United States Patent [19]

Tawara et al.

[11] **3,839,102**

[45] **Oct. 1, 1974**

[54] **PERMANENT MAGNET**

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[22] Filed: **Nov. 10, 1970**

[21] Appl. No.: **88,479**

Related U.S. Application Data

[62] Division of Ser. No. 775,651, Nov. 14, 1968.

[30] **Foreign Application Priority Data**

Mar. 18, 1968 Japan 43-18154

[52] **U.S. Cl.** **148/102,** 148/31.57

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

[58] **Field of Search** 148/100, 101, 102, 103, 148/31.57, 121; 75/170, 122

[56] **References Cited**

UNITED STATES PATENTS

3,211,592	10/1965	Masumoto et al.	148/121
3,350,240	10/1967	Higuchi et al.	148/121
3,421,889	1/1969	Ostertag et al.	75/170
3,424,578	1/1969	Strnat et al.	75/213
3,523,836	8/1970	Buschow et al.	148/31.57
3,546,030	12/1970	Buschow et al.	148/31.57
3,560,200	2/1971	Nesbitt et al.	75/122

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[57] **ABSTRACT**

Permanent magnet material having a high coercive force and a high residual flux density is constituted by an alloy of cerium (15 to 20 mol percent), cobalt (52 to 77 mol percent) and copper (8 to 30 mol percent). The cerium can be replaced by Ce-mischmetal in an amount providing the equivalent quantity of cerium. The material has a novel microstructure. The material can be prepared by melting together the ingredient materials and furnace-cooling to room temperature. Superior results are obtained with specially scheduled heat-treatments including controlled cooling rates. It is not necessary to use a fine particle magnet material.

3 Claims, 4 Drawing Figures

FIG. 1

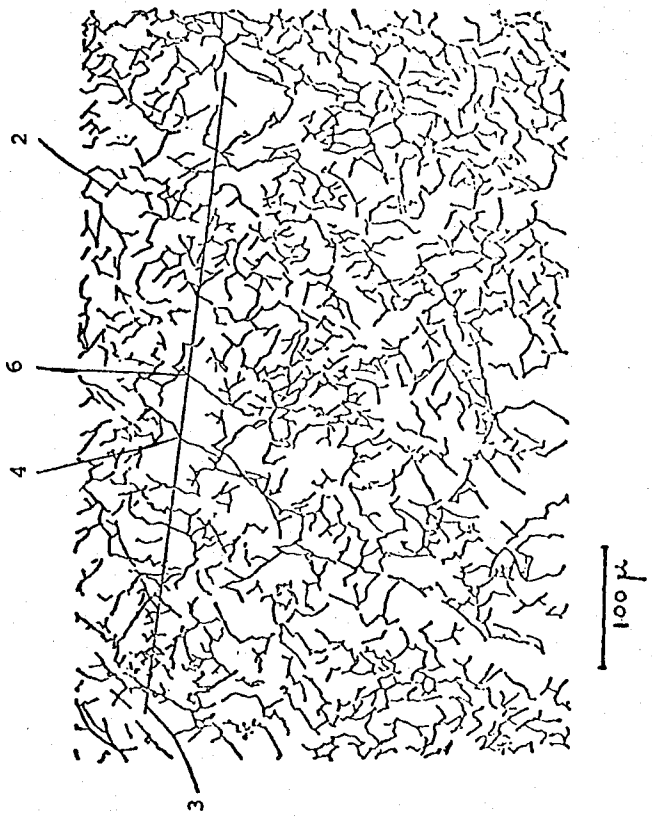


FIG.2

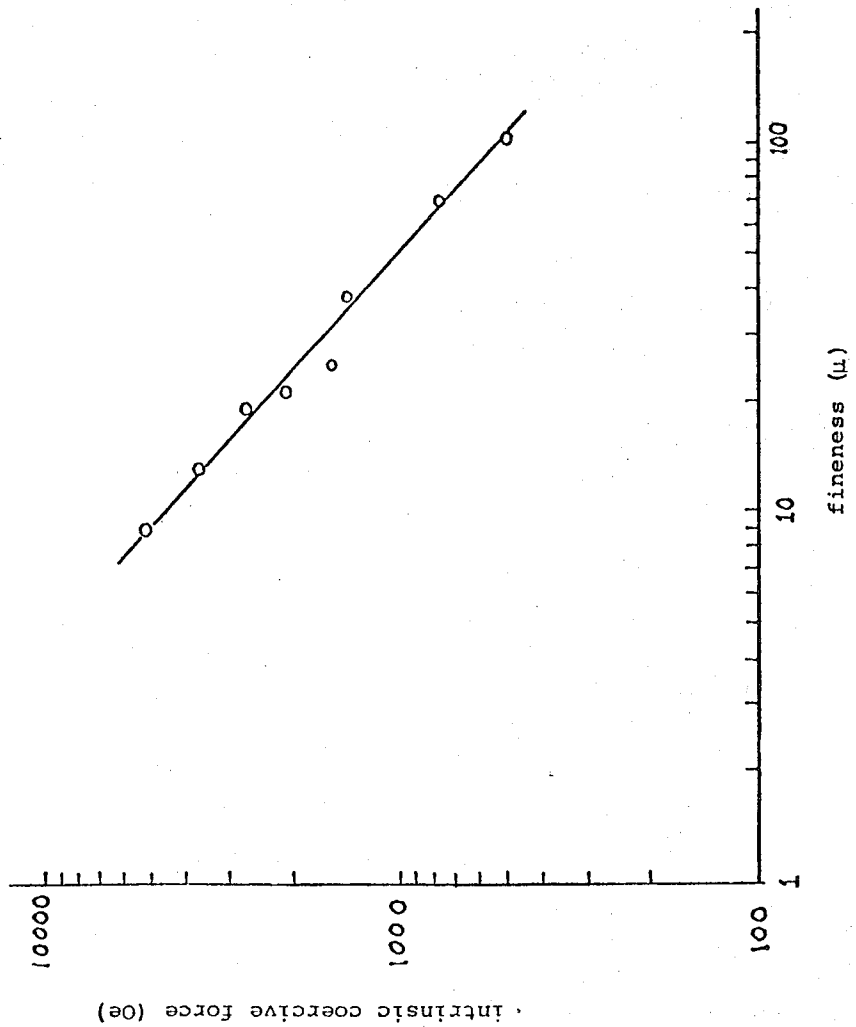

intrinsic coercive force (Oe)
10000
1000
100
1
10
100
fineness (μ)

FIG. 3

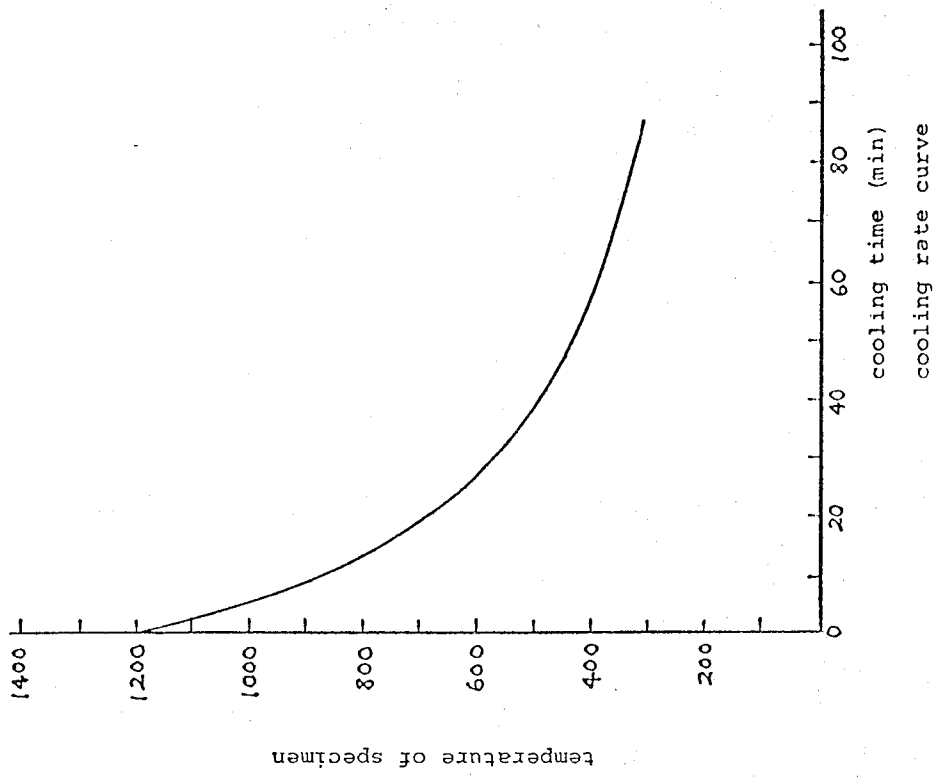
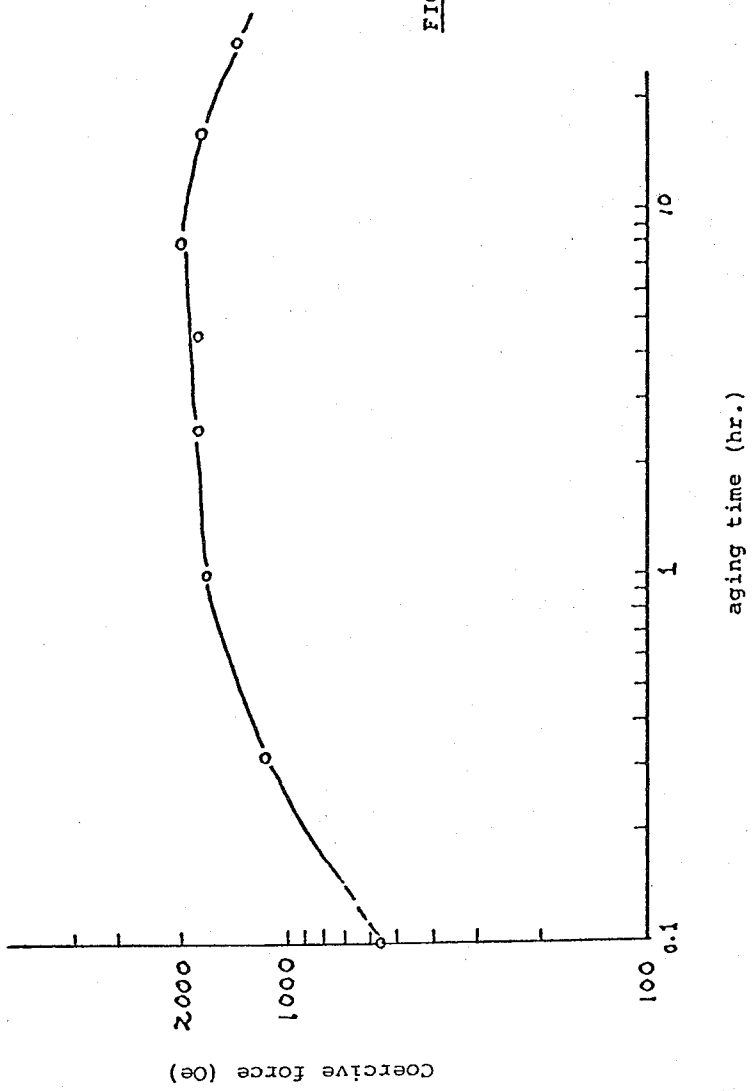

temperature of specimen
1400
1200
1000
800
600
400
200
0
20
40
60
80
100
cooling time (min)
cooling rate curve

FIG. 4



PERMANENT MAGNET

This application is a division of Ser. No. 775,651, filed Nov. 14, 1968.

This invention relates to a permanent magnet material characterized by a high coercive force and a high residual flux density and to a manufacturing method thereof.

It has been suggested that the alloy composed of a rare earth metal and a transition metal such as YCo_5 is a promising candidate for a fine particle magnet material. It has been a problem; however, how to make a fine and chemically stable particle of the material. In general, a mechanically crushed particle of the material is liable to be oxidized in air and the oxidation is accelerated by the coexistence of moisture even at room temperature. Therefore, it is desired to make a magnet of the material without using the pulverized form thereof.

An object of the invention is to provide a novel magnetic material characterized by a high coercive force and a high residual flux density.

A further object of the invention is to provide a permanent magnet material comprising Ce, Co and Cu.

A still further object of the invention is to provide a composition of the alloy consisting of Ce, Co and Cu, which gives a high coercive force, without pulverizing the alloy.

A further object of the invention is to provide a permanent magnet material comprising Ce-mischmetal including Fe, La, Pr and Nd as minor constituents, Co and Cu.

Another object of the invention is to provide a method of manufacturing a permanent magnet material.

These and other objects which are achieved by the present invention will be apparent upon consideration of the following detailed description taken together with the accompanying drawings wherein:

FIG. 1 is a schematic drawing which shows a structure, enlarged by 200 times, of the alloy according to the present invention;

FIG. 2 shows the relation between the intrinsic coercive force in oersteds and the fineness of the fiber-like structure in microns, which is characteristic of the alloy of the present invention;

FIG. 3 shows an example of cooling rate applicable to the method of manufacturing the magnet material of the invention;

FIG. 4 is a graph showing the relation between the intrinsic coercive force and the aging time according to one example of the invention.

According to the present invention, an alloy which consists of proper amounts of Ce, Co and Cu has excellent magnetic properties for use as a permanent magnet. A novel composition of ferromagnetic alloy according to the invention comprises 15 to 20 mol percent of Ce, 52 to 77 mol percent of Co and 8 to 30 mol percent of Cu. The 15 to 20 mol percent of Ce can be replaced by the less expensive Ce-mischmetal without impairing the magnetic properties. The Ce-mischmetal

is a Ce-rich metal and is widely used in industry because of the lower cost than that of pure Ce metal. As is well known, the Ce-mischmetal contains, as a main ingredient, Ce, rare earth metals such as La, Pr and Nd in a small amount, and other metals such as Fe, Mg and Al in a very small amount.

Ce-mischmetal, in the present specification, refers to an alloy having a composition according to Table 1.

Table 1

	Ce	La	Pr	Nd	other rare earth metal	Fe	Mg	Al
Ce-mischmetal wt. %	40–94	3–30	0.1–4	0.1–1.5	0.1–1.0	0.1–8.0	0–1.0	0–1.0

The alloy specimens of the present invention have an interesting microstructure which has not been found in any other similar magnetic alloy consisting of any other combination of rare earth metals and transition metals. The microstructure consists of a fiber-like structure as shown in FIG. 1. It is observed with a conventional microscope on tha flat surface of specimens etched by conc. HCl for a few minutes. It has been discovered that a high coercive force is closely related to the microstructure. In a specimen having a high coercive force, quite definite and fine fiber structure are found, whereas, in a specimen with a low coercive force, such a structure as above mentioned is hardly found.

The alloy body of the invention as heated is polished at one surface thereof with a suitable abrasive such as SiC powder or Cr_2O_3 powder in a particle size of 0.5 to 10μ in order that it may be provided with a flat surface. The surface is etched by a 12N HCl solution (aqueous) for several minutes at room temperature (15° to 30°C). The etched surface shows an etch pattern when observed microscopically as shown in FIG. 1. Said etch pattern is composed of many etch fibers 2, with a characteristic fineness defined as the average distance between two adjacent points 4 and 6 on a straight line 3 taken on the etch pattern, crossed by the etch fibers. In order to determine the fineness of the fiber-like structure, it is convenient to measure the same on a microscopic photograph. It can be made by drawing a sufficiently long straight line on the microscopic photograph in an arbitrary direction, so that there will be many cross points of the line with the etch fibers. The average distance is obtained by dividing the line length by the number of all such cross points on the line.

According to the present invention, the smaller the fineness of the alloy, the higher the coercive force thereof. The alloy having a fineness larger than 100μ has a poor coercive force such as lower than 500 Oe regardless of the composition. A coercive force higher than 2000 Oe is obtained with an alloy having a fineness smaller than 20μ. FIG. 2 shows the relation between intrinsic coercive force and the fineness of the fiber-like structure of various specimens of the invention. It is clearly seen from FIG. 2 that the finer the structure the higher is the coercive force.

The alloy according to the present invention with the aforedescribed structure was crushed to a fine particle size and examined by X-ray powder diffractometry. An example of the analysis for the alloy having a composition of 16.7 mol percent Ce, 75 mol percent Co and 8.3 mol percent Cu is shown in Table 2. In the measurement, Fe-Kαradiation generated in an X-ray tube working at an anode voltage of 35 kV and an anode current

of 8 mA through a Mn filter was used as X-ray source. The diffracted X-ray from the specimen was counted by a conventional counter at a counting rate of 400 c/s and a scanning velocity of 1°/min. and recorded at a time constant of 2 sec.

Table 2

2θ	intensity*	d	index*
38.5	s	2.94	101
46.2	m	2.47	uk.
46.8	s	2.44	110
52.8	w	2.18	uk.
53.6	m	2.15	200
54.7	s	2.11	uk.
55.1	ss	2.09	111
56.8	m	2.04	002
62.0	w	1.88	201

*uk. = unknown, w = weak, m = medium, s = strong, ss = very strong

The observed diffraction angles, 2θ, are listed in the first column of Table 2. In the second column, is shown the line intensity. The interplanar spacings [d] corresponding to each line are shown in the third column. Some of the diffraction lines can be indexed as shown in the fourth column, assuming that the crystal phase has a $CaCu_5$-type structure which is well verified in the case of many RCo_5 compounds. The other lines, however, remain unexplained. The most intense ones among these unexplained lines appear at slightly lower angles than the main lines of (**111**) and (**110**). This looks like a splitting of the main line into two lines. Although the origin of these extra lines are unknown at present, it should be noted that these lines are characteristic of the alloy of the present invention.

The materials according to the present invention have a residual flux density higher than 3500 G, a coercive force higher than 600 Oe, and a maximum energy product higher than 1.3 MG·Oe. The best results are obtained with compositions consisting essentially of 17.1 to 17.4 mol percent of Ce, 64 to 72.6 mol percent of Co and 10.3 to 18.57 mol percent of Cu in which the fine fiber-structure is easily formed. It is possible to replace Ce with Ce-mischmetal so that the amount of total rare earth elements in said Ce-Mischmetal is equivalent to that of said Ce, without impairing the resultant magnetic properties. The material of said optimal composition with a markedly developed fiber-structure has a residual flux density higher than 4250 G, a coercive force higher than 1500 Oe, and a maximum energy product higher than 4.0 MG·Oe.

The magnetic alloys according to the invention can be prepared by a conventional metallurgical method. For example, the ingredient metals are melted together in an alumina crucible in air at 10^{-3} mmHg using a graphite heater, and the molten alloy is furnace-cooled to room temperature. The alloy thus prepared has a more or less developed fiber-structure. However, in order to obtain a clearly and finely developed fiber-structure with the alloy materials and accordingly a high coercive force, it is effective to give the materials specially scheduled heat-treatments.

According to one manufacturing method of the present invention, the mixed ingredient metals are melted at a temperature higher than 1200°C, said melt is solidified at a temperature slightly lower than the melting point of the desired alloy, the solidified alloy is maintained at a temperature between the solidifying temperature and about 1000°C to obtain a homogenized alloy, the homogenized alloy is cooled to a temperature of 650° to 250°C at an average rate of 35° to 3°C per minute, and then the resultant alloy is quenched to room temperature. The homogenizing treatment, although not necessary, has a favorable effect on the magnetic properties.

An important feature of the process is the controlled cooling after the homogenizing heat treatment in order to obtain superior magnetic properties. The magnetic properties are highly dependent on the said cooling rate from 1100°C to 250°C.

The cooling rate should be higher in a relatively high temperature region than in a relatively low temperature region. The most important process feature is the controlled cooling from 1000°C to 650°C of which the average rate should be 35° to 10°C per minute.

An example of a proper cooling rate which is realized during the furnace cooling process is shown in FIG. **3**.

According to an alternative method of producing the magnet material of the invention, the mixed ingredient metals are melted at a temperature higher than 1200°C, said melt is quenched to room temperature, for instance, in a metal mold cooled by a cooling means such as water, the quenched alloy is aged at a temperature of 400° to 650°C for 20 minutes to 10 hours, and then the aged alloy is cooled to room temperature.

The quenched alloy exhibits a low coercive force value such as about 200 Oe. The coercive force, however, increases to value as high as 1250 Oe during the aging period of 1 to 5 hours at a temperature of 400° to 650°C. An aging treatment below 400°C requires too prolonged a period to obtain a sufficiently high coercive force value. In some cases for a higher aging temperature, for example of 700°C, the coercive force value decreases.

Illustrative embodiments of the invention are as follows:

Example 1

The alloy of 16.67 mol percent of Ce-mischmetal, 75.0 mol percent of Co and 8.33 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at **1000**°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. A sphere of about 3 mm in diameter was prepared from the ingot. The demagnetization curve was measured by means of a conventional vibrating specimen magnetometer. The magnetic properties were:

$Br = 6250$ G

$bHc = 630$ Oe

$(BH)max = 3.3$ MG·Oe

Example 2

The alloy of 17.4 mol percent of Ce-mischmetal, 70.2 mol percent of Co and 12.4 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at 1000°C, cooled to 400°C, according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. A sphere of about 3 mm in diameter was prepared from the ingot. The demagnetization curve was measured by means of a conventional vibrating specimen magnetometer. The magnetic properties were:

$Br = 5960$ G

$bHc = 3240$ Oe

$(BH)max = 8.0$ MG·Oe

Example 3

The alloy of 16.67 mol percent of Ce-mischmetal, 66.7 mol percent of Co and 16.63 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at 1000°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4750$ G

$bHc = 2900$ Oe

$(BH)max = 5.0$ MG·Oe

Example 4

The alloy of 16.67 mol percent of Ce-mischmetal, 54.13 mol percent of Co and 29.2 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at 1000°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 3700$ G

$bHc = 1250$ Oe

$(BH)max = 1.3$ MG·Oe

The influence of the Cu-content in the Ce-mischmetal-Co-Cu alloy system is shown explicitly from the above examples.

Example 5

The alloy of 15.25 mol percent of Ce-mischmetal, 67.8 mol percent of Co and 16.95 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at 1000°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4250$ G

$bHc = 1200$ Oe

$(BH)max = 3.4$ MG·Oe

Example 6

The alloy of 16.67 mol percent of Ce-mischmetal, 66.7 mol percent of Co and 16.63 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at 1000°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4750$ G

$bHc = 2900$ Oe

$(BH)max = 5.0$ MG·Oe

Example 7

The alloy of 19.35 mol percent of Ce-mischmetal, 64.52 mol percent of Co and 16.13 mol percent of Cu was melted at 1670°C, maintained for 30 minutes at 1000°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 3600$ G

$bHc = 750$ Oe

$(BH)max = 1.7$ MG·Oe

The influence of the Ce-mischmetal content in the Ce-mischmetal-Co-Cu alloy system is shown explicitly from the preceding three examples.

Examples 8

The alloy of 16.67 mol percent of Ce-mischmetal, 66.7 mol percent of Co and **16.63** mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 300°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4300$ G

$bHc = 2750$ Oe

$(BH)max = 3.8$ MG·Oe

Example 9

The alloy of 16.67 mol percent of Ce-mischmetal, 66.7 mol percent of Co and 16.63 mol of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 400°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4750$ G

$bHc = 2900$ Oe

$(BH)max = 5.0$ MG·Oe

Example 10

The alloy of 16.67 mol % of Ce-mischmetal, 66.67 mol percent of Co and 16.63 mol % of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 530°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 5050$ G

$bHc = 2730$ Oe

$(BH)max = 5.8$ MG·Oe

Example 11

The alloy of 16.67 mol percent of Ce-mischmetal, 66.7 mol percent of Co and **16.63** mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 600°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 5050$ G

$bHc = 2000$ Oe

(BH)max = 4.3 MG·Oe

Example 12

The alloy of 16.67 mol percent of Ce-mischmetal, 66.7 mol percent of Co and 16.63 mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 790°C according to the cooling curve shown in FIG. **3** and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4650$ G

$bHc = 150$ Oe

(BH)max = 0.25 MG·Oe

It is apparent from the preceding five examples that the temperature at which the sample is taken out from the electric furnace influences explicitly the magnetic properties.

Example 13

The alloy of 17.4 mol percent of Ce, 66.1 mol percent of Co and 16.5 mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 400°C at the average rate of 28°C/min. between 1000°C and 650°C and at the overall rate of 16.5°C/min. and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 4550$ G

$bHc = 800$ Oe

(BH)max = **2.4** MG·Oe

Example 14

The alloy of **17.4** mol percent of Ce, 66.1 mol percent of Co and 16.5 mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 400°C at the average rate of 24°C/min. between 1000°C and 650°C and the overall average rate of 13.2°C/min. and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

Br = 4720 G

bHc = 2300 Oe

(BH)max = 3.8 MG·Oe

Example 15

The alloy of 17.4 mol percent of Ce, 66.1 mol percent of Co and 16.5 mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 400°C at the average cooling rate of 19.5°C/min. between 1000°C and 650°C and at the overall average rate of 10.5°C/min. and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 6050$ G

$bHc = 2570$ Oe

(BH)max = 7.1 MG·Oe

Example 16

The alloy of 17.4 mol percent of Ce, 66.1 mol percent of Co and 16.5 mol percent of Cu was melted at 1550°C, maintained for 30 minutes at 1000°C, cooled to 400°C at an average cooling rate of 12°C/min. between 1000°C and 650°C and at the overall average rate of 4°C/min. and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 6500$ G

$bHc = 900$ Oe

(BH)max = **1.6** MG·Oe

It is apparent from the preceding four examples that cooling rate influences the magnetic properties of the materials.

Example 17

The alloy of 18.03 mol percent of Ce-mischmetal, 55.32 mol percent of Co and 26.65 mol percent of Cu was melted at 1550°C, and quenched in water. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

$Br = 2300$ G

$bHc = 260$ Oe

Example 18

The alloy of 18.03 mol percent of Ce-mischmetal, 55.32 mol percent of Co and 26.65 mol percent of Cu was melted at 1550°C, quenched in water, aged for 1 hour at 300°C and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

Br = 2600 G

bHc = 490 Oe

Example 19

The alloy of 18.03 mol percent of Ce-mischmetal, 55.32 mol percent of Co and 26.65 mol percent of Cu was melted at 1550°C, quenched in water, aged for 1 hour at 400°C and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

Br = 2900 G

bHc = 890 Oe

Example 20

The alloy of 18.03 mol percent of Ce-mischmetal, 55.32 mol percent of Co and 26.65 mol percent of Cu was melted at 1550°C, quenched in water, aged for 1 hour at 520°C and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

Br = 3000 G

bHc = 1250 Oe

Example 21

The alloy of 18.03 mol percent of Ce-mischmetal, 55.32 mol percent of Co and 26.65 mol percent of Cu was melted at 1550°C, quenched into water, aged for 1 hour at 600°C and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

Br = 3000 G

bHc = 970 Oe

Example 22

The alloy of 18.03 mol percent of Ce-mischmetal, 55.52 mol percent of Co and 26.65 mol percent of Cu was melted at 1550°C, quenched in water, aged for 1 hour at 700°C and then rapidly cooled to room temperature. The measurement of magnetic properties was carried out by the same method as in the previous examples. The magnetic properties were:

Br = 2500 G

bHc = 260 Oe

The influence of aging temperature is explicitly confirmed from the six preceding examples.

Example 23

The alloy of 18.03 mol percent Ce-mischmetal, 55.32 mol percent of Co and 26.65 mol percent of Cu which was prepared by melting the ingredient metals at 1550°C and quenching in water, was heated at 520°C for various times. The intrinsic coercive force $_iH_c$ of thus - obtained alloy is plotted against the aging time in FIG. **4.**

The intrinsic coercive force increased rapidly with increasing the aging time in the range from about 20 min. to 1 hour, and was followed by a gradual increase up to the aging time of about 8 hours, then by a gradual decrease with the aging time over 10 hours.

What is claimed is:

1. A method for making a permanent magnet material having a fiber-like microstructure of fineness smaller than 20 microns and having a maximum energy product of at least **1.3** MG.oe, comprising heating a mixture of 15 to 20 mol percent of Ce or Ce mischmetal, 52 to 77 mol percent of Co and 8 to 30 mol percent of Cu to a melt at a temperature higher than 1200°C, quenching said melt to room temperature, aging the quenched alloy at a temperature of 400°C to 650°C for 20 minutes to 10 hours and then rapidly cooling the aged alloy to room temperature.

2. A method for making a permanent magnet material according to claim **1,** wherein Ce-mischmetal is employed.

3. A method for making a permanent magnet material according to claim **1** wherein Ce is employed.

* * * * *