maximum applied magnetic field: 15T) manufactured by Toei Industry Co., Ltd. was used. Both the coercive force and the residual magnetization were measured at 23°C, 100°C, 140°C and 160°C.

[0126] The results are shown in Tables 1-1 to 1-4 and Tables 2-1 and 2-2. In Tables 1-1 and Table 1-3, the composition of each sample is shown together. As for the coercive force and the residual magnetization, the gradient ΔHc from 23 to 160°C and the gradient ΔBr from 23 to 160°C are shown together, respectively. In Table 2-1, the conditions in hot upsetting and the average grain size are shown together. Here, the average grain size means the average grain size t of a crystal grain composed of a main phase 10 and an intermediate phase 30 (see, Fig. 3). Fig. 4 is a graph illustrating the relationship between the temperature and the cohesive force with respect to the samples of Example 15 and Comparative Example 1. Fig. 5 is a diagram illustrating the relationship between the temperature and the residual magnetization with respect to the samples of Example 15 and Comparative Example 1.

[0127] With respect to the samples of Examples 6, 12, 17, 39 and 40, the texture was observed using a scanning transmission electron microscope (STEM), and the component analysis (EDX analysis) was performed.

[0128] Figs. 6 to 26 illustrate the evaluation results. Of these, Figs. 6 to 14 are evaluation results regarding Examples and Comparative Examples shown in Tables 1-1 to 1-4, and Figs. 15 to 26 are the evaluation results regarding Examples shown in Tables 2-1 and 2-2.

[0129] Fig. 6 is a diagram illustrating the positions for texture observation and composition analysis with respect to the sample of Example 6. Fig. 7 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 6 (first visual field). Fig. 8 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 6 (second visual field). Fig. 9 is a diagram illustrating the positions for texture observation and composition analysis with respect to the sample of Example 12. Fig. 10 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 12 (first visual field). Fig. 11 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 12 (second visual field). Fig. 12 is a diagram illustrating the positions for texture observation and composition analysis with respect to the sample of Example 17. Fig. 13 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 17 (first visual field). Fig. 14 is a diagram illustrating the results of texture observation and composition analysis with respect to the sample of Example 17 (second visual field).

[0130] Fig. 15 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 39. Fig. 16 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 40. Fig. 17 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 6. Fig. 18 is a diagram illustrating one example of the grain size t of a crystal grain with respect to the sample of Example 12. In each of Figs. 15 to 18, the average grain size of Table 2 is an average of respective grain sizes t of crystal grains included in the visual field.

[0131] Fig. 19 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 39. Fig. 20 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 19. Fig. 21 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 40. Fig. 22 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 21. Fig. 23 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 6. Fig. 24 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 23. Fig. 25 is a diagram illustrating the results of texture observation and the positions for composition analysis with respect to the sample of Example 12. Fig. 26 is a diagram illustrating the results of composition analysis at a position indicated by a white line in Fig. 25. Furthermore, with respect to Examples 39, 40, 6 and 12, the peak concentrations of La and Ce in the grain boundary phase and the total peak concentration thereof are determined from Figs. 20, 22, 24 and 26, and the results are shown in Table 3.

[Table 1-1]

[0132]

Table 1-1

	Composition of Rare Earth Magnet Precursor (at%)							Modifier			Ratio of Rare Earths			
								Composition Ratio		Infiltration Amount (at%)	Percentage			Ratio
	Nd	Ce	La	Fe	B	Ga	Cu	Nd	Cu		Nd	Ce	La	La/Ce
Example 1	6.555	5.8995	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	1.593	50	45	5	1/9
Example 2	6.555	5.8995	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	50	45	5	1/9
Example 3	6.555	5.8995	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	50	45	5	1/9
Example 4	6.555	3.933	2.622	80.43	5.99	0.37	0.1	0.7	0.3	1.593	50	30	20	2/3
Example 5	6.555	3.933	2.622	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	50	30	20	2/3
Example 6	6.555	3.933	2.622	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	50	30	20	2/3
Example 7	7.866	4.7196	0.5244	80.43	5.99	0.37	0.1	0.7	0.3	1.593	60	36	4	1/9
Example 8	7.866	4.7196	0.5244	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	60	36	4	1/9
Example 9	7.866	4.7196	0.5244	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	60	36	4	1/9
Example 10	7.866	3.1464	2.0976	80.43	5.99	0.37	0.1	0.7	0.3	1.593	60	24	16	2/3
Example 11	7.866	3.1464	2.0976	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	60	24	16	2/3
Example 12	7.866	3.1464	2.0976	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	60	24	16	2/3
Example 13	9.177	3.5397	0.3933	80.43	5.99	0.37	0.1	0.7	0.3	1.593	70	27	3	1/9
Example 14	9.177	3.5397	0.3933	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	70	27	3	1/9
Example 15	9.177	3.5397	0.3933	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	70	27	3	1/9
Example 16	9.177	2.9498	0.9833	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	70	22.5	7.5	1/3
Example 17	9.177	2.9498	0.9833	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	70	22.5	7.5	1/3
Example 18	9.177	2.3598	1.5732	80.43	5.99	0.37	0.1	0.7	0.3	1.593	70	18	12	1/3
Example 19	9.177	2.3598	1.5732	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	70	18	12	2/3
Example 20	9.177	2.3598	1.5732	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	70	18	12	2/3
Example 21	5.244	5.8995	1.9665	80.43	5.99	0.37	0.1	0.7	0.3	1.593	40	45	15	2/3

(continued)

	Composition of Rare Earth Magnet Precursor (at%)							Modifier			Ratio of Rare Earths			
								Composition Ratio		Infiltration Amount (at%)	Percentage			Ratio
	Nd	Ce	La	Fe	B	Ga	Cu	Nd	Cu		Nd	Ce	La	La/Ce
Example 22	5.244	5.8995	1.9665	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	40	45	15	1/3
Example 23	5.244	5.8995	1.9665	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	40	45	15	1/3
Example 24	10.488	1.9665	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	1.593	80	15	5	1/3
Example 25	10.488	1.9665	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	80	15	5	1/3
Example 26	10.488	1.9665	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	80	15	5	1/3
Comp. Ex. 1	13.11	0	0	80.43	5.99	0.37	0.1	0.7	0.3	0	100	0	0	0

[Table 1-2]

[0133]

Table 1-2

	Hc (kA/m)				ΔHc	Br (T)				ΔBr
	23°C	100°C	140°C	160°C		23°C	100°C	140°C	160°C	
Example 1	814.419	535.629	399.056	331.710	-3.523	1.078	0.969	0.891	0.804	-0.001997
Example 2	1028.451	664.597	486.864	394.509	-4.627	1.086	0.972	0.880	0.808	-0.002026
Example 3	992.544	602.112	450.800	328.810	-4.845	1.156	1.037	0.905	0.826	-0.002408
Example 4	624.456	460.678	351.232	331.162	-2.141	1.071	0.939	0.809	0.746	-0.002378
Example 5	993.877	654.091	531.552	452.211	-3.954	1.041	0.910	0.835	0.785	-0.001874
Example 6	1056.989	718.458	554.758	473.301	-4.260	1.087	0.964	0.882	0.840	-0.001803
Example 7	1024.061	626.259	447.194	375.379	-4.735	1.072	0.910	0.832	0.791	-0.002048
Example 8	1145.189	720.261	536.178	441.157	-5.139	1.078	0.991	0.934	0.893	-0.001350
Example 9	1091.798	662.166	500.819	412.070	-4.962	1.308	1.139	1.061	1.038	-0.001972
Example 10	671.026	461.698	378.515	288.120	-2.795	1.243	1.147	1.060	0.945	-0.002175
Example 11	1123.707	774.906	599.760	514.147	-4.449	1.088	0.999	0.933	0.868	-0.001608
Example 12	1259.810	828.061	634.413	537.040	-5.276	1.097	0.964	0.911	0.826	-0.001982
Example 13	1015.358	610.109	454.955	373.106	-4.688	1.320	1.192	1.082	1.040	-0.002041
Example 14	1298.931	814.498	610.030	503.485	-5.806	1.173	1.091	1.018	0.930	-0.001776
Example 15	1250.872	753.659	555.621	465.461	-5.733	1.327	1.162	1.039	0.987	-0.002483
Example 16	1380.781	932.803	723.162	609.482	-5.630	1.121	1.027	0.953	0.950	-0.001247
Example 17	1559.062	1022.101	780.158	638.960	-6.716	1.103	0.978	0.927	0.861	-0.001762
Example 18	918.613	612.147	472.674	427.437	-3.585	1.166	1.019	0.924	0.913	-0.001844
Example 19	1252.048	807.128	628.219	530.611	-5.266	1.285	1.159	1.047	0.976	-0.002256
Example 20	1460.435	933.822	721.123	608.854	-6.216	1.114	1.026	0.972	0.896	-0.001589
Example 21	456.288	337.826	271.656	224.067	-1.695	1.181	1.078	0.903	0.869	-0.002275
Example 22	893.054	593.880	459.346	379.221	-3.751	1.116	0.989	0.915	0.767	-0.002549
Example 23	977.178	631.120	460.286	385.728	-4.317	1.034	0.931	0.824	0.747	-0.002097
Example 24	736.254	489.216	367.931	344.882	-2.857	0.971	0.900	0.841	0.757	-0.001561
Example 25	640.606	446.174	358.366	312.032	-2.398	0.900	0.855	0.807	0.778	-0.000894
Example 26	956.480	613.323	476.829	430.730	-3.838	0.885	0.781	0.715	0.695	-0.001388
Comp. Ex. 1	2111.200	1278.200	0.000	753.600	-9.909	1.227		1.061	1.020	-0.001511

[Table 1-3]

[0134]

Table 1-3

	Composition of Rare Earth Magnet Precursor (at%)							Modifier			Ratio of Rare Earths			
								Composition Ratio		Infiltration Amount (at%)	Percentage			Ratio
	Nd	Ce	La	Fe	B	Ga	Cu	Nd	Cu		Nd	Ce	La	La/Ce
Example 27	9.177	0.9833	2.9498	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	70	7.5	23	3
Example 28	9.177	0.9833	2.9498	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	70	7.5	23	3
Example 29	7.866	1.3110	3.9330	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	60	10	30	3
Example 30	7.866	1.3110	3.9330	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	60	10	30	3
Example 31	6.555	1.6388	4.9163	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	50	12.5	38	3
Example 32	6.555	1.6388	4.9163	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	50	12.5	38	3
Example 33	9.177	0.9833	2.9498	80.43	5.99	0.37	0.1	0	0	0	70	7.5	23	3
Example 34	7.866	1.3110	3.9330	80.43	5.99	0.37	0.1	0	0	0	60	10	30	3
Example 35	9.177	2.9498	0.9833	80.43	5.99	0.37	0.1	0	0	0	70	22.5	7.5	1/3
Example 36	6.555	1.6388	4.9163	80.43	5.99	0.37	0.1	0	0	0	50	12.5	38	3
Example 37	9.177	2.9498	0.9833	80.80	5.99	0	0.1	0.7	0.3	3.7218	70	22.5	7.5	1/3
Example 38	9.177	2.9498	0.9833	80.80	5.99	0	0.1	0.7	0.3	5.3184	70	22.5	7.5	1/3
Comp. Ex. 1	13.110	0	0	80.43	5.99	0.37	0.1	0.7	0.3	0	100	0	0	0
Comp. Ex. 2	13.110	0	0	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	100	0	0	0
Comp. Ex. 3	9.833	3.2775	0	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	75	25	0	0
Comp. Ex. 4	6.555	6.5550	0	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	50	50	0	0
Comp. Ex. 5	3.278	9.8325	0	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	25	75	0	0
Comp. Ex. 6	0	13.1100	0	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	0	100	0	0
Comp. Ex. 7	0	9.8325	3.2775	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	0	75	25	1/3
Comp. Ex. 8	12.979	0	0.1311	80.43	5.99	0.37	0.1	0	0	0	99	0	1	-
Comp. Ex. 9	12.979	0	0.1311	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	99	0	1	-

(continued)

	Composition of Rare Earth Magnet Precursor (at%)							Modifier			Ratio of Rare Earths			
								Composition Ratio		Infiltration Amount (at%)	Percentage			Ratio
	Nd	Ce	La	Fe	B	Ga	Cu	Nd	Cu		Nd	Ce	La	La/Ce
Comp. Ex. 10	12.455	0	0.6555	80.43	5.99	0.37	0.1	0	0	0	95	0	5	-
Comp. Ex. 11	12.455	0	0.6555	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	95	0	5	-
Comp. Ex. 12	10.488	0	2.6220	80.43	5.99	0.37	0.1	0.7	0.3	3.7218	80	0	20	-

[Table 1-4]

[0135]

Table 1-4

	Hc (kA/m)				ΔHc	Br (T)				ΔBr
	23°C	100°C	140°C	160°C		23°C	100°C	140°C	160°C	
Example 27	1209.320	773.416	610.893	538.765	-4.895	1.140	1.000	0.963	0.909	-0.001688
Example 28	1321.902	874.709	676.984	587.216	-5.363	1.070	0.990	0.915	0.845	-0.001644
Example 29	843.584	553.896	451.270	393.333	-3.287	1.113	1.028	0.937	0.876	-0.001726
Example 30	1011.438	655.267	527.789	469.067	-3.959	1.003	0.892	0.812	0.760	-0.001773
Example 31	227.909	174.283	138.376	120.266	-0.786	1.167	1.007	0.954	0.885	-0.002055
Example 32	759.147	513.050	422.654	380.318	-2.765	1.068	0.903	0.819	0.768	-0.002194
Example 33	309.445	192.002	157.662	143.394	-1.212	1.188	0.903	0.833	0.797	-0.002857
Example 34	204.389	140.493	112.896	87.651	-0.852	1.179	1.023	0.856	0.859	-0.002335
Example 35	464.050	300.899	245.706	226.890	-1.731	1.299	1.141	1.007	0.948	-0.002561
Example 36	172.166	87.886	79.890	69.776	-0.747	1.141	1.079	1.022	0.999	-0.001037
Example 37	924.101	555.778	407.837	338.923	-4.271	1.312	1.162	1.021	0.993	-0.002331
Example 38	978.118	572.242	438.178	350.134	-4.584	1.267	1.105	0.969	0.940	-0.002383
Comp. Ex. 1	2111.200	1278.200	857.905	753.600	-9.909	1.227	1.132	1.061	1.020	-0.001511
Comp. Ex. 2	2213.500	1380.240	956.376	850.460	-9.949	1.110	1.016	0.960	0.930	-0.001314
Comp. Ex. 3	1593.680	962.400	708.184	589.760	-7.328	1.090	0.999	0.922	0.875	-0.001569
Comp. Ex. 4	1344.000	756.000	524.000	378.080	-7.051	1.040	0.953	0.880	0.835	-0.001497
Comp. Ex. 5	518.160	353.440	250.400	196.640	-2.347	0.845	0.614	0.541	0.432	-0.003012
Comp. Ex. 6	405.600	262.400	160.800	105.600	-2.190	0.805	0.619	0.546	0.383	-0.003081
Comp. Ex. 7	405.600	262.400	160.800	105.600	-2.190	0.851	0.581	0.544	0.431	-0.003064
Comp. Ex. 8	1076.746	648.603	489.373	412.541	-4.848	1.347	1.217	1.117	1.062	-0.002078
Comp. Ex. 9	1745.654	1101.520	775.611	691.174	-7.697	1.235	1.102	1.031	1.003	-0.001694
Comp. Ex. 10	1085.370	663.813	517.440	445.234	-4.673	1.341	1.201	1.085	1.016	-0.002374
Comp. Ex. 11	1766.587	1114.926	855.344	707.403	-7.731	1.238	1.127	1.092	1.026	-0.001547
Comp. Ex. 12	1337.739	845.701	670.085	578.435	-5.542	1.222	1.057	0.978	0.931	-0.002123

[0136] It could be confirmed from Tables 1-1 to 1-4 that in all of the samples of Examples 1 to 38, the absolute value of ΔHc is smaller than in Comparative Examples 1 to 4. In addition, it could be confirmed that in all of the samples of Examples 1 to 38, the absolute value of ΔBr is very small. Furthermore, it could be confirmed that in Comparative Examples 5 to 7, the decrease of magnetization at high temperatures is large. These results could verify that in the rare earth magnet of the present disclosure, reduction in the coercive force at high temperatures can be suppressed without greatly affecting the magnetization. The same could also be verified in Figs. 4 and 5. In addition, from Figs. 6 to 11, formation of an intermediate phase 30 could be confirmed.

[0137] With regard to the samples in which the modifier are infiltrated, the samples of Examples 1 to 32 and Examples 37 to 38 are compared with the samples of Comparative Examples 9, 11, and 12. Then, it could be confirmed that, with regard to rare earth elements, the absolute value of ΔHc is smaller in the samples of Examples 1 to 32 and Examples 37 to 38 that contain Nd, Ce, and La than in the samples of Comparative Examples 9, 11, and 12 that contain only Nd and La. With regard to the samples in which the modifier are not infiltrated, the same could also be confirmed between the samples of Examples 33 to 36 and the samples of Comparative Examples 8 and 10.

[Table 2-1]

[0138]

Table 2-1

	Composition of Rare Earth Magnet Precursor (at%)							Modifier			Ratio of Rare Earths				Hot Upsetting Conditions			Average Grain Size (μm)
								Composition Ratio		Infiltration Amount (at%)	Percentage			Ratio	Strain Rate (/s)	Reduction Ratio (%)	Temperature (°C)	
	Nd	Ce	La	Fe	B	Ga	Cu	Nd	Cu		Nd	Ce	La	La/Ce				
Example 6	6.555	3.933	2.622	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	50	30	20	2/3	0.01	70	780	527.72
Example 12	7.866	3.1464	2.0976	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	60	24	16	2/3	0.01	70	780	579.33
Example 39	6.555	3.933	2.622	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	50	30	20	2/3	0.001	70	780	595.82
Example 40	7.866	3.1464	2.0976	80.43	5.99	0.37	0.1	0.7	0.3	5.3184	60	24	16	2/3	0.001	70	780	638.27

[Table 2-2]

[0139]

Table 2-2

	Hc (kA/m)				ΔHc	Br (T)				ΔBr
	23°C	100°C	140°C	160°C		23°C	100°C	140°C	160°C	
Example 6	1056.989	718.458	554.758	473.301	-4.260	1.087	0.964	0.882	0.840	-0.001803
Example 12	1259.810	828.061	634.413	537.040	-5.276	1.097	0.964	0.911	0.826	-0.001982
Example 39	857.696	543.939	406.739	336.650	-3.803	1.221	1.110	0.979	0.887	-0.002436
Example 40	1054.088	637.862	479.888	399.840	-4.776	1.244	1.124	1.023	0.971	-0.001993

[Table 3]

[0140]

Table 3

	Example 6	Example 12	Example 39	Example 40
Ce (at%)	13.85	11.01	9.46	9.21
La (at%)	11.52	5.73	16.19	16.91
Ce+La (at%)	25.37	16.74	25.65	26.12

[0141] It could be confirmed from Table 2 that even when the strain rate is low, the increase in the average grain size of a crystal grain is suppressed and consequently, the coercive force is not deteriorated. In addition, it could be confirmed that when the strain rate is low, the magnetization is enhanced. Furthermore, it could be confirmed from Table 3 that the concentrations of Ce and La, particularly La, in the grain boundary phase 20 are high when the strain rate is low, compared with the case where the strain rate is high, and the maintenance of coercive force and the enhancement of magnetization possibly have high relevance to the expelling of Ce and La to the grain boundary phase 20 from the main phase 10.

[0142] From the results above, the effects of the rare earth magnet of the present disclosure and the production method thereof could be verified.

[Description of Numerical References]

[0143]

10 Main phase
20 Grain boundary phase
30 Intermediate phase
100 Rare earth magnet (precursor)

Claims

1. A rare earth magnet comprising:

a main phase, and
a grain boundary phase present around the main phase,
wherein the overall composition is represented by the formula: $(Nd_x(Ce, La)_{(1-x-y)}R^1_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1_s\cdot(R^2_zR^3_wM^2_{1-z-w})_t$,
wherein R^1 is one or more members selected from rare earth elements other than Nd, Ce and La, R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd, R^3 is one or more members selected from rare earth

elements other than R^2, M^1 represents one or more members selected from Ga, Al, Cu, Au, Ag, Zn, In and Mn, and an unavoidable impurity element, M^2 represents an alloy element for decreasing the melting point of $R^2_zR^3_wM^2_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element,
wherein p, q, r, s, and t are, in at%,

$5.0 \leq p \leq 20.0$,
$0 \leq q \leq 8.0$,
$4.0 \leq r \leq 6.5$,
$0 \leq s \leq 2.0$, and
$0 \leq t \leq 10.0$, and

wherein x, y, z, and w are, by molar ratio,

$0.4 \leq x \leq 0.8$,
$0 \leq y \leq 0.1$,
$0.5 \leq z \leq 0.8$, and
$0 \leq w \leq 0.1$), and

wherein La is contained in an amount of 1/9 to 3 times by molar ratio relative to Ce.

2. The rare earth magnet according to claim 1, wherein La is contained in an amount of 1/9 to 2 times by molar ratio relative to Ce.

3. The rare earth magnet according to claim 1 or 2,

wherein an intermediate phase is further provided between the main phase and the grain boundary phase,
wherein t is $0.1 \leq t \leq 10.0$, and
wherein the concentration of R^2 is higher in the intermediate phase than in the main phase.

4. The rare earth magnet according to any one of claims 1 to 3, wherein R^2 is Nd.

5. The rare earth magnet according to claim 3 or 4, wherein the concentration of R^2 is higher by 1.5 to 8.0 times in the main phase than in the intermediate phase.

6. The rare earth magnet according to any one of claims 3 to 5, wherein the thickness of the intermediate phase is from 2 to 100 nm.

7. A method for producing a rare earth magnet, comprising:

preparing a molten metal having a composition represented by the formula:

$$(Nd_x(Ce, La)_{(1-x-y)}R^1_y)_pFe_{(100-p-q-r-s)}Co_qB_rM^1_s,$$

wherein R^1 is one or more members selected from rare earth elements other than Nd, Ce and La, M^1 represents one or more members selected from Ga, Al, Cu, Au, Ag, Zn, In and Mn, and an unavoidable impurity element,
wherein p, q, r, and s are, in at%,

$5.0 \leq p \leq 20.0$,
$0 \leq q \leq 8.0$,
$4.0 \leq r \leq 6.5$, and
$0 \leq s \leq 2.0$, and

wherein x and y are, by molar ratio,

$0.4 \leq x \leq 0.8$, and

$0 \leq y \leq 0.1$, and

wherein La is contained in an amount of 1/9 to 3 times by molar ratio relative to Ce, and

quenching the molten metal to obtain a ribbon,
compressing a plurality of ribbons by hot working to obtain a molded body, and
compressing the molded body by hot working to obtain a compressed body.

8. The method according to claim 7, wherein the molten metal contains La in an amount of 1/9 to 2 times by molar ratio relative to Ce.

9. The method according to claim 7 or 8, comprising:

preparing a modifier containing an alloy represented by the formula:

$$R^2_zR^3_wM^2_{1z-w},$$

wherein R^2 is one or more members selected from Pr, Nd, Pm, Sm, Eu and Gd, R^3 is one or more members selected from rare earth elements other than R^2, M^2 represents an alloy element for decreasing the melting point of $R^2_zR^3_wM^2_{1-z-w}$ to be lower than the melting point of R^2 by alloying with R^2 and R^3, and an unavoidable impurity element, and
wherein z and w are, by molar ratio, $0.5 \leq z \leq 0.8$ and $0 \leq w \leq 0.1$,

contacting the compressed body and the modifier with each other to obtain a contact body, and
heat-treating the contact body to infiltrate a melt of the modifier into the inside of the compressed body.

10. The method according to claim 9, wherein R^2 is Nd.

11. The method according to any one of claims 7 to 10,

wherein the molded body is compressed at a strain rate of 0.001/s or more and less than 0.01/s, a reduction ratio of 50 to 70%, and a temperature of 700 to 800°C to obtain a compressed body.

FIG. 1

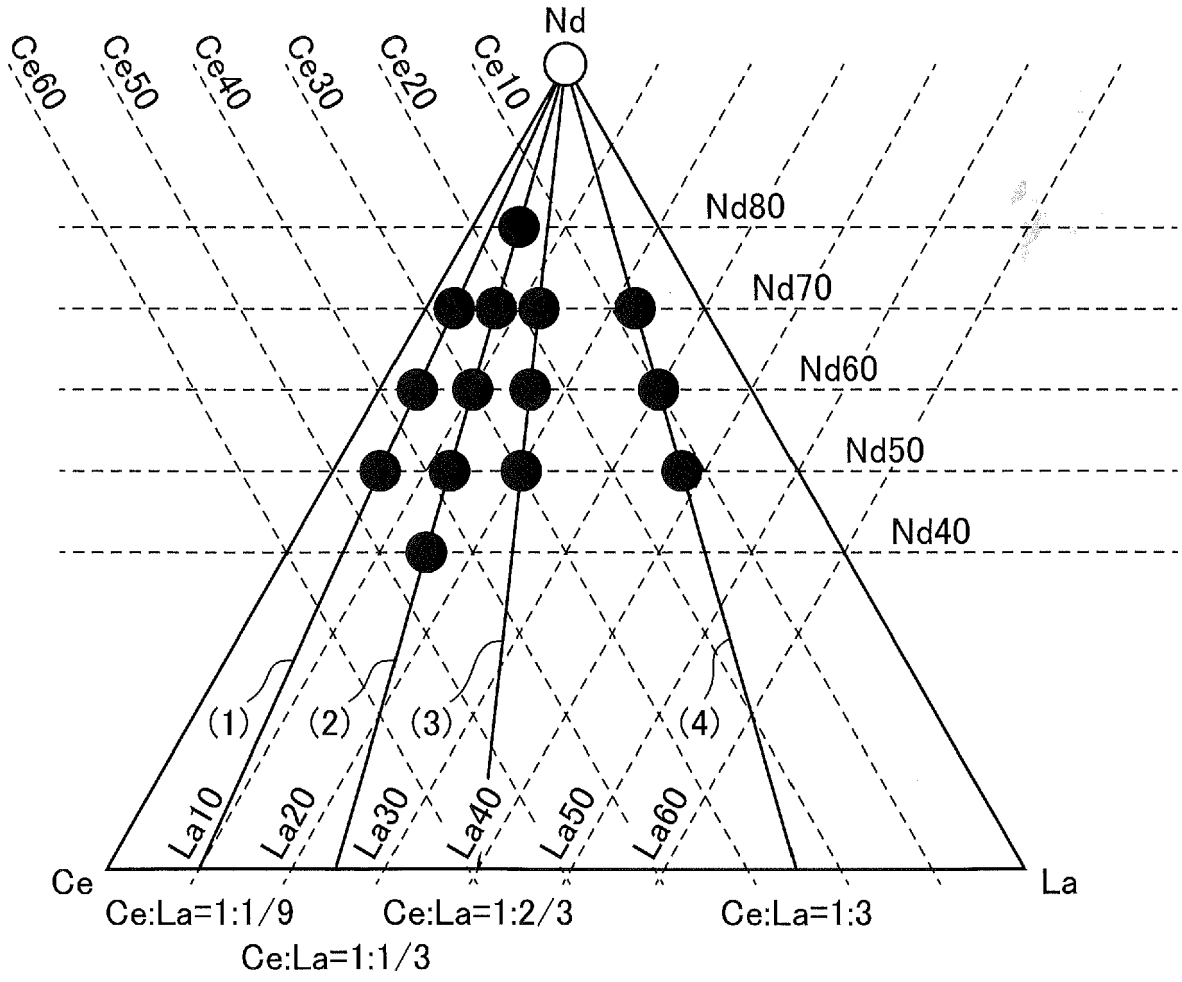

Nd
Ce60
Ce50
Ce40
Ce30
Ce20
Ce10
Nd80
Nd70
Nd60
Nd50
Nd40
(1)
(2)
(3)
(4)
La10
La20
La30
La40
La50
La60
Ce
La
Ce:La=1:1/9
Ce:La=1:1/3
Ce:La=1:2/3
Ce:La=1:3

FIG. 2

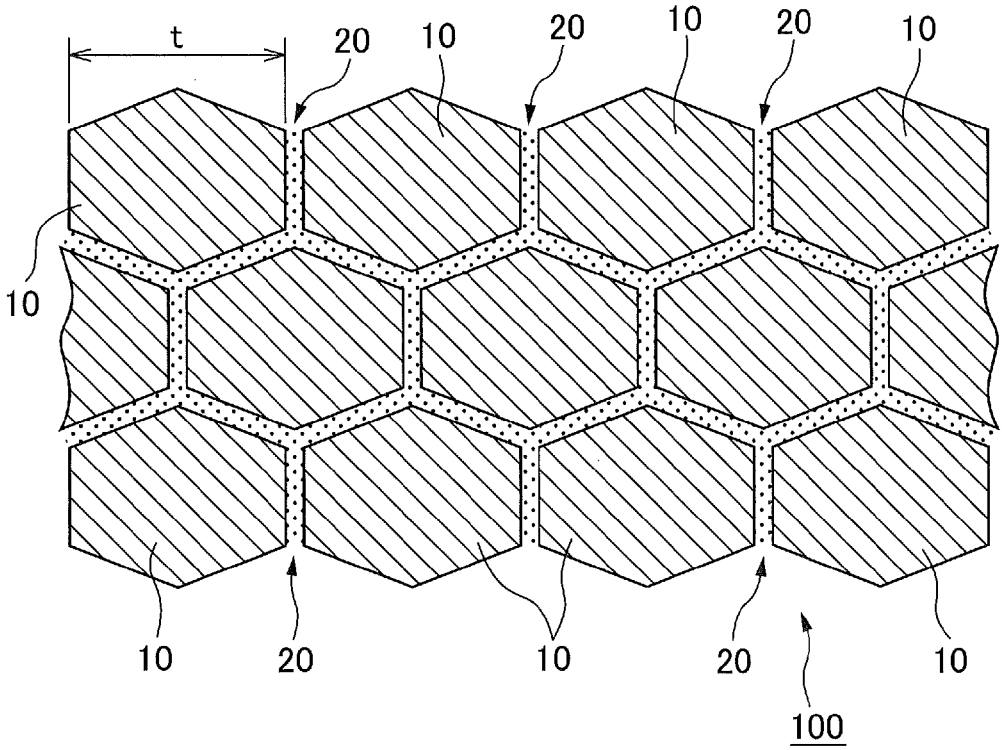

t
20
10
20
10
20
10
10
10
20
10
20
10
100

FIG. 3

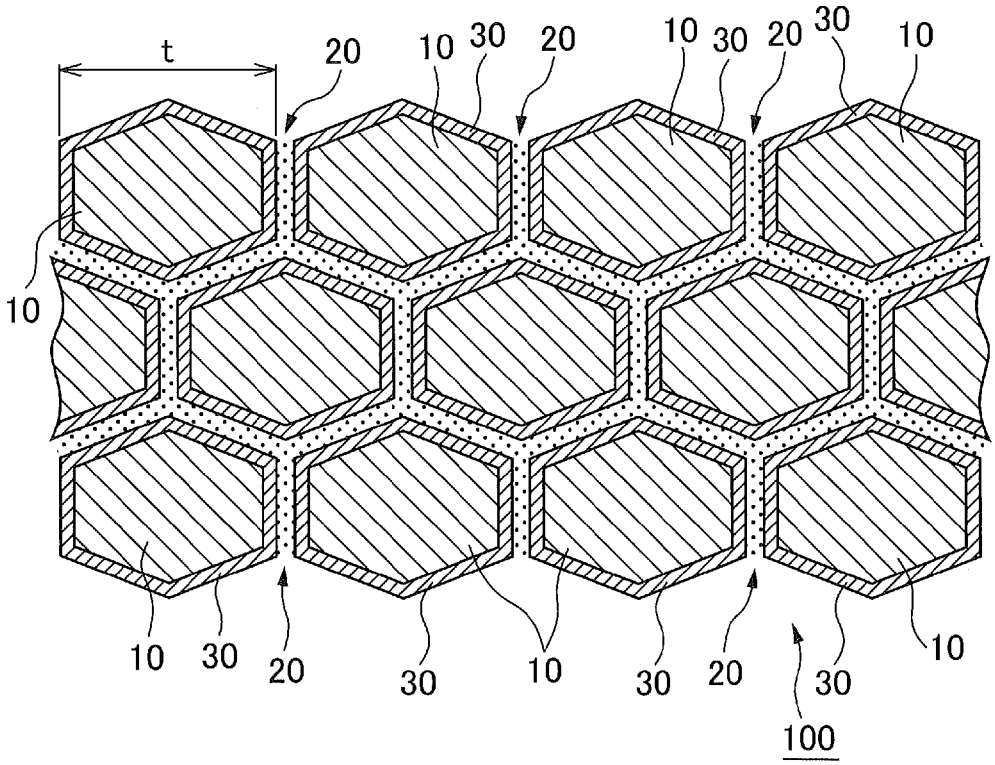

t
20
10
30
20
10
30
20
30
10
10
10
30
20
30
10
30
20
30
10
100

FIG. 4

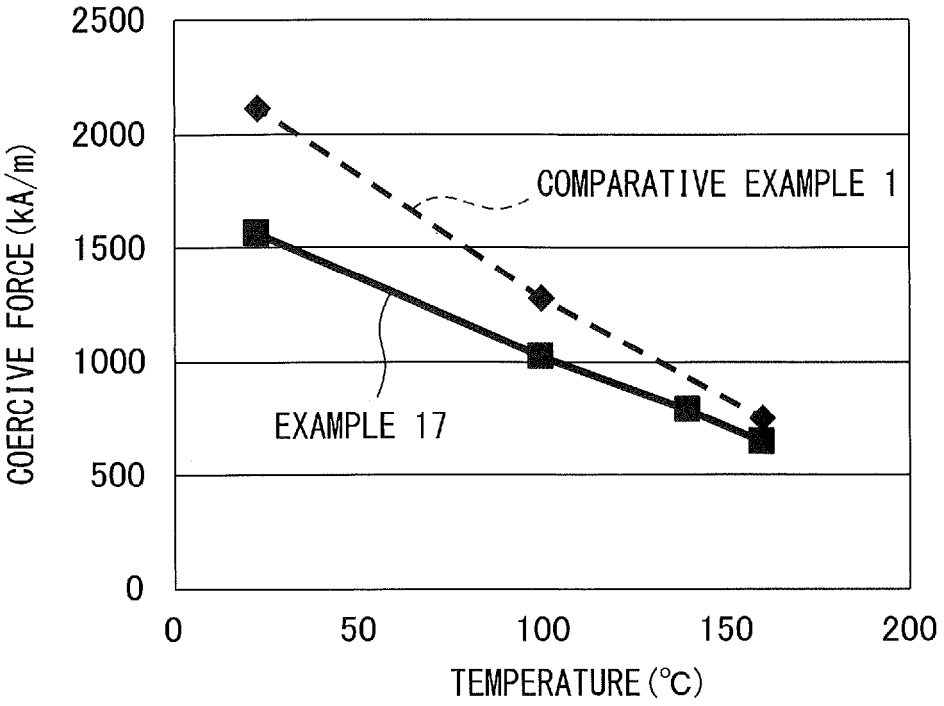
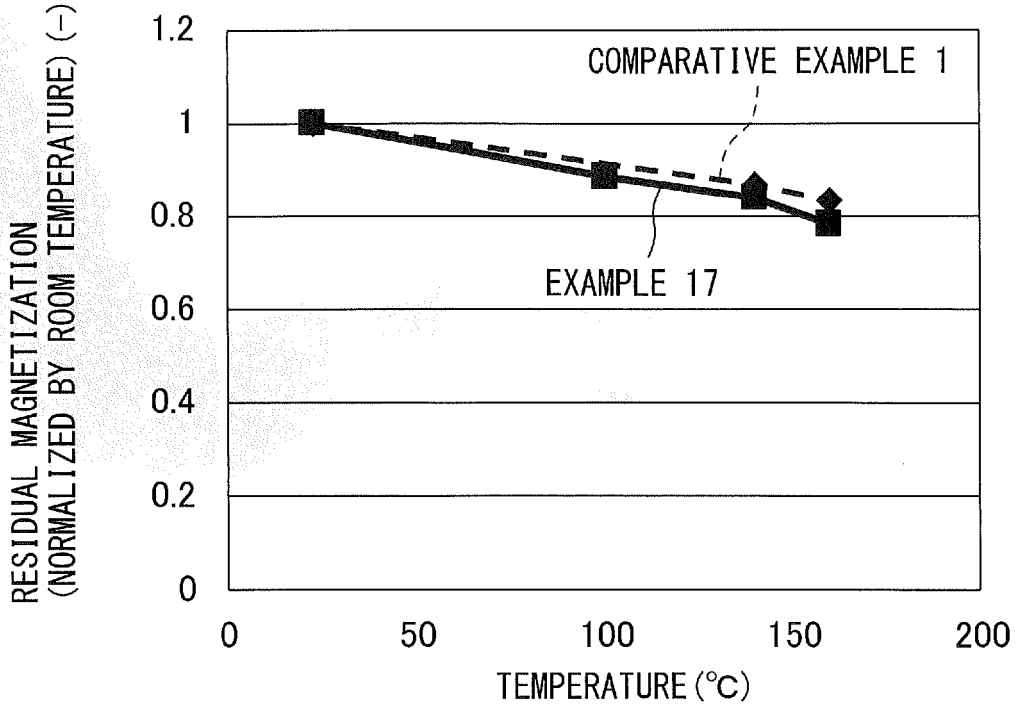

2500
2000
1500
1000
500
0
COERCIVE FORCE (kA/m)
COMPARATIVE EXAMPLE 1
EXAMPLE 17
0
50
100
150
200
TEMPERATURE (°C)

FIG. 5


1.2
1
0.8
0.6
0.4
0.2
0
RESIDUAL MAGNETIZATION
(NORMALIZED BY ROOM TEMPERATURE) (-)
COMPARATIVE EXAMPLE 1
EXAMPLE 17
0
50
100
150
200
TEMPERATURE (°C)

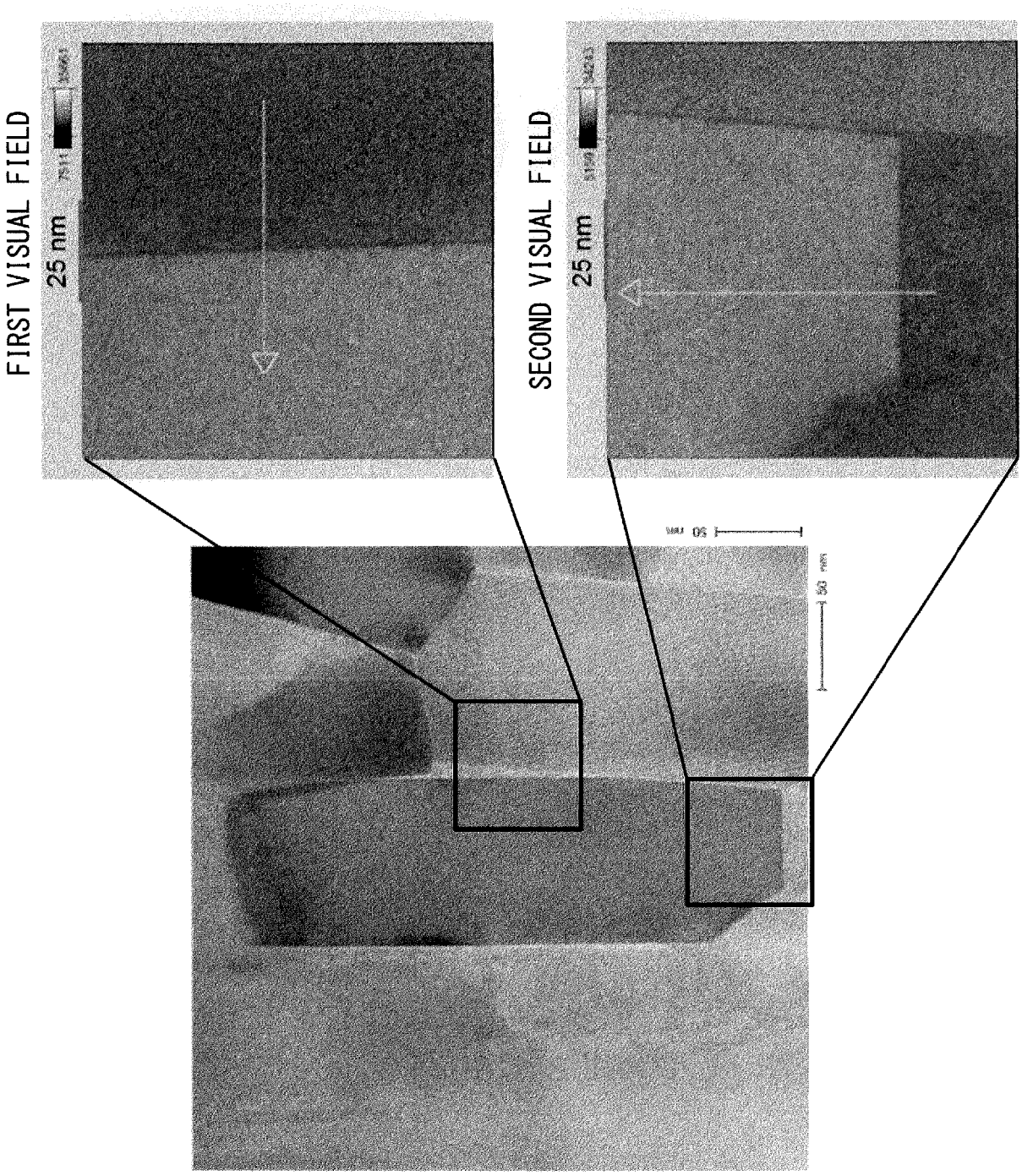
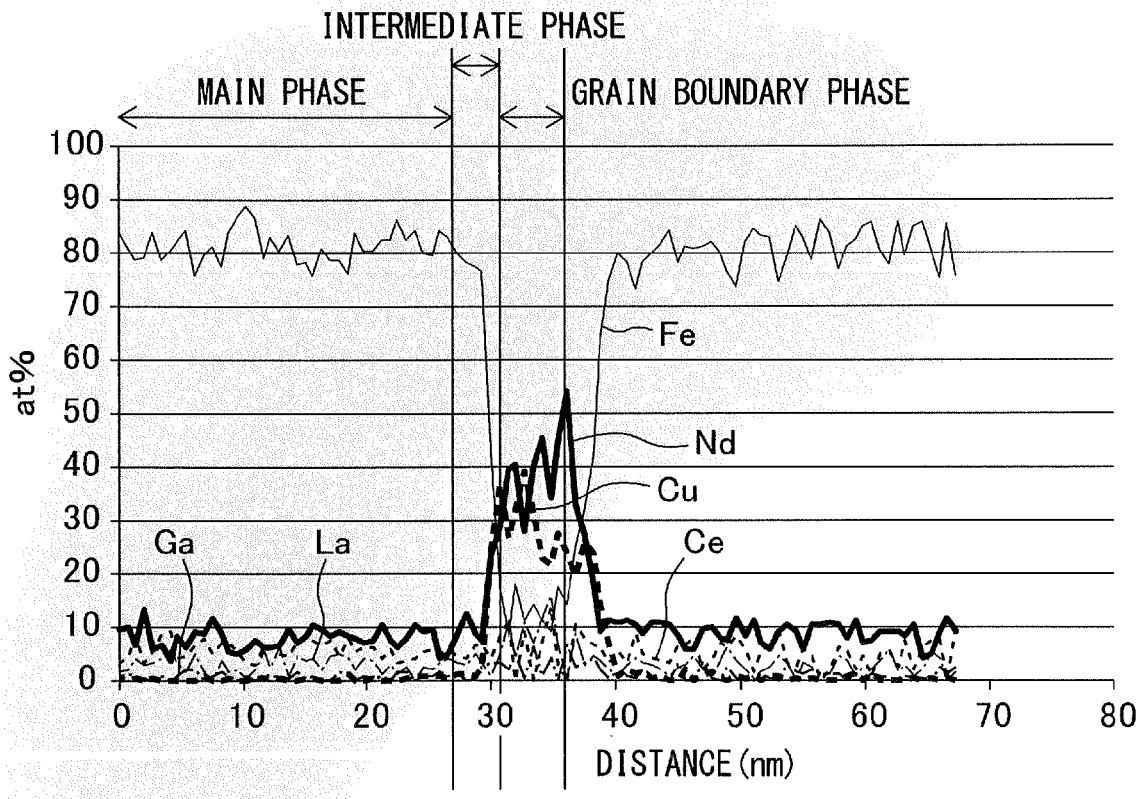


FIG. 6

FIG. 7



FIRST VISUAL FIELD

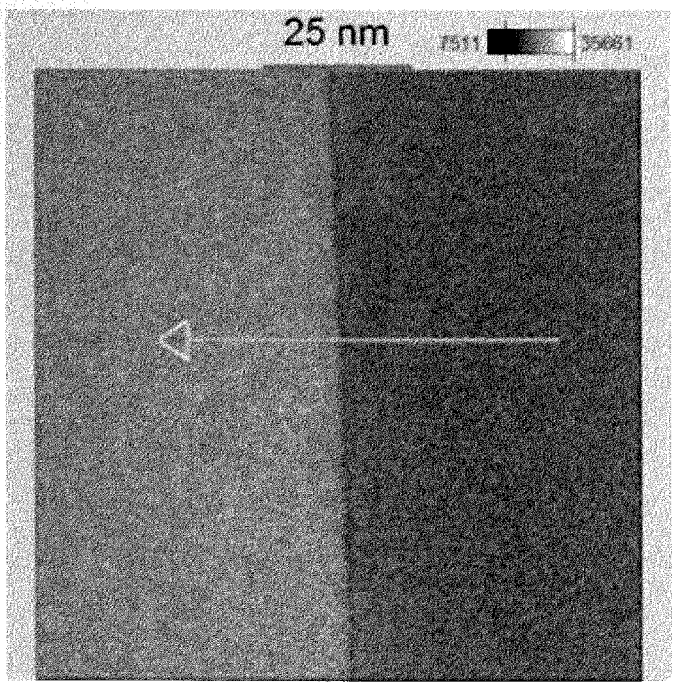
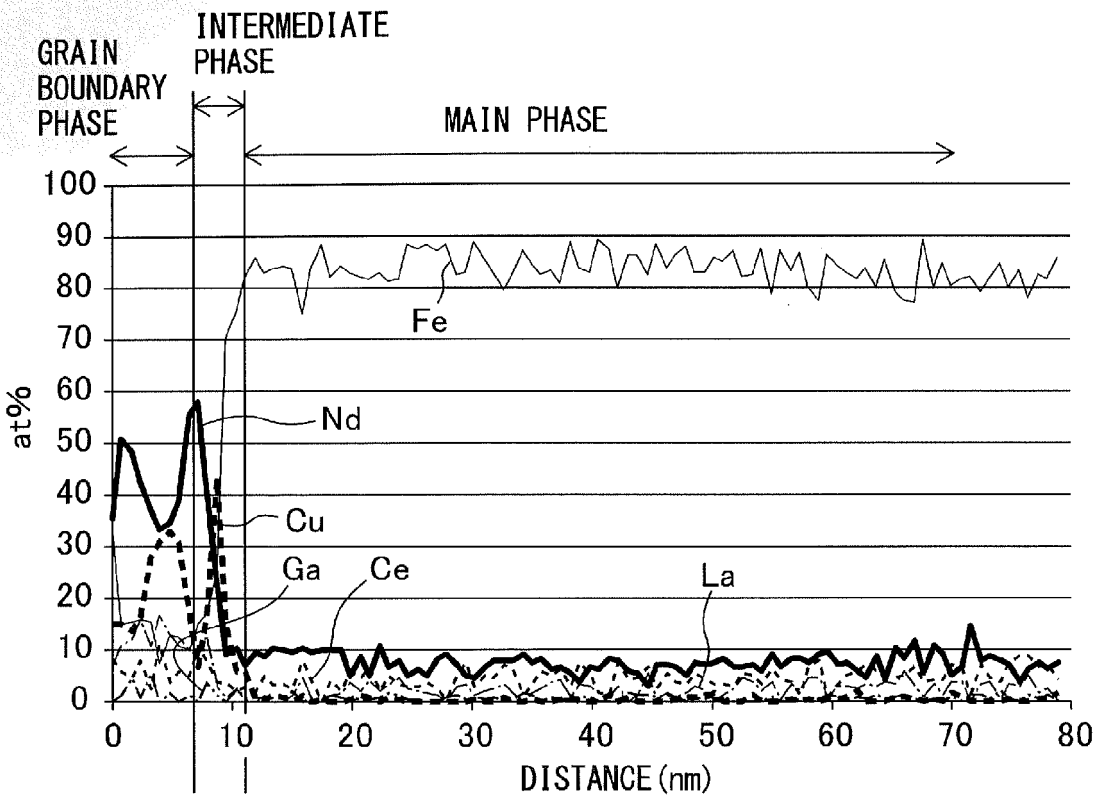
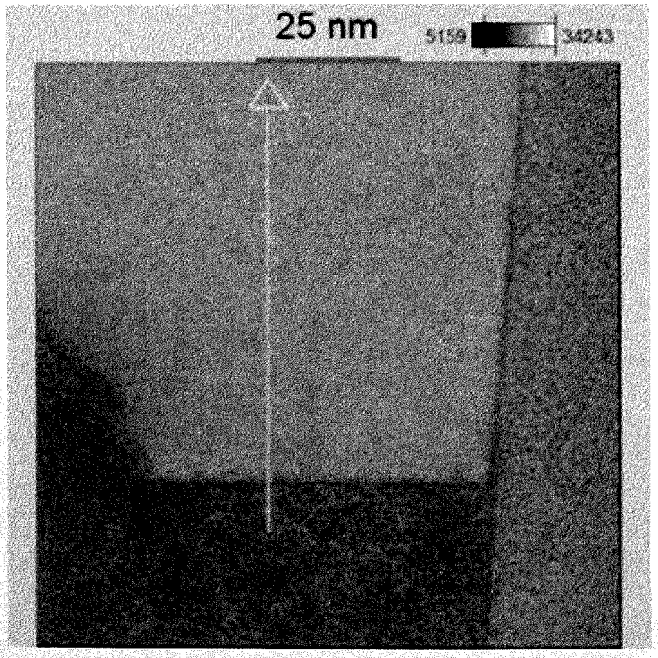


FIG. 8



SECOND VISUAL FIELD



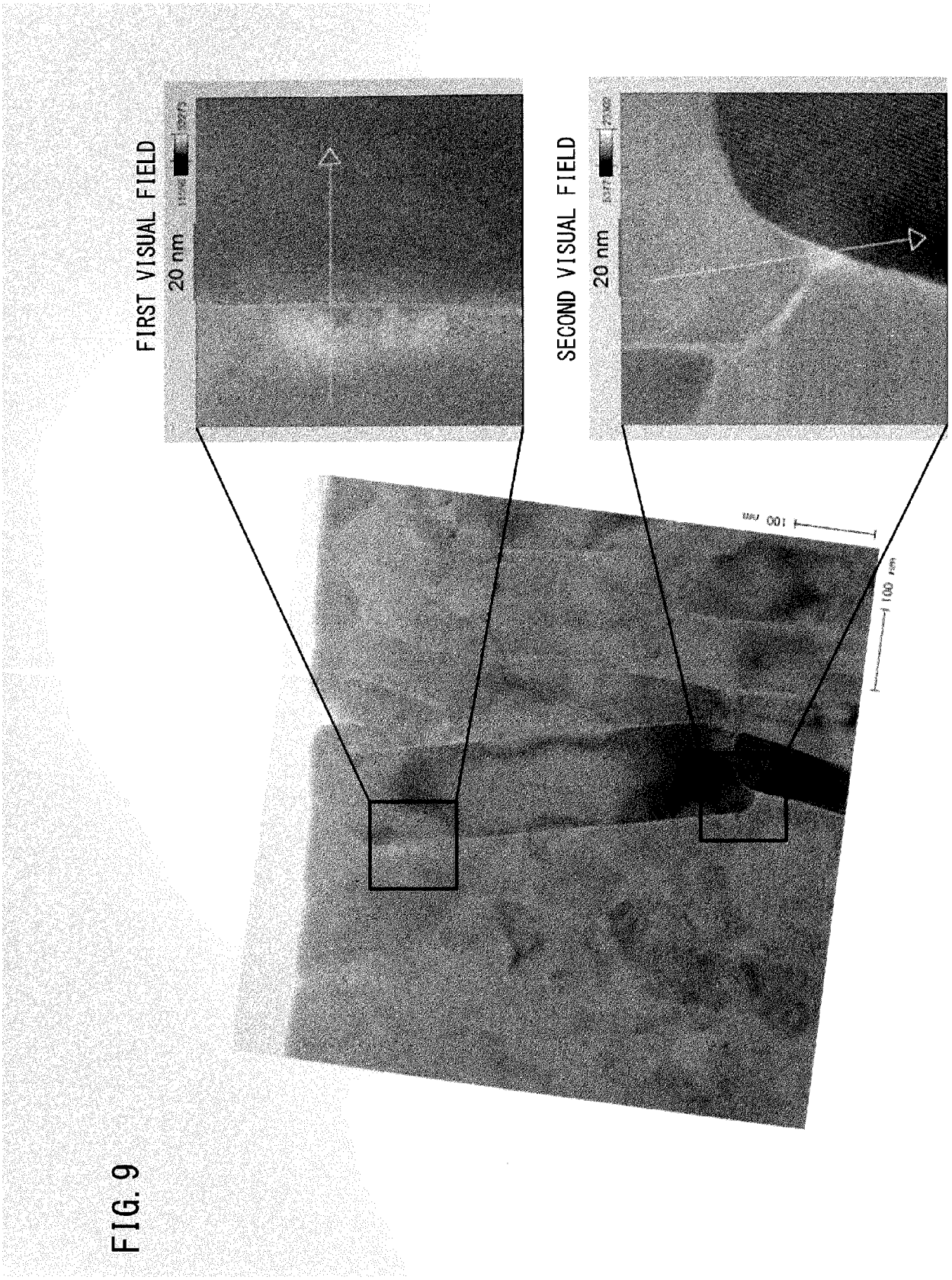
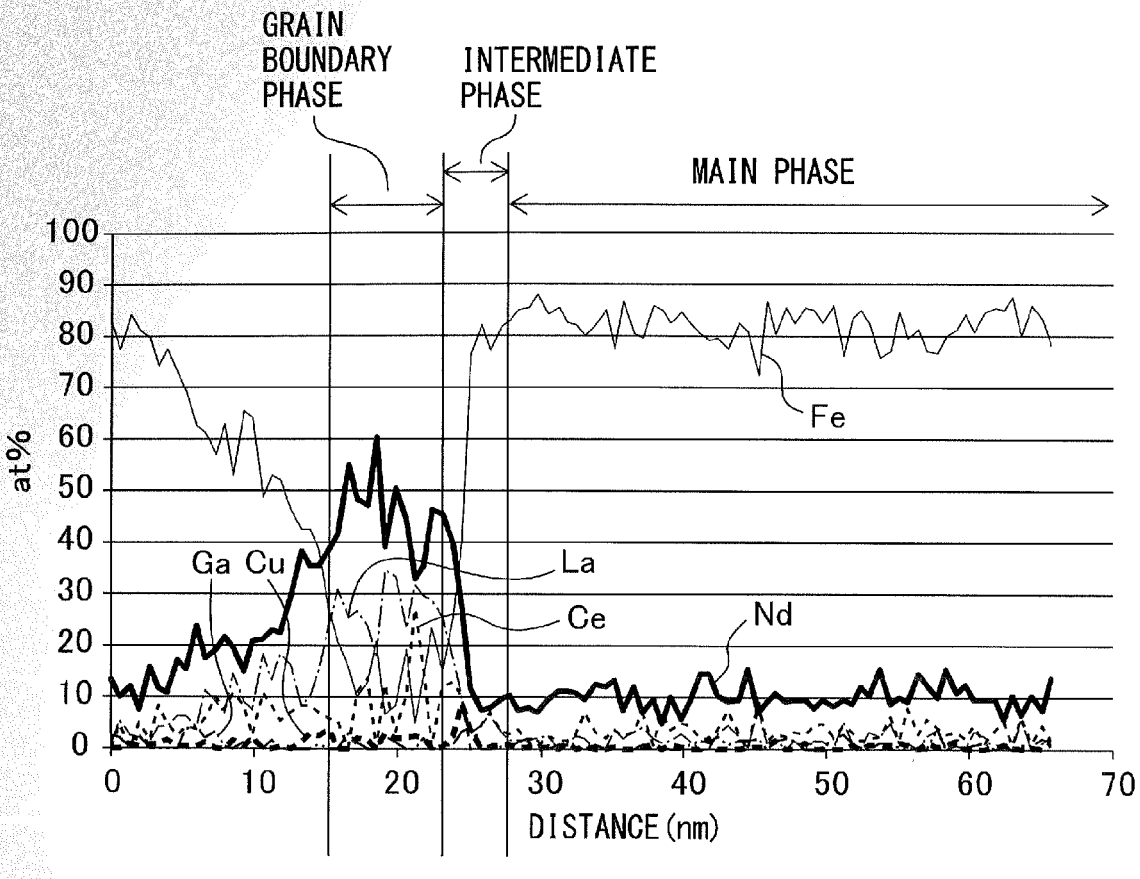

FIRST VISUAL FIELD
20 nm
SECOND VISUAL FIELD
20 nm
100 nm
100 nm

FIG. 9

FIG. 10



FIRST VISUAL FIELD

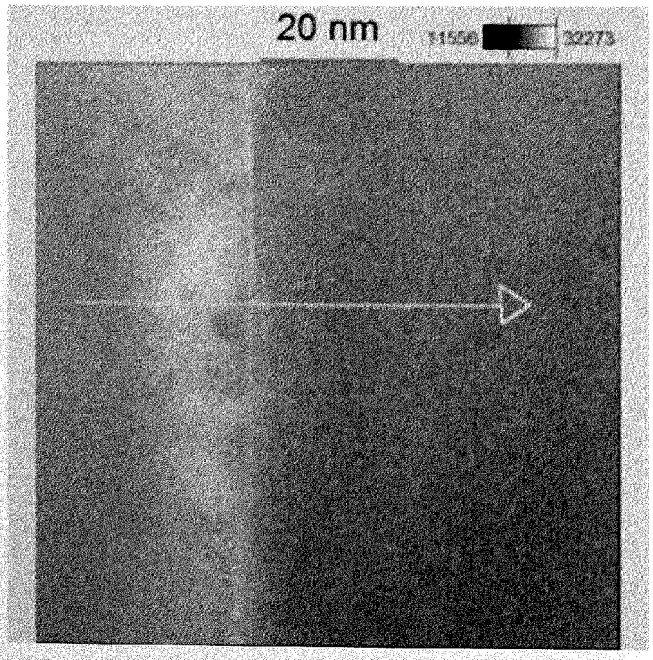
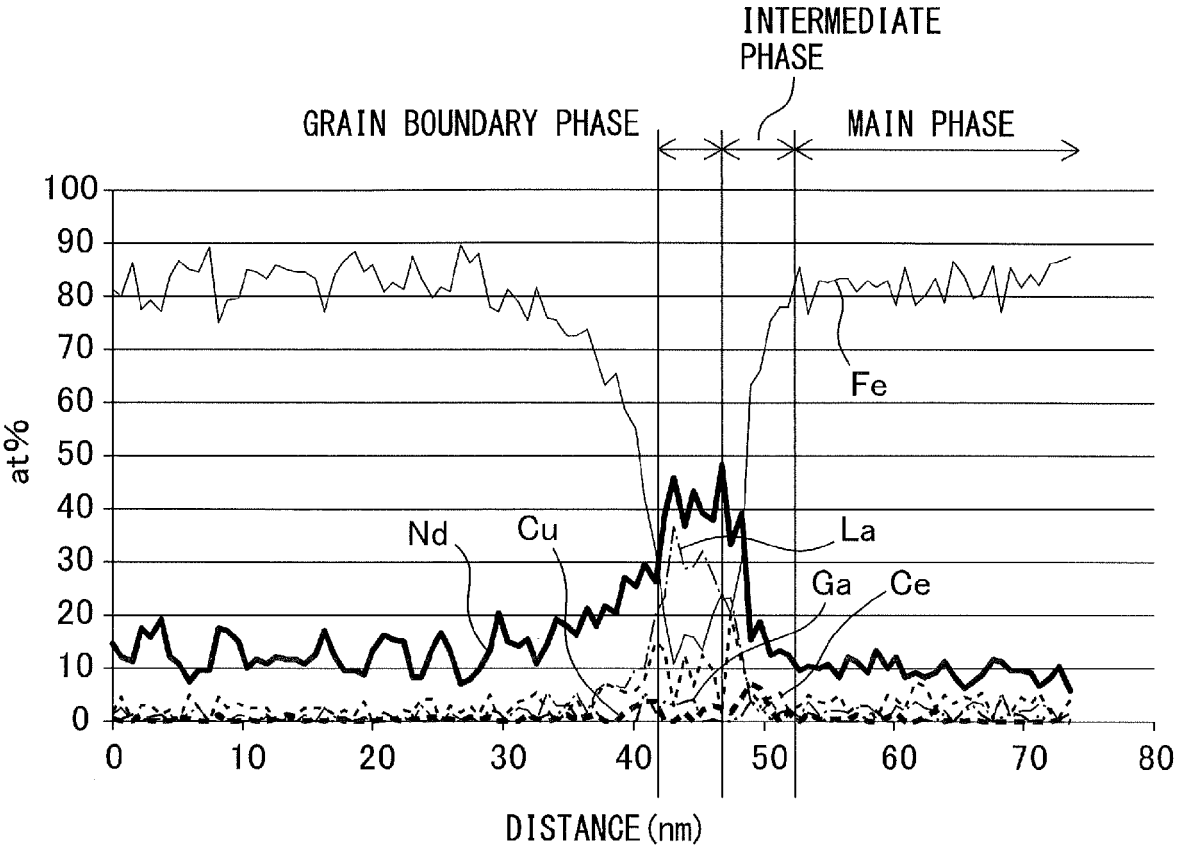
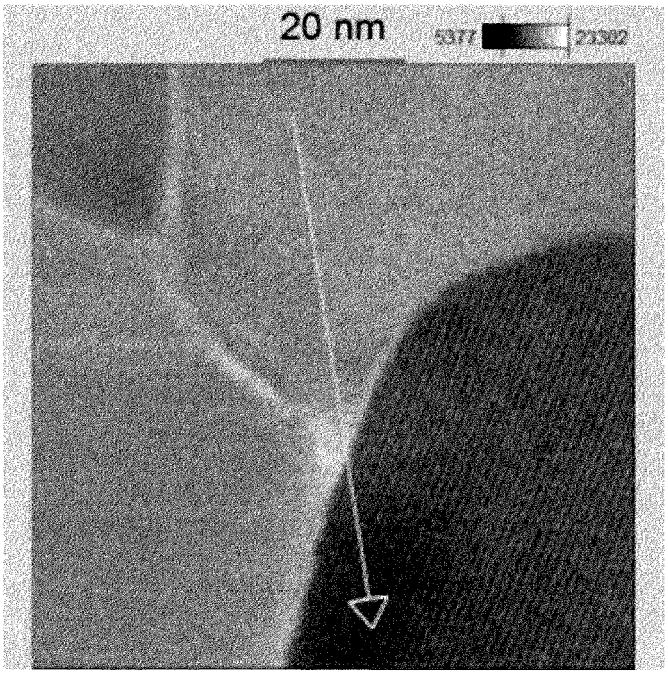


FIG. 11



SECOND VISUAL FIELD



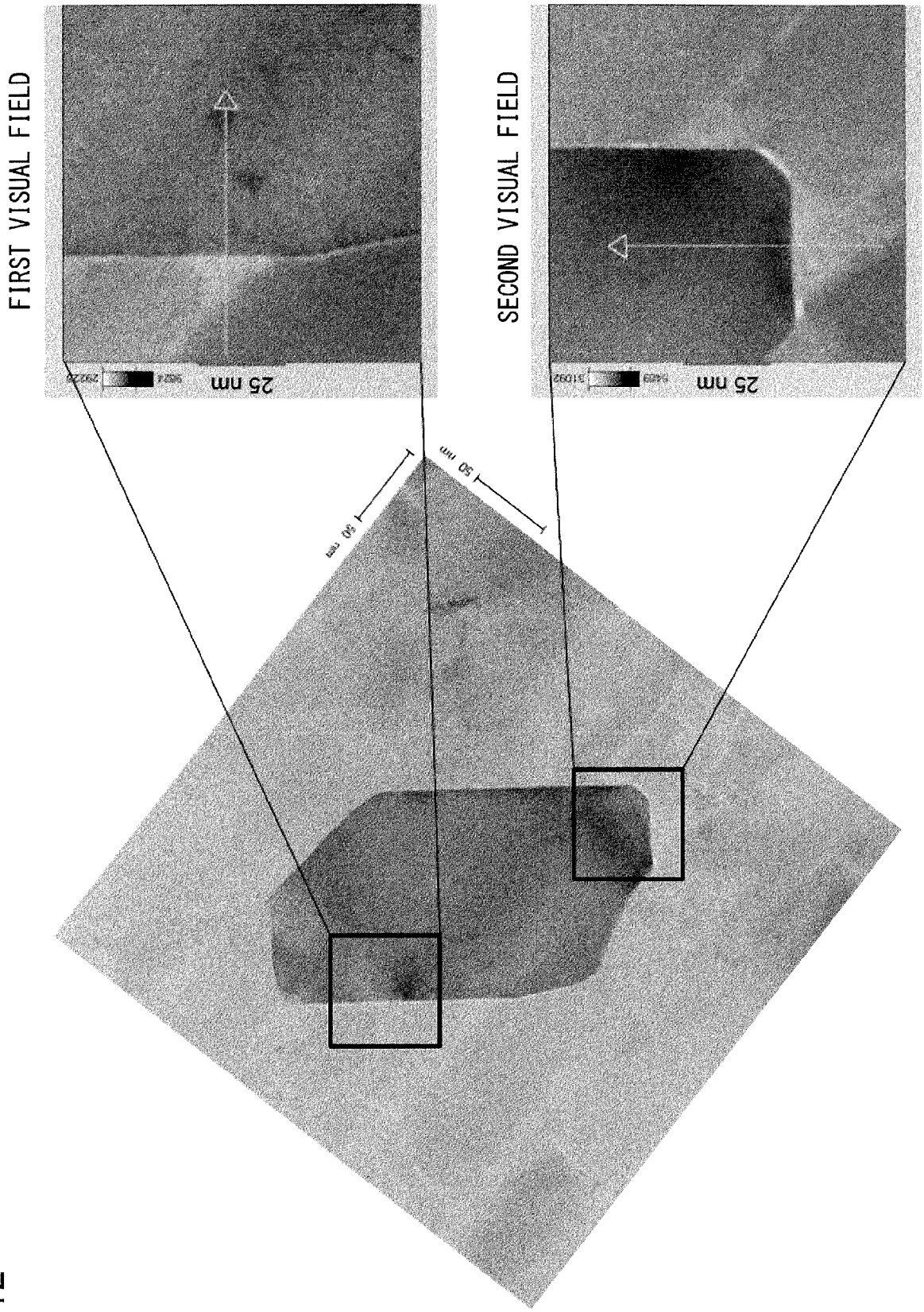
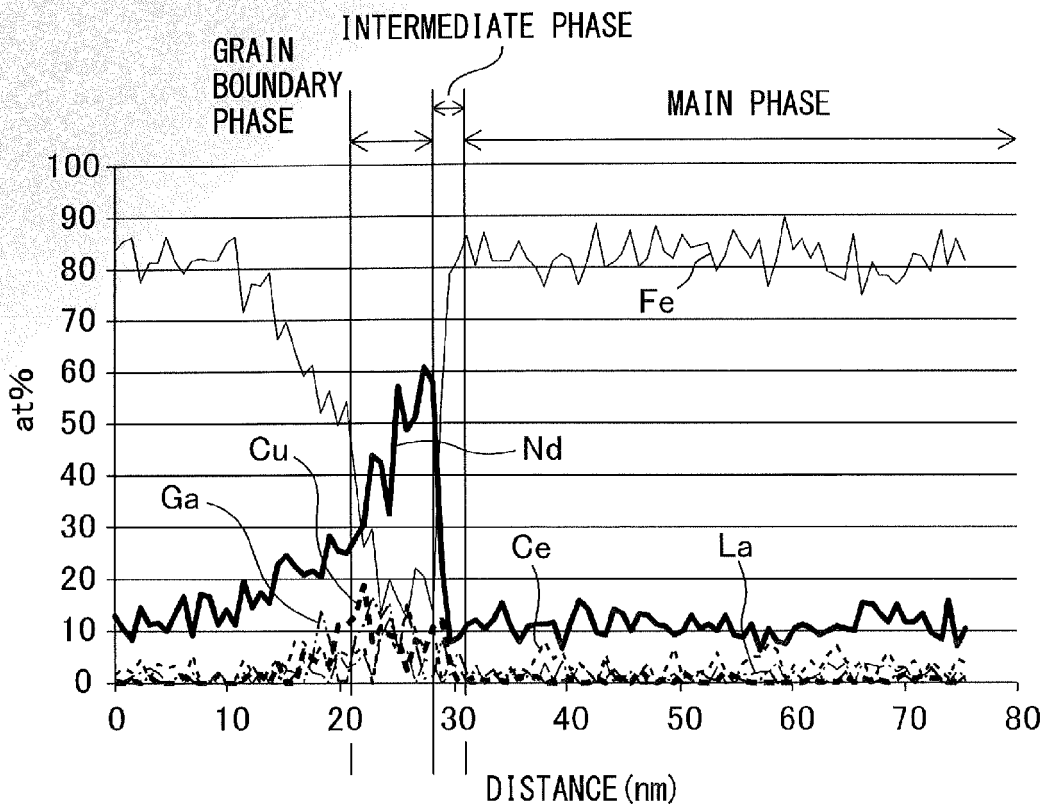


FIG. 12

FIG. 13



FIRST VISUAL FIELD

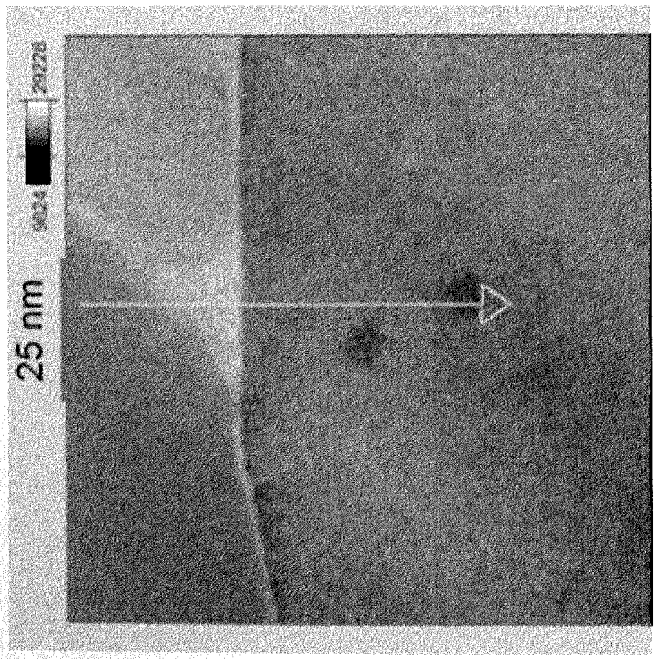
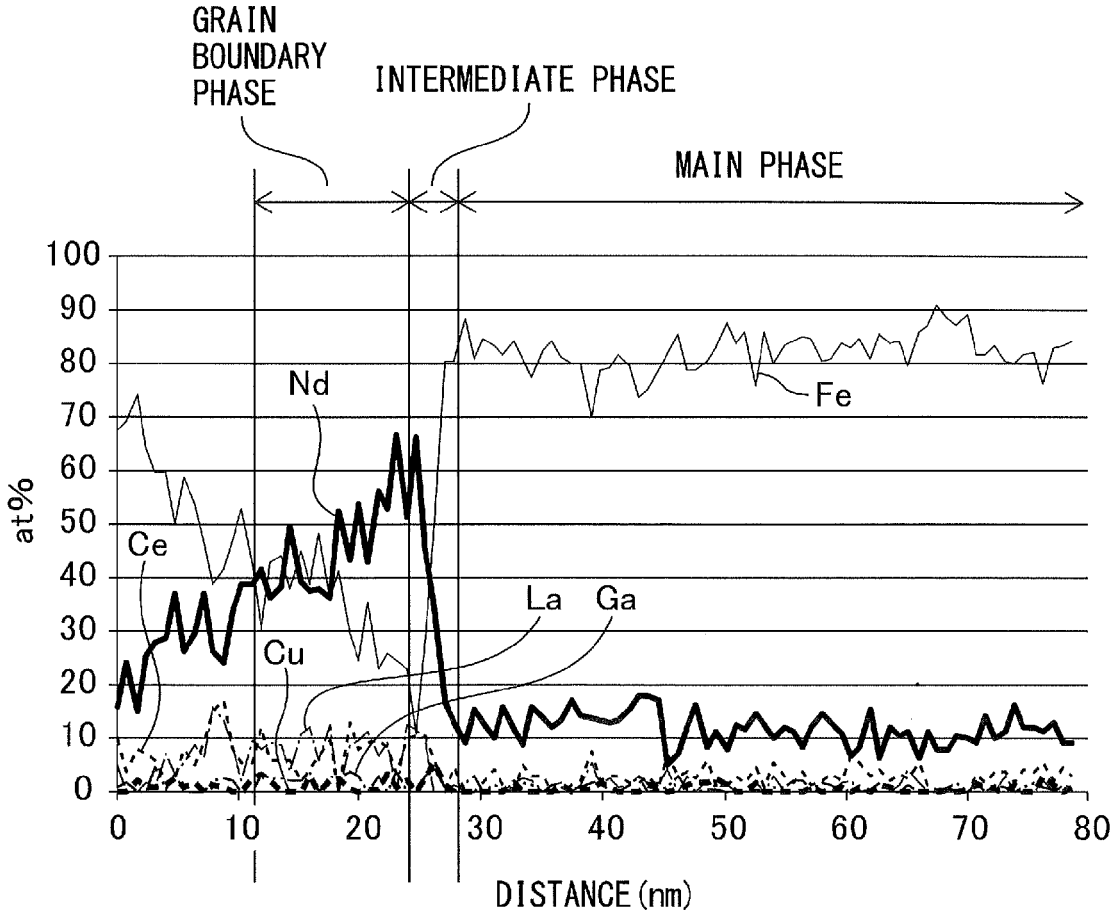


FIG. 14



SECOND VISUAL FIELD

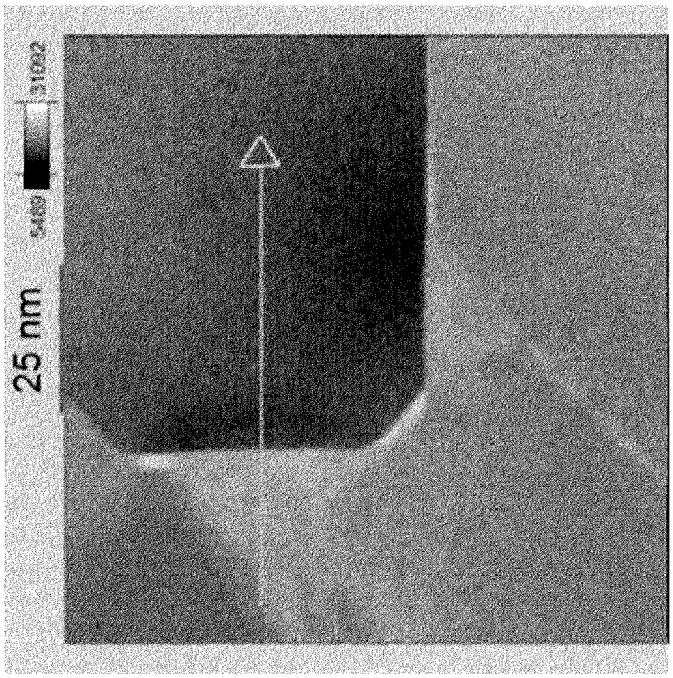


FIG. 15

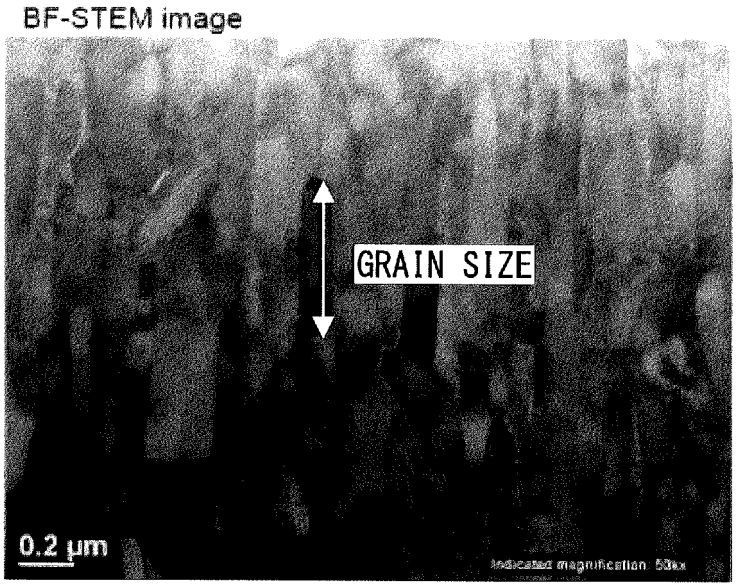


FIG. 16

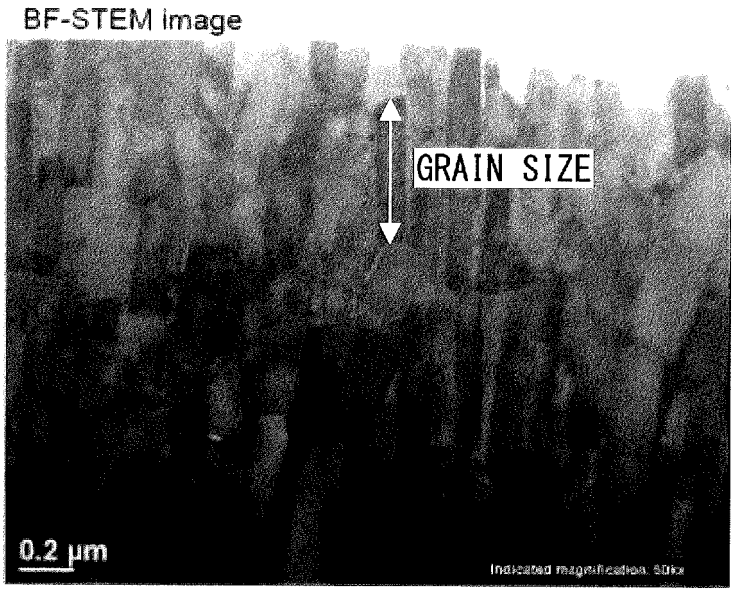


FIG. 17

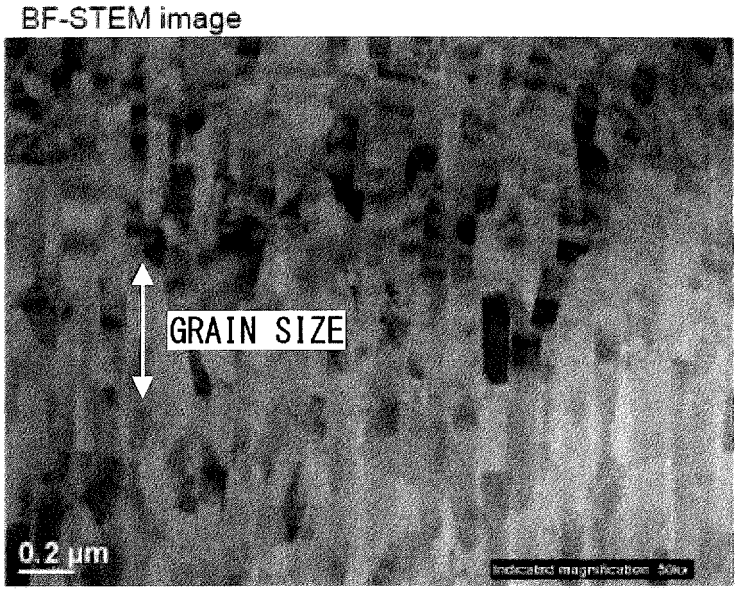


FIG. 18

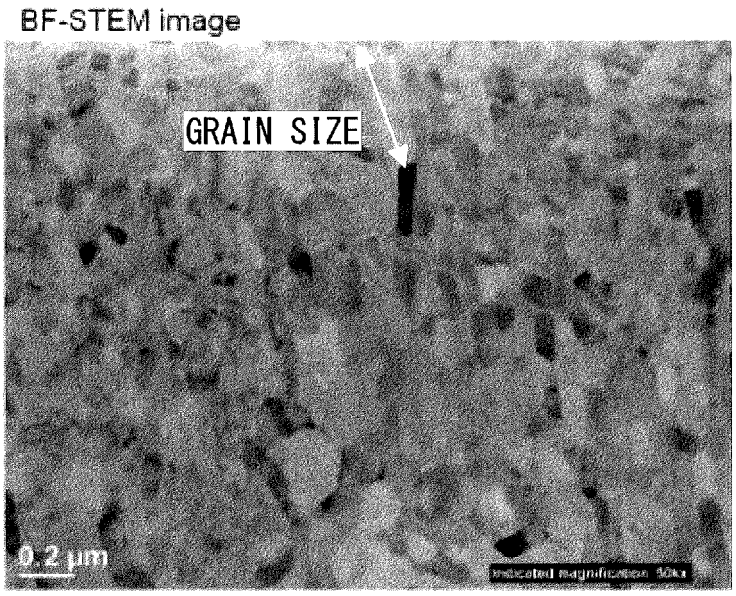


FIG. 19

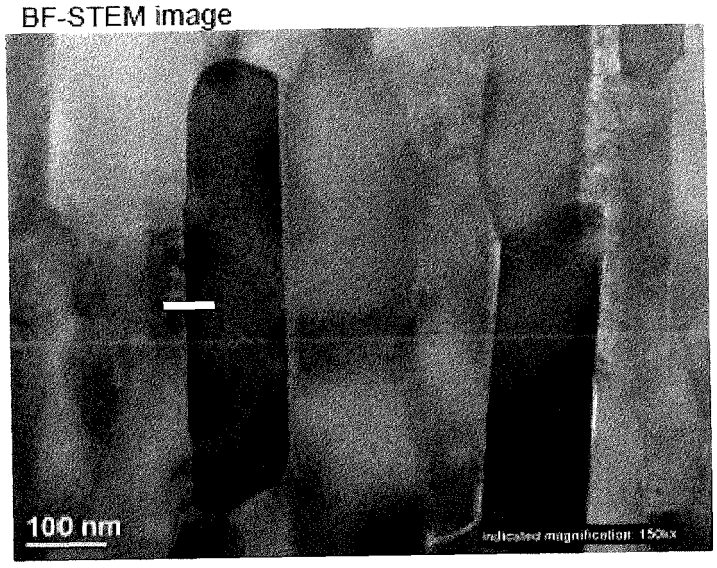


FIG. 20

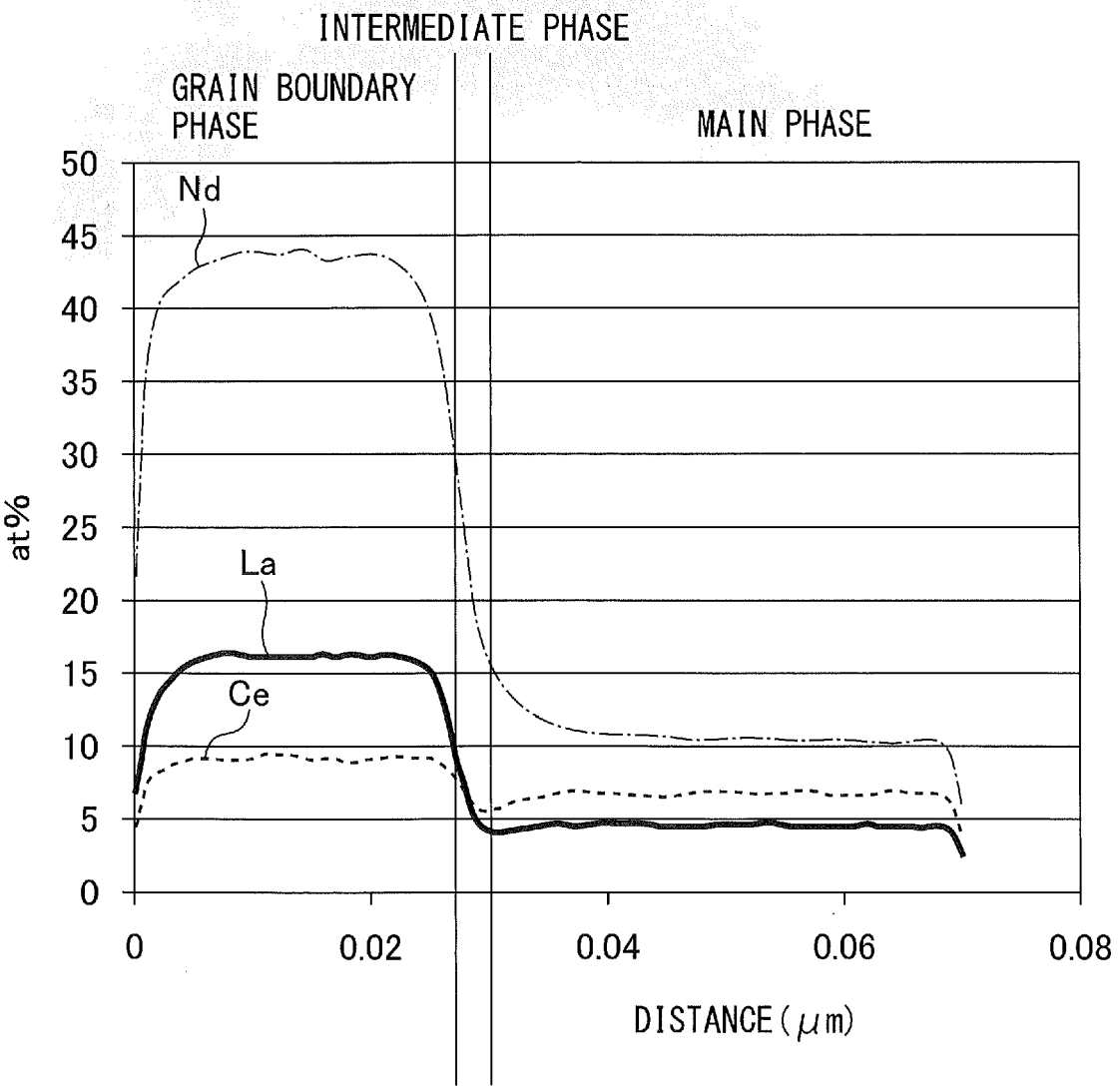

INTERMEDIATE PHASE
GRAIN BOUNDARY PHASE
MAIN PHASE
Nd
La
Ce
at%
50
45
40
35
30
25
20
15
10
5
0
0
0.02
0.04
0.06
0.08
DISTANCE(μm)

FIG. 21

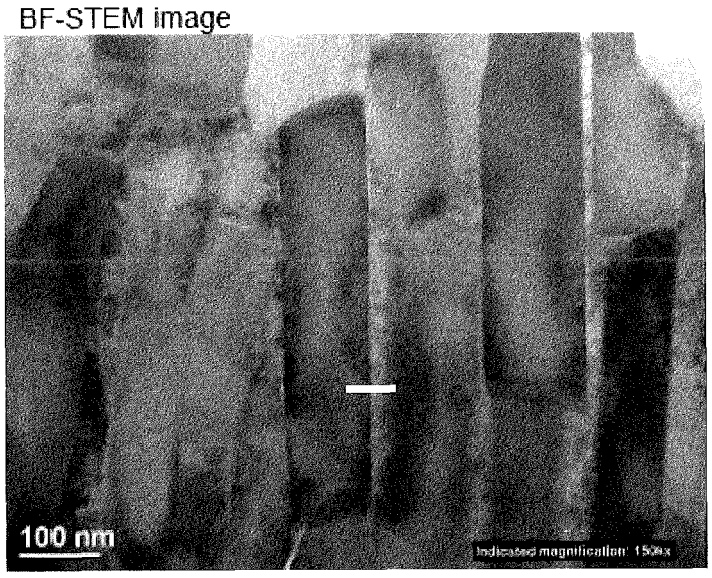


FIG. 22

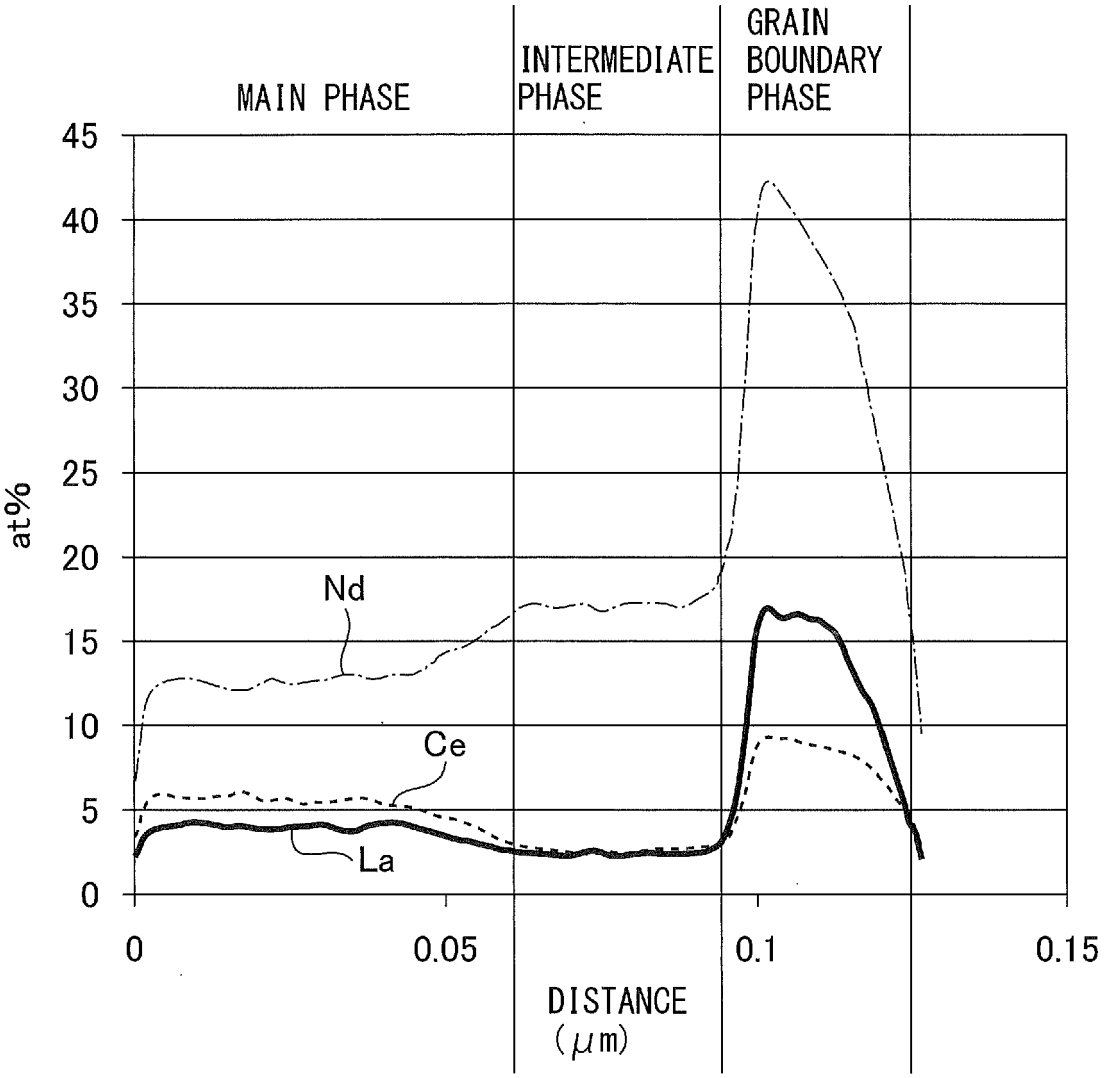

MAIN PHASE
INTERMEDIATE PHASE
GRAIN BOUNDARY PHASE
45
40
35
30
25
20
15
10
5
0
at%
Nd
Ce
La
0
0.05
0.1
0.15
DISTANCE (μm)

FIG. 23

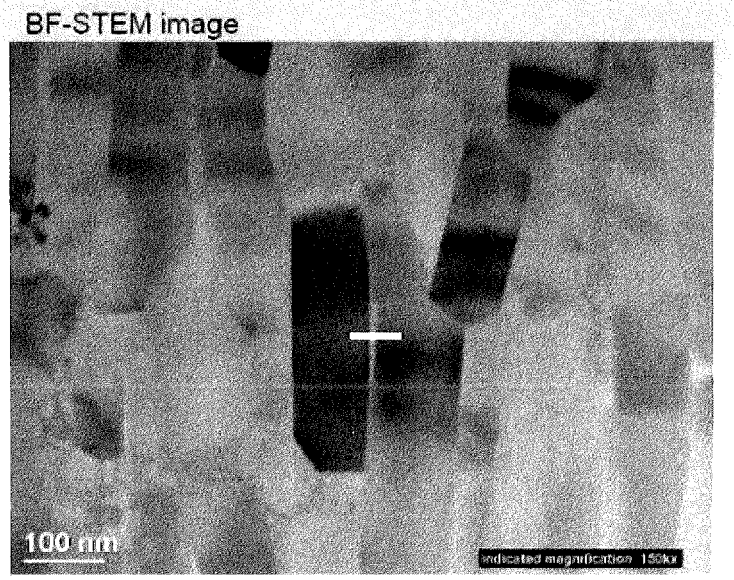


FIG. 24

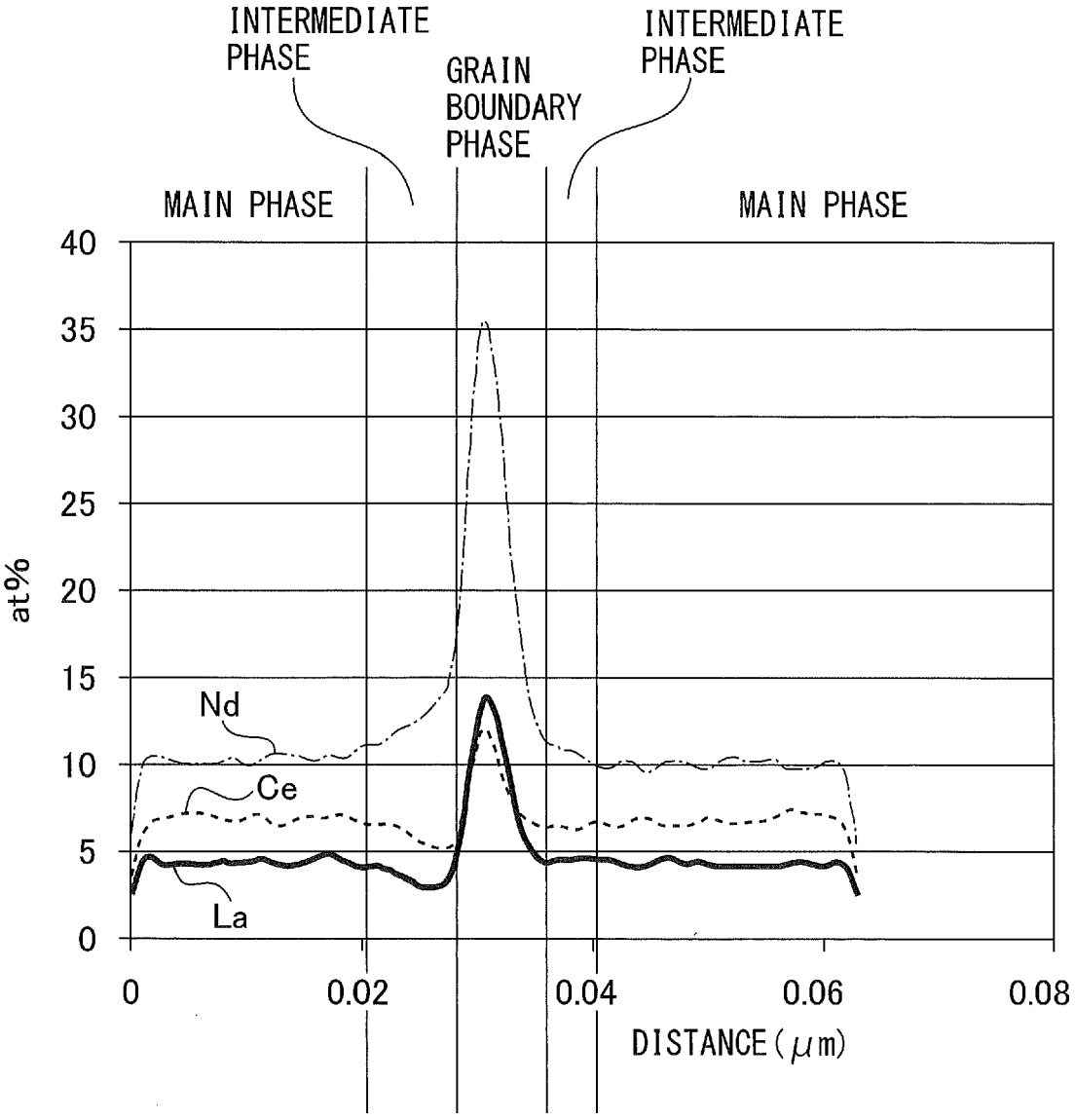

INTERMEDIATE PHASE
GRAIN BOUNDARY PHASE
INTERMEDIATE PHASE
MAIN PHASE
MAIN PHASE
40
35
30
25
20
15
10
5
0
at%
Nd
Ce
La
0
0.02
0.04
0.06
0.08
DISTANCE(μm)

FIG. 25

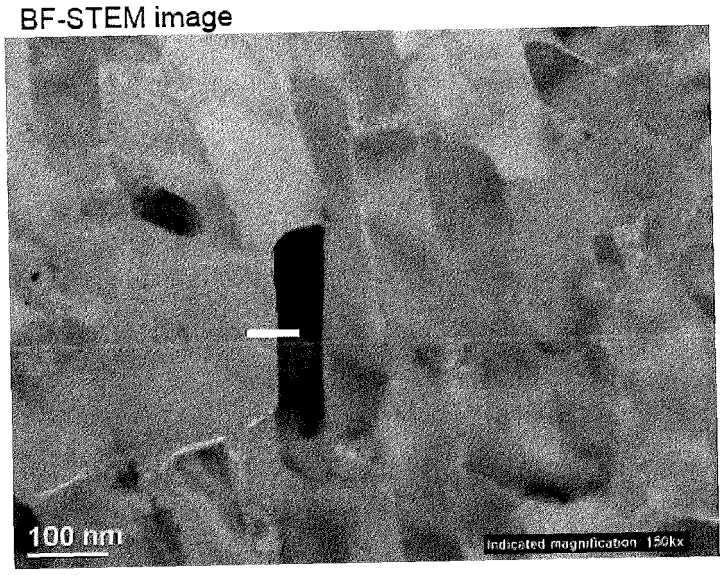
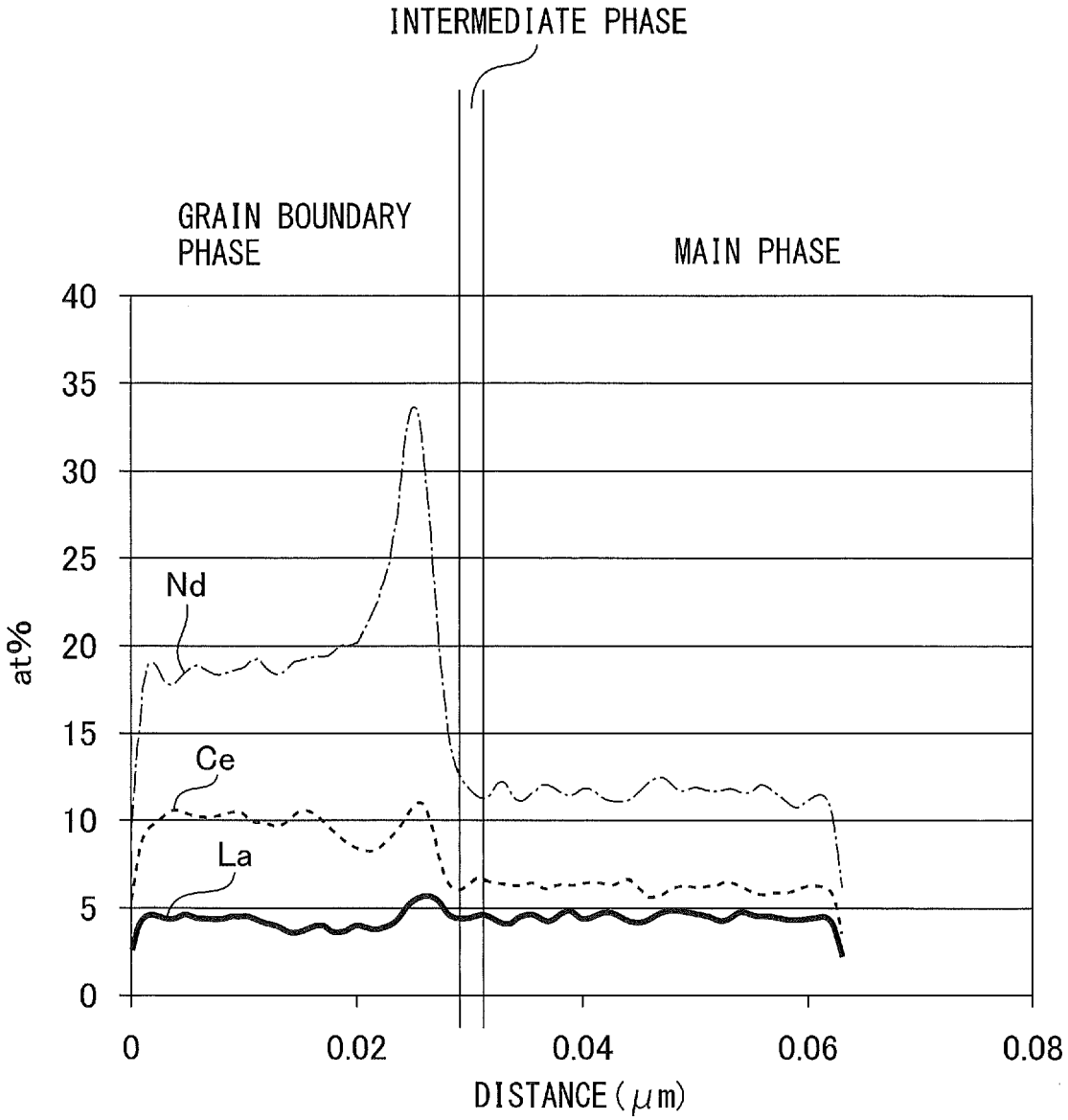


FIG. 26


INTERMEDIATE PHASE
GRAIN BOUNDARY PHASE
MAIN PHASE
40
35
30
25
20
15
10
5
0
at%
Nd
Ce
La
0
0.02
0.04
0.06
0.08
DISTANCE (μm)

Europäisches Patentamt
European Patent Office
Office européen des brevets

EUROPEAN SEARCH REPORT

Application Number
EP 18 21 5888

DOCUMENTS CONSIDERED TO BE RELEVANT

Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 6 136 099 A (AKIOKA KOJI [JP] ET AL) 24 October 2000 (2000-10-24) * claims 4,5,12; table 15 *	1,2,7,8, 11	INV. H01F1/057 H01F41/02
X,D	US 2016/141083 A1 (ITO MASAAKI [JP] ET AL) 19 May 2016 (2016-05-19) * figures 1,9; example 1; table 2 *	1-11	
X	JP 2016 111136 A (TOYOTA MOTOR CORP) 20 June 2016 (2016-06-20) * example 2; table 1 *	1-11	
A	US 5 129 963 A (PANCHANATHAN VISWANATHAN [US] ET AL) 14 July 1992 (1992-07-14) * column 2, line 48; figure 2; example 1 *	1-11	

TECHNICAL FIELDS SEARCHED (IPC)

H01F

The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	19 June 2019	Primus, Jean-Louis

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
Y : particularly relevant if combined with another document of the same category
A : technological background
O : non-written disclosure
P : intermediate document

T : theory or principle underlying the invention
E : earlier patent document, but published on, or after the filing date
D : document cited in the application
L : document cited for other reasons

& : member of the same patent family, corresponding document

EPO FORM 1503 03.82 (P04C01)

ANNEX TO THE EUROPEAN SEARCH REPORT ON EUROPEAN PATENT APPLICATION NO. EP 18 21 5888

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report. The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

19-06-2019

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 6136099 A	24-10-2000	NONE	
US 2016141083 A1	19-05-2016	CN 105518809 A	20-04-2016
		CN 109300640 A	01-02-2019
		JP 6183457 B2	23-08-2017
		JP WO2014196605 A1	23-02-2017
		US 2016141083 A1	19-05-2016
		WO 2014196605 A1	11-12-2014
JP 2016111136 A	20-06-2016	NONE	
US 5129963 A	14-07-1992	JP 3033127 B2	17-04-2000
		JP H0421744 A	24-01-1992
		US 5129963 A	14-07-1992

EPO FORM P0459

For more details about this annex : see Official Journal of the European Patent Office, No. 12/82

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- WO 2014196605 A1 **[0005]**