⑲ Europäisches Patentamt
European Patent Office
Office européen des brevets

⑪ Publication number : **0 342 922 B1**

⑫ EUROPEAN PATENT SPECIFICATION

㊺ Date of publication of patent specification : **08.02.95 Bulletin 95/06**

(51) Int. Cl.^{6} : **H01F 1/14,** C22C 38/16, C21D 6/00

㉑ Application number : **89304926.2**

㉒ Date of filing : **16.05.89**

(54) Fe-based soft magnetic alloy and dust core made therefrom.

㉚ Priority : **17.05.88 JP 118335/88**
30.11.88 JP 300686/88

㊸ Date of publication of application : **23.11.89 Bulletin 89/47**

㊺ Publication of the grant of the patent : **08.02.95 Bulletin 95/06**

(84) Designated Contracting States : **DE FR GB**

(56) References cited :
EP-A- 0 271 657
EP-A- 0 302 355
CH-A- 443 505
DE-B- 2 005 371
JP-A- 4 992 600
JP-A- 5 273 120
JP-A- 5 449 936

(73) Proprietor : **KABUSHIKI KAISHA TOSHIBA**
72, Horikawa-cho
Saiwai-ku
Kawasaki-shi Kanagawa-ken 210 (JP)

(72) Inventor : **Sawa, Takao c/o Toshiba Corporation**
Intellectual Pro. Div.
1-1 Shibaura 1-chome
Minato-ku Tokyo 105 (JP)
Inventor : **Okamura, Masami c/o Toshiba Corporation**
Intellectual Pro. Div.
1-1 Shibaura 1-chome
Minato-ku Tokyo 105 (JP)

(74) Representative : **BATCHELLOR, KIRK & CO.**
2 Pear Tree Court
Farringdon Road
London EC1R 0DS (GB)

Note : Within nine months from the publication of the mention of the grant of the European patent, any person may give notice to the European Patent Office of opposition to the European patent granted. Notice of opposition shall be filed in a written reasoned statement. It shall not be deemed to have been filed until the opposition fee has been paid (Art. 99(1) European patent convention).

Jouve, 18, rue Saint-Denis, 75001 PARIS

Description

This invention relates to Fe-based, soft magnetic alloys and a dust core of said alloy.

Conventionally, iron cores of crystalline materials such as permalloy or ferrite have been employed in high frequency devices such as switching regulators. However, the resistivity of permalloy is low, so it is subject to large core loss at high frequency. Also, although the core loss of ferrite at high frequencies is small, the magnetic flux density is also small, at best 0,5 T (5,000 G). Consequently, in use at high operating magnetic flux densities, ferrite becomes close to saturation and as a result the core loss is increased.

Recently, it has become desirable to reduce the size of transformers that are used at high frequency, such as the power transformers employed in switching regulators, smoothing choke coils, and common mode choke coils. However, when the size is reduced, the operating magnetic flux density must be increased, so the increase in core loss of the ferrite becomes a serious practical problem.

For this reason, amorphous magnetic alloys, i.e., alloys without a crystal structure, have recently attracted attention and have to some extent been used because they have excellent soft magnetic properties such as high permeability and low coercive force. Such amorphous magnetic alloys are typically base alloys of Fe, Co, Ni, etc., and contain metalloids as elements promoting the amorphous state, (P, C, B, Si, Al, and Ge, etc.).

However, not all of these amorphous magnetic alloys have low core loss in the high frequency region. Iron-based amorphous alloys are cheap and have extremely small core loss, about one quarter that of silicon steel, in the frequency region of 50 to 60 Hz. However, they are extremely unsuitable for use in the high frequency region for such applications as in switching regulators, because they have an extremely large core loss in the high frequency region of 10 to 50 kHz. In order to overcome this disadvantage, attempts have been made to lower the magnetostriction, lower the core loss, and increase the permeability be replacing some of the Fe with non-magnetic metals such as Nb, Mo, or Cr. However, the deterioration of magnetic properties due to hardening, shrinkage, etc., of resin, for example, on resin moulding, is large compared to Co-based alloys, so satisfactory performance of such materials is not obtained when used in the high frequency region.

Co-based, amorphous alloys also have been used in magnetic components for electronic devices such as saturable reactors, since they have low core loss and high squareness ratio in the high frequency region. However, the cost of Co-based alloys is comparatively high making such materials uneconomical.

As explained above, although Fe-based amorphous alloys constitute cheap soft magnetic materials and have comparatively large magnetostriction, they suffer from various problems when used in the high frequency region and are inferior to Co-based amorphous alloys in respect of both core loss and permeability. On the other hand, although Co-based amorphous alloys have excellent magnetic properties, they are not industrially practical due to the high cost of such materials.

In the technical field of dust cores, use is made of iron powder, Mo permalloy, etc. for dust cores in noise filters and choke coils, since they can be produced in a variety of shapes more easily than can thin strips. However, there are problems in their use in power sources at high frequency owing to the comparatively large core loss.

As described above, Fe-based amorphous alloys constitute an inexpensive soft magnetic material, but their magnetostriction is comparatively large, and they are inferior to Co-based amorphous alloys in respect of core loss and permeability, so that there are problems in using these materials in the high frequency region. On the other hand, although Co-based amorphous alloys have excellent magnetic properties, as hereinbefore pointed out, the high price of the raw material makes them commercially disadvantageous. Such materials also suffer disadvantages where used for dust cores since they too have comparatively large core losses, causing problems in their use in power sources of high frequency.

Document EP-A-302355 discloses a Fe-base, soft magnetic alloy powder and dust core having the composition represented by the general formula:

$$(Fe_{1-a}M_a)_{100-x-y-z-\alpha-\beta-\gamma}Cu_xSi_yB_zM'_\alpha M''_\beta X_\gamma$$

wherein M is Co and/or Ni, M′ is at least one element selected from the group consisting of Nb, W, Ta, Zr, Hf, Ti and Mo, M″ is at least one element selected from the group consisting of V, Cr, Mn, Al, elements in the platinum group, Sc, Y, rare earth elements, Au, Zn, Sn and Re, X is at least one element selected from the group consisting of C, Ge, P, Ga, Sb, In, Be and As, and a, x, y, z, α, β and γ respectively satisfy $0 \leqq \alpha \leqq 0.5$, $0.1 \leqq x \leqq 3$, $0 \leqq y \leqq 30$, $0 \leqq z \leqq 25$, $0 \leqq y+z \leqq 35$, $0.1 \leqq \alpha \leqq 30$, $0 \leqq \beta \leqq 10$ and $0 \leqq \gamma \leqq 10$, at least 50% of the alloy structure being fine crystalline particles having an average particle size of 500nm or less.

Document EP-A-271657 discloses a Fe-base soft magnetic alloy having the composition represented by the general formula:

$$[Fe_{1-a}M_a]_{100-x-y-z-\alpha}Cu_xSi_yB_zM'_\alpha$$

wherein M is Co and/or Ni, M′ is at least one element selected from the group consisting of Nb, W, Ta, Zr, Hf, Ti and Mo, and a, x, y, z and α respectively satisfy $0 \leqq a \leqq 0.5$, $0.1 \leqq x \leqq 3$, $0 \leqq y \leqq 30$, $0 \leqq z \leqq 25$, $5 \leqq y+z \leqq 30$ and

$0.1 \leqq \alpha \leqq 30$, at least 50% of the alloy structure being occupied by fine crystalline particles, and

an Fe-base soft magnetic alloy having the composition represented by the general formula: $[Fe_{1-a}M_a]_{100-x-y-z-\alpha-\beta-\gamma}Cu_xSi_yB_zM'_\alpha M''_\beta X_\gamma$ wherein M is Co and/or Ni, M′ is at least one element selected from the group consisting of Nb, W, Ta, Zr, Hf, Ti and Mo, M″ is at least one element selected from the group consisting of V, Cr, Mn, Al, elements in the platinum group, Sc, Y, rare earth elements, Au, Zn, Sn and Re, X is at least one element selected from the group consisting of C, Ge, P, Ga, Sb, In, Be and As, and a, x, y, z, α, β and γ respectively satisfy $0 \leqq a \leqq 0.5$, $0.1 \leqq x \leqq 3$, $0 \leqq y \leqq 30$, $0 \leqq z \leqq 25$, $5 \leqq y + z \leqq 30$, $0.1 \leqq \alpha \leqq 30$, $\beta \leqq 10$ and $\gamma \leqq 10$, at least 50% of the alloy structure being fine crystalline particles having an average particle size of 1000Å or less.

Consequently, having regard to the above problems, the object of this invention is to provide an Fe-based soft magnetic alloy having high saturation magnetic flux density in the high frequency region, with attractive soft magnetic characteristics.

Another object of this invention is to provide an Fe-based dust core capable of being produced in various shapes and also having attractive soft magnetic characteristics with high saturation magnetic flux density in the high frequency region.

According to a first aspect of the invention, there is provided an Fe-based soft magnetic alloy having an area ratio of fine crystal grains in the range of 5 to 30nm (50Å to 300Å) of at least 30% and is defined by formula (I)

$$Fe_{100-a-b-c}Cu_aM_bZ_c; \qquad (I)$$

wherein

"M" is at least one element from the following: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al and the Platinum group;

"Z" is at least one element from the following:

Si, B, P, and C;

and wherein "a", "b", and "c", expressed in atomic % are as follows:

$$3 < a \leqq 8$$
$$0.1 \leqq b \leqq 8$$
$$3.1 \leqq a + b \leqq 12$$
$$15 \leqq c \leqq 28$$

In accordance with a second aspect, the invention provides a dust core made from an alloy powder characterised in that it has an area ratio of fine crystal grains in the range of 5 to 30nm (50Å to 300Å) of at least 30% and is defined by formula (II),

$$Fe_{100-a-b-c-d-e}Cu_aM'_bM''_cSi_dB_e \qquad (II)$$

wherein

"M′" is at least one element from the following: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W;

"M″" is at least one element from the following:

Mn, Co, Ni, Al, and the Platinum group;

and wherein "a", "b", "c", "d" and "e", expressed in atomic %, are as follows:

$$3 < a \leqq 8$$
$$0.1 < b \leqq 8$$
$$0 \leqq c \leqq 15$$
$$8 \leqq d \leqq 22$$
$$3 \leqq e \leqq 15$$
$$15 \leqq d + e \leqq 28.$$

Fine crystal grains are present to the extent of at least 30% in terms of the area ratio in the alloy. It is further desirable that at least 80% of the fine crystal grains be of a size in the range of 5 to 30nm (50Å to 300Å). The term "area ratio" of fine crystal grains as used herein means the ratio of the surface of the fine grains to the total surface in a plane of the alloy as measured, for example, by photomicrography or by microscopic examination of ground and polished specimens.

In order to attain the above objects, and desired properties it is important to control the composition of the alloy and to balance the constituents as hereinafter described. In particular, fine crystal grains should be present to the extent of 30% or more in terms of area ratio in the alloy. It is further desirable that 80% or more of the fine crystal grains be of a size in the range of 5 to 30nm (50Å to 300Å).

In the second aspect of the invention it was also discovered that an alloy powder having fine crystal grains and defined by formula (II) above can also possess excellent properties and is especially suitable for manufacture of dust cores.

Optimum properties of such alloy powders can be achieved by including fine crystal grains to the extent of at least 30% in terms of area ratio in the alloy. It is preferable that, of these fine crystal grains, at least 80%

should be crystal grains of 5 to 30nm (50Å to 300Å).

In order that the invention may be illustrated and readily carried into effect, preferred embodiments of first and second aspects will now be described by way of non-limiting examples only, with reference to the accompanying drawings, wherein:

Fig. 1 is a graph of the variation of corrosion resistance and saturation magnetization resulting from the addition of Cu to an alloy of this invention:

Fig. 2 is a graph showing the effect of changes in the amount of Cu on packing ratio;

Fig. 3 is a graph showing the μ', Q-F characteristics of embodiments of the invention and of comparative examples;

Fig. 4 is a graph showing the DC superposition characteristic of embodiments of the invention and of comparative examples; and

Fig. 5 is a graph showing the effect of changes in the amount of Cu on saturation magnetization.

In accordance with the invention, it is important that the alloy components are within the proportions indicated. Copper is especially important because it is effective in increasing corrosion resistance, preventing coarsening of the crystal grains, and improving soft magnetic characteristics such as core loss and permeability. However, if too little Cu is present, the benefit of the addition is not obtained. On the other hand, if too much Cu is present, the magnetic characteristics are adversely affected. A range of more than 3 and less than 8 atomic % is therefore selected. This is particularly desirable in the use of the alloy for dust cores, since the packing ratio is increased by increased amounts of Cu. Preferably, the amount of Cu is more than 3 and less than 5 atomic %.

In the first aspect "M" is at least one element from: Ti, Zr, H*f*, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al and the Platinum group, i.e., Ru, Rh, Pd, Os, Ir and Pt as elements of the Platinum group. These elements are effective in making the crystal grain size uniform, and in improving the soft magnetic properties by reducing magnetostriction and magnetic anisotropy. It is also effective in improving the magnetic properties in respect of temperature change. However, if the amount of "M" is too small, the benefit of addition is not obtained and if the amount is too large, the saturation magnetic flux density is lowered. An amount in the range 0.1 to 8 atomic % is selected. Preferably the amount is 1 to 7 atomic %, and even more preferably 1.5 to 5 atomic %. In addition to the above-mentioned effects, the various elements comprising "M" have the following respective effects: in the case of Group IVa elements Ti, Zr, Hf, increase of the range of heat treatment conditions for obtaining optimum magnetic properties; in the case of Group Va elements V, Nb, Ta, increase in the resistance to embrittlement and in workability such as by cutting; in the case of Group VIa elements Cr, Mo, Wo, improvement of corrosion resistance and surface morphology; in the case of Al, increased fineness of the crystal grains and reduction of magnetic anisotropy, thereby improving magnetostriction and soft magnetic properties.

The elements Nb, Mo, Cr, Mn, Ni and W are desirable to lower core loss, and Co is desirable in particular to increase saturation magnetic flux density.

In the second aspect "M′" is at least one element from : Groups IVa, Va, VIa of the Japanese periodic table. These elements are effective in making the crystal grain size uniform, and in improving the soft magnetic properties by lowering magnetostriction and magnetic anisotropy. They also improve the magnetic properties with respect to change of temperature. However, if too little is used, the benefit of the addition is not obtained. On the other hand, if too much is used, the saturation magnetic flux density is lowered. An amount of 0.1 to 8 atomic % is therefore selected. Preferably the range is 1 to 7 atomic %, and even more preferably 1.5 to 5 atomic %. In this connection, the additive elements in M′ have, in addition to the aforementioned benefits, the following benefits: in the case of Group IVa elements, an expansion of the range of heat treatment conditions that are available in order to obtain optimum magnetic properties; in the case of the Group Va elements, increase in resistance to embrittlement and increase in workability such as cutting; in the case of the Group VIa elements, increase in corrosion resistance and improvement in surface configuration, resulting in improvement in magnetostriction and soft magnetic properties.

The elements Nb, Mo, Ta, W, Zr and Hf are particularly preferable in lowering core loss.

In the second aspect "M″" is at least one element from: Mn, Co, Ni, Al, and the Platinum group. These elements are effective in improving soft magnetic characteristics. However, it is undesirable to use too much, since this results in lowered saturation magnetic flux density. An amount of less than 15 atomic % is therefore specified. Preferably the amount is less than 10 atomic %.

Preferably the total amount of Cu, M′ and M″ is 3.1 to 25 atomic %. If the total amount is too small, the benefit of the addition is slight. On the other hand, if it is too large, the saturation magnetic flux density tends to be reduced.

In the first aspect "Y" is at least one element from: Si, B, P and C.
These elements are effective in making the alloy amorphous during manufacture, or in directly segregating fine crystals. If the amount is too small, the benefit of superquenching in manufacture is difficult to obtain and

the above condition is not obtained but if the amount is too large saturation magnetic flux density becomes low, making the above condition difficult to obtain, with the result that superior magnetic properties are not obtained. An amount in the range 15 to 28 atomic % is therefore selected. Preferably the range is 18 to 26 atomic %. In particular, the ratio of (Si,C) / (P,B) is preferably more than 1.

Thus the atomic ratio Si:B or C:P is preferably > 1, whichever is present.

In the second aspect, Si is effective in obtaining the amorphous state of the alloy during manufacture or in directly segregating fine crystals. If the amount of Si used is too small, there is little benefit from superquenching during manufacture and the aforementioned condition is not obtained but if the amount is too large, the saturation magnetic flux density is lowered and the aforesaid condition becomes difficult to obtain, so that superior magnetic properties are not obtained. An amount in the range 8 to 22 atomic % is therefore selected. Preferably the range is 10 to 20 atomic %, and even more preferably 12 to 18 atomic %. Boron, like silicon, is an element that is effective in obtaining the amorphous condition of the alloy, or in directly segregating fine crystals. If the amount is too small, the benefit of superquenching in manufacture is difficult to obtain an aforementioned condition is not obtained. On the other hand, if the amount used is too large, problems with magnetic characteristics result. An amount in the range 3 to 15 atomic % is therefore selected. Preferably, the range is 5 to 10 atomic %. If the total of Si and B is too small, the benefit of their addition is not obtained. On the other hand, if the total amount is too large, the benefit is likewise difficult to obtain, and there is a lowering of saturation magnetic flux density. A total amount in the range 15 to 28 at. % is therefore preferable.

Fe-based soft magnetic alloys and alloy powders of this invention may be obtained by the following method.

An amorphous alloy thin strip is obtained by liquid quenching. A quenched powder is obtained by grinding, or by an atomizing method or by mechanical alloying method, etc.. The alloy is heat treated for from one minute to 10 hours preferably 10 minutes to 5 hours at a temperature of from 50C° below the crystallization temperature to 120C° above the crystallization temperature preferably 30C° to 100C° above the crystalization temperature of the amorphous alloy, to segregate the fine crystal grains. Alternatively, segregation of the fine crystals may be obtained by controlling the quenching speed in the quenching method.

With respect to the importance of the fine crystal grains, it has been determined that if there are too few fine crystal grains in the alloy of this invention i.e. if there is too much amorphous phase, an adverse effect on the magnetic properties during moulding is increased, with increased core loss, lower permeability and higher magnetostriction. It is therefore preferable that the fine crystal grains in the alloy should be present to the extent of at least 30% in terms of area ratio.

Furthermore, if the crystal grain size in the aforementioned fine crystal grains is too small, maximum improvement in magnetic properties is not obtained. On the other hand, if too large, the magnetic properties are adversely affected. It is therefore preferable that, in the fine crystal grains, crystals of grain size 50Å to 300Å should be present to the extent of that least 80%.

Fe-based soft magnetic alloys according to this invention can have excellent soft magnetic properties at high frequency. They are useful as alloys for magnetic materials for magnetic components such as for example magnetic heads, thin film heads, radio frequency transformers including transformers for high power use, saturable reactors, common mode choke coils, normal mode choke coils, high voltage pulse noise filters, and magnetic switches used in laser and other power sources, magnetic cores, etc. used at high frequency, and for sensors of various types, such as power source sensors, direction sensors, and security sensors, etc.

As indicated previously, alloys according to the second aspect of the invention are also particularly useful for dust cores. However in this application, if the size of the particles is too small, the packing ratio is lowered. On the other hand, if the particle size is too large, losses become considerable, making the core unfit for high frequency use. A particle size 1 to 100 μm is therefore preferable.

The shape of the particles is not prescribed, which could be, for example, spherical or flat. These shapes depend on the method of manufacture. For example, in the case of the atomizing method, spherical powder is obtained, but if this is subjected to rolling treatment, flat powder is obtained.

The alloy powders, can be subjected to ordinary press forming and sintering is advantageously carried out while performing heat treatment for 10 minutes to 10 hours at 450°C to 650°C.

In this process, an inorganic insulating material such as a metallic alkoxide, water glass, or low melting point glass is used as a binder.

The following examples further illustrate the invention.

Examples of First Aspect

Amorphous alloy thin strips of about 15 μm were obtained by the single rolling method from master alloy consisting of $Fe_{75-a}Cu_aNb_3Si_{12}B_{10}$, for a = 0, 2, 4, 6, 8, and 10.

These thin strips were then subjected to heat treatment for about 80 minutes at a temperature about 20C° higher than the crystallization temperature of this alloy (measured with a rate of temperature rise 10C°/min.).

The corrosion resistance of the thin strip that was obtained was measured as the loss in initial weight on immersion for 100 hours in 1N HCl. The results are described in Fig. 1. The amorphous alloy strip was then wound to form a toroidal magnetic core of external diameter 18 mm, internal diameter 12 mm, and height 4.5 mm, which was then subjected to heat treatment in the same way as above.

The saturation magnetization of the magnetic core obtained was measured by a vibrating sample magnetometer (VSM). These results are also shown in Fig. 1.

It can be seen from Fig. 1 that the corrosion resistance is greatly improved by the Cu addition; the value falling to below 0.5% when the Cu addition exceeds 3 atomic %. Also, if the Cu addition exceeds 8 atomic %, the saturation magnetization becomes 7.5 KG, which is a value equal to that of Co-based amorphous alloy. To satisfy corrosion resistance and saturation magnetization, the value of the Cu content should therefore be more than 3 atomic % and less than 8 atomic %.

When the core loss was measured at B = 0,2 T (2 KG), f = 100 KHz, low core loss of 290 to 330 mW/cc was found except at X = 0 at. %.

Thin alloy strips of the above alloy compositions $Fe_{71.5}Cu_{3.5}Nb_{13}Si_{13}B_9$ were wound to form a toroidal core of external diameter 18 mm, internal diameter 12 mm, and height 4.5 mm, which was then subjected to heat treatment under the conditions shown in Table 1. For comparison, a core was manufactured by performing heat treatment at about 430°C for about 80 min. It was found by TEM observation that fine crystal grains had not segregated in the magnetic core that was obtained.

Five samples of the magnetic core material according to this invention in which fine crystal grains were present, were prepared for evaluation with five samples of comparative magnetic core material in which fine crystal grains were not present. The core loss after heat treatment at B = 0,2 T (2 KG) and f = 100 KHz and the core loss and magnetostriction after epoxy resin moulding were measured, and the permeability and saturation flux density at 1 KHz, $1{,}592 \cdot 10^4$A/m (2 Oe) were measured. The mean values are shown in Table I.

TABLE I

Alloy Composition	Whether fine crystal grains are present	Core loss (mw/cc)		Magnetostriction ($X10^{-4}$)	Permeability μ' IKHz ($X10^{4}$)	Saturation magnetic flux density (kG)*
		Before moulding	After moulding			
$Fe_{71.5}Cu_{3.5}Nb_3Si_{13}B_9$	Yes	210	250	1.1	12.8	11.7
$Fe_{71.5}Cu_{3.5}Nb_3Si_{13}B_9$	No	670	2860	13.5	1.2	11.7

* 1G = 10^{-4}T

As is clear from the above Table I, in comparison with the magnetic cores consisting of amorphous alloy thin strip of the same composition, the alloy of this invention, owing to the presence of fine crystal grains, shows excellent soft magnetic properties at high frequencies, has high permeability with low core loss, in particular, after resin moulding, and low magnetostriction.

With the present invention, an Fe-based soft magnetic alloy can be provided having excellent soft magnetic properties, owing to the presence of fine crystal grains in the desired alloy composition and high saturated magnetic flux density in the high frequency region.

Examples of the Second Aspect

With an alloy system consisting of $Fe_{75-x}Cu_xNb_3Si_{15}B_7$, spherical powders of 10 to 50 μm were manufactured by the atomizing method for X = 1, 2, 3, 4, 5, 6, and 7.

Toroidal cores of 38 X 19 X 12.5 mm were pressure formed from these powders using water glass as a binder. Sintering was then performed at 550°C for 60 minutes in the case of X = 1 to 3°; 530°C and 60 minutes in the case of X = 4 and 5, and 500°C and 60 minutes in the case of X = 6 and 7.

The packing ratio for these cores was then examined. As shown in Fig. 2, it was found that the packing ratio increased with increasing amounts of Cu.

Also, for X = 2 and X = 4 of these samples, the μ′, Q - f characteristics were measured. In this measurement, an LCR meter was used, winding 20 turns onto the magnetic core and using a voltage of 1 V. The results are shown in Fig. 3. As is clear from Fig. 3, the alloy of this invention performed much better than another alloy where (X = 2) shown for comparison, and would be effective as a magnetic core for a choke core transformer or the like.

The DC superposition characteristic was also measured using the same samples. The results are shown in Fig. 4. It is clear from these results that the magnetic core of this invention is superior.

The various alloy powders shown in Table II were manufactured by the atomizing method. The powders obtained were spherical powders, of powder size 10 to 50 μm.

The powders were pressure formed into toroidal cores of 38 X 19 X 12.5 mm, using water glass as binder. The cores were subjected to heat treatment at 540°C for 60 minutes in the case of samples 1 to 6, and used for carrying out the measurements.

For comparison, a sample 7 was manufactured in the same way and an $Fe_{79}Si_{10}B_{11}$ amorphous thin strip. Evaluations were performed also for an iron powder dust core of the same shape, and for a toroidal core sample 8 which was wound to the same shape, and subjected to heat treatment, resin impregnation and gap forming.

Table II shows the results obtained by measuring μ′10 kHz and q10 kHz for these cores. It can be seen that high μ′ and high Q values are obtained with the cores of this invention.

TABLE II

	Sample	Composition	μ' 1KHz	Q_{100KHz}
	1	$Fe_{72}Cu_4Ta_3Si_{14}B_7$	160	50
	2	$Fe_{72}Cu_4W_3Si_{14}B_7$	160	50
	3	$Fe_{72}Cu_4Mo_3Si_{14}B_7$	157	48
	4	$Fe_{72}Cu_4Nb_3Si_{14}B_7$	165	53
	5	$Fe_{72}Cu_4Nb_2Cr_2Si_{14}B_6$	165	52
	6	$Fe_{72}Cu_4Nb_2Ru_2Si_{14}B_6$	167	55
comparative	7	$Fe_{71}Cu_1Mo_3Si_{13}B_{12}$	105	28
comparative	8	$Fe_{79}Si_{10}B_{11}$ (cut core)	100	25
comparative	9	Iron powder dust	30	11

Alloy powder of the composition Fe_{79}-xCuxNb$_2$Si$_{13}$B$_6$ was manufactured by the atomization method. The powder obtained was a spherical powder of particle size 10 to 50 μm.

This powder was pressure formed into toroidal cores of 38 X 19 X 12.5 mm, using water glass as binder, and measurement samples were prepared by carrying out heat treatment at 500°C for 90 minutes.

Saturation magnetization for the samples obtained was measured, using a VSM, in a magnetic field of $7.96 \cdot 10^4$A/m (10 KOe). The results are shown in Fig. 5.

It is clear from Fig. 5 that saturation magnetization is reduced by replacing Fe by Cu, and there are practical problems when the Cu exceeds 8 at. %.

As described above, this invention makes it possible to provide an Fe-based dust core that has a high saturation magnetic flux density, excellent soft magnetic characteristics at high frequency and that is capable of being made in various shapes.

The foregoing description and examples have been set forth merely to illustrate the invention and are not intended to be limiting. Since modifications of the described embodiments incorporating the spirit and substance of the invention may occur to persons skilled in the art, the scope of the invention should be limited only by the appended claims and equivalents.

Claims

1. An Fe-based soft magnetic alloy having an area ratio of fine crystal grains in the range of 5 to 30nm (50Å to 300Å) of at least 30% and is defined by formula (I)

$$Fe_{100-a-b-c}Cu_aM_bZ_c; \qquad (I)$$

wherein

"M" is at least one element from the following: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al and the Pla-

tinum group;
"Z" is at least one element from the following:

Si, B, P, and C;

and wherein "a", "b", and "c", expressed in atomic % are as follows:

$$3 < a \leqq 8$$
$$0.1 \leqq b \leqq 8$$
$$3.1 \leqq a + b \leqq 12$$
$$15 \leqq c \leqq 28$$

2. An alloy according to claim 1 wherein at least 80% of fine crystal grains present in the alloy are in the range of 5-30nm (50 Å to 300 Å).

3. An alloy according to claim 1 or 2 wherein the amount of Cu is less than 5 atomic %.

4. An alloy according to any preceding claim wherein the amount of "M" is 1 to 7 atomic %, preferably 1.5 to 5 atomic %.

5. An alloy according to any preceding claim wherein the amount of "Z" is 18 to 26 atomic %.

6. An alloy according to any preceding claim wherein the ratio of (Si and/or C) to (B and/or P) is more than 1.

7. A dust core made from an alloy powder characterised in that it has an area ratio of fine crystal grains in the range of 5 to 30nm (50Å to 300Å) of at least 30% and is defined by formula (II),

$$Fe_{100-a-b-c-d-e}Cu_aM'_bM''_cSi_dB_e \qquad (II)$$

wherein
"M'" is at least one element from the following: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo and W;
"M″" is at least one element from the following:
Mn, Co, Ni, Al, and the Platinum group;
and wherein "a", "b", "c", "d" and "e", expressed in atomic %, are as follows:

$$3 < a \leqq 8$$
$$0.1 < b \leqq 8$$
$$0 \leqq c \leqq 15$$
$$8 \leqq d \leqq 22$$
$$3 \leqq e \leqq 15$$
$$15 \leqq d + e \leqq 28.$$

8. A dust core according to claim 7 wherein at least 80% of the fine crystal grains are in the range 5-30nm (50 Å to 300Å).

9. A dust core according to claim 7 or 8 wherein the amount of Cu is less than 5 atomic %.

10. A dust core according to any one of claims 7 to 9 wherein the amount of M′ is 1 to 7 atomic %, preferably 1.5 to 5 atomic %.

11. A dust core according to any one of claims 7 to 10 wherein the amount of M″ is less than 10 atomic %.

12. A dust core according to any one of claims 7 to 11 wherein the amount of Cu, M′ and M″ is 3.1 to 25 atomic %.

13. A dust core according to any one of claims 7 to 12 wherein the amount of Si is 10 to 22 atomic %, preferably 12 to 18 atomic %.

14. A dust core according to any one of claims 7 to 13 wherein the amount of B is 5 to 10 atomic %.

15. A dust core according to any one of claims 7 to 14 wherein the particle size of the alloy powder is in the range 1 to 100 μm.

16. A method of treating an Fe-based soft magnetic alloy according to any one of claims 1 to 6 comprising heat treating said alloy for from one minute to ten hours at a temperature of from 50C° below the crystallization temperature to 120C° above the crystallization temperature to segregate the fine crystal grains; said heat treatment preferably being carried out for from ten minutes to five hours.

Patentansprüche

1. Weichmagnetische Legierung auf Eisenbasis, die ein Flächenverhältnis von feinen Kristallkörnern im Größenbereich von 5 bis 30 nm (50 Å bis 300 Å) von wenigstens 30% aufweist und die definiert ist durch die Formel (I)
$$Fe_{100-a-b-c}Cu_aM_bZ_c; \qquad (I)$$
wobei
"M" wenigstens ein Element aus den folgenden ist: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al und die Platingruppe;
"Z" wenigstens ein Element aus den folgenden ist:
Si, B, P und C;
und wobei "a", "b" und "c" ausgedrückt in Atomprozent folgendermaßen sind:
$$3 < a \leqq 8$$
$$0,1 \leqq b \leqq 8$$
$$3,1 \leqq a + b \leqq 12$$
$$15 \leqq c \leqq 28.$$

2. Legierung gemäß Anspruch 1, wobei wenigstens 80% der in der Legierung vorhandenen Kristallkörner im Bereich von 5 bis 30 nm (50 Å bis 300 Å) sind.

3. Legierung nach Anspruch 1 oder 2, wobei der Gehalt an Cu geringer als 5 Atomprozent ist.

4. Legierung nach einem der vorhergehenden Ansprüche, wobei der Gehalt an "M" 1 bis 7 Atomprozent, vorzugsweise 1,5 bis 5 Atomprozent beträgt.

5. Legierung nach einem der vorhergehenden Ansprüche, wobei der Gehalt an "Z" 18 bis 26 Atomprozent beträgt.

6. Legierung nach einem der vorhergehenden Ansprüche, wobei das Verhältnis von (Si und/oder C) zu (B und/oder P) mehr als 1 beträgt.

7. Massekern hergestellt aus einem Legierungspulver, **dadurch gekennzeichnet**, daß es ein Flächenverhältnis von feinen Kristallkörnern im Größenbereich von 5 bis 30 nm (50 Å bis 300 Å) von wenigstens 30% aufweist und durch die Formel (II) definiert ist
$$Fe_{100-a-b-c-d-e}Cu_aM'_bM''_cSi_dB_e \qquad (II)$$
wobei
"M′" wenigstens ein Element aus den folgenden ist: Ti, Zr, Hf, V, Nb, Ta, Cr, Mo und W;
"M″" wenigstens ein Element aus den folgenden ist: Mn, Co, Ni, Al und die Platingruppe;
und wobei "a", "b", "c", "d" und "e" ausgedrückt in Atomprozent folgendermaßen sind:
$$3 < a \leqq 8$$
$$0,1 < b \leqq 8$$
$$0 \leqq c \leqq 15$$
$$8 \leqq d \leqq 22$$
$$3 \leqq e \leqq 15$$
$$15 \leqq d + e \leqq 28.$$

8. Massekern nach Anspruch 7, wobei wenigsten 80% der feinen Kristallkörner im Bereich von 5 bis 30 nm (50 Å bis 300 Å) sind.

9. Massekern nach Anspruch 7 oder 8, wobei der Gehalt an Kupfer weniger als 5 Atomprozent beträgt.

10. Massekern nach einem der Ansprüche 7 bis 9, wobei der Gehalt an M′ 1 bis 7 Atomprozent, vorzugsweise 1, 5 bis 5 Atomprozent beträgt.

11. Massekern nach einem der Ansprüche 7 bis 10, wobei der Gehalt an M″ weniger als 10 Atomprozent be-

trägt.

12. Massekern nach einem der Ansprüche 7 bis 11, wobei der Gehalt an Cu, M′ und M″ von 3,1 bis 25 Atomprozent beträgt.

13. Massekern nach einem der Ansprüche 7 bis 12, wobei der Gehalt an Si 10 bis 22 Atomprozent, vorzugsweise 12 bis 18 Atomprozent beträgt.

14. Massekern nach einem der Ansprüche 7 bis 13, wobei der Gehalt an B 5 bis 10 Atomprozent beträgt.

15. Massekern nach einem der Ansprüche 7 bis 14, wobei die Teilchengrößen des Legierungspulvers im Bereich von 1 bis 100 μm liegen.

16. Verfahren zum Behandeln einer weichmagnetischen Legierung auf Eisenbasis gemäß einem der Ansprüche 1 bis 6, mit einer Wärmebehandlung der Legierung zwischen einer und zehn Stunden bei einer Temperatur zwischen 50°C unterhalb der Kristallisierungstemperatur bis 120°C oberhalb der Kristallisierungstemperatur, um die feinen Kristallkörner abzuscheiden, wobei die Wärmebehandlung vorzugsweise von zehn Minuten bis fünf Stunden ausgeführt wird.

Revendications

1. Alliage magnétique mou à base de fer ayant un rapport de surface des grains cristallins fins dans l'intervalle de 15 à 30 nm (50 Å à 300 Å) d'au moins 30 % et qui répond à la formule (I)

$$Fe_{100-a-b-c}Cu_aM_bZ_c; \qquad (I)$$

dans laquelle

"M" est au moins un élément choisi parmi : Ti, Zr, Hf, V, Nb, Ta, Cr, Mo, W, Mn, Co, Ni, Al, et le groupe du platine ;

"Z" est au moins un élément choisi parmi :

Si, B, P et C ;

et dans laquelle "a", "b" et "c", exprimés en atomes %, sont les suivants :

$$3 < a \leqq 8$$
$$0,1 \leqq b \leqq 8$$
$$3,1 \leqq a + b \leqq 12$$
$$15 \leqq c \leqq 28$$

2. Alliage selon la revendication 1, dans lequel au moins 80 % des grains cristallins fins présents dans l'alliage sont dans l'intervalle de 15 à 30 nm (50 Å à 300 Å).

3. Alliage selon la revendication 1 ou 2, dans lequel la quantité de Cu est inférieure à 5 atomes %.

4. Alliage selon l'une quelconque des revendications précédentes, dans lequel la quantité de "M" est de 1 à 7 atomes %, de préférence de 1,5 à 5 atomes %.

5. Alliage selon l'une quelconque des revendications précédentes, dans lequel la quantité de "Z" est de 18 à 26 atomes %.

6. Alliage selon l'une quelconque des revendications précédentes, dans lequel le rapport de (Si et/ou C) à (B et/ou P) est supérieur à 1.

7. Tore à poudre de ferrite fabriqué à partir d'une poudre d'alliage, caractérisé en ce qu'il a un rapport de surface des grains cristallins fins de 5 à 30 nm (50 Å à 300 Å) d'au moins 30 % et répond à la formule (II)

$$Fe_{100-a-b-c-d-e}Cu_aM'_bM''_cSi_dB_e \qquad (II)$$

dans laquelle

"M′" est au moins un élément choisi parmi : Ti, Zr, Hf, V, Nb, Ta, Cr, Mo et W ;

"M″" est au moins un élément choisi parmi : Mn, Co, Ni, Al, et le groupe du platine ;

et dans laquelle "a", "b", "c", "d" et "e", exprimés en atomes %, sont les suivants :

$$3 < a \leqq 8$$
$$0,1 < b \leqq 8$$

$$0 \leqq c \leqq 15$$
$$8 \leqq d \leqq 22$$
$$3 \leqq e \leqq 15$$
$$15 \leqq d + e \leqq 28.$$

8. Tore à poudre de ferrite selon la revendication 7, dans lequel au moins 80 % des grains cristallins fins sont dans l'intervalle de 5 à 30 nm (50 Å à 300 Å).

9. Tore à poudre de ferrite selon la revendication 7 ou 8, dans lequel la quantité de Cu est inférieure à 5 atomes %.

10. Tore à poudre de ferrite selon l'une quelconque des revendications 7 à 9, dans lequel la quantité de M′ est de 1 à 7 atomes %, de préférence de 1,5 à 5 atomes %.

11. Tore à poudre de ferrite selon l'une quelconque des revendications 7 à 10, dans lequel la quantité de M′ est inférieure à 10 atomes %.

12. Tore à poudre de ferrite selon l'une quelconque des revendications 7 à 11, dans lequel la quantité de Cu, M′ et M″ est de 3,1 à 25 atomes %.

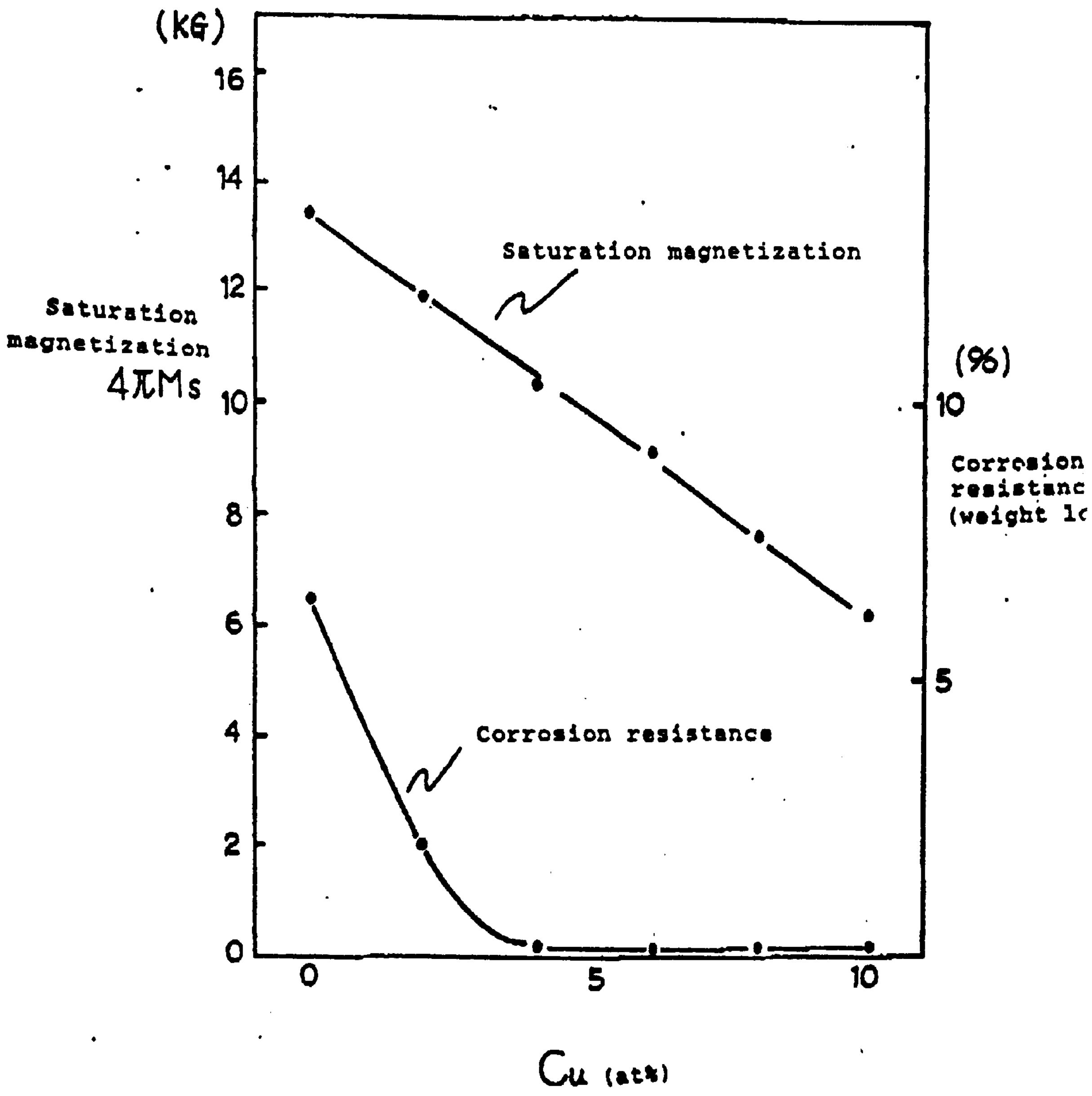
13. Tore à poudre de ferrite selon l'une quelconque des revendications 7 à 12, dans lequel la quantité de Si est de 10 à 22 atomes %, de préférence de 12 à 18 atomes %.

14. Tore à poudre de ferrite selon l'une quelconque des revendications 7 à 13, dans lequel la quantité de B est de 5 à 10 atomes %.

15. Tore à poudre de ferrite selon l'une quleconque des revendications 7 à 14, dans lequel la taille de particules de la poudre d'alliage est dans l'intervalle de 1 à 100 µm.

16. Procédé de traitement d'un alliage magnétique mou à base de Fe selon l'une quelconque des revendications 1 à 6, comprenant le fait de traiter thermiquement cet alliage pendant 1 minute à 10 heures à une température allant de 50°C au-dessous de la température de cristallisation à 120°C au-dessus de la température de cristallisation, pour effectuer la ségrégation des grains cristallins fins ; ce traitement thermique étant de préférence effectué pendant 10 minutes à 5 heures.

Fig. 1


(KG)
16
14
12
10
8
6
4
2
0
Saturation magnetization 4πMs
(%)
10
5
Corrosion resistanc
(weight lo
Saturation magnetization
Corrosion resistance
0
5
10
Cu (at%)

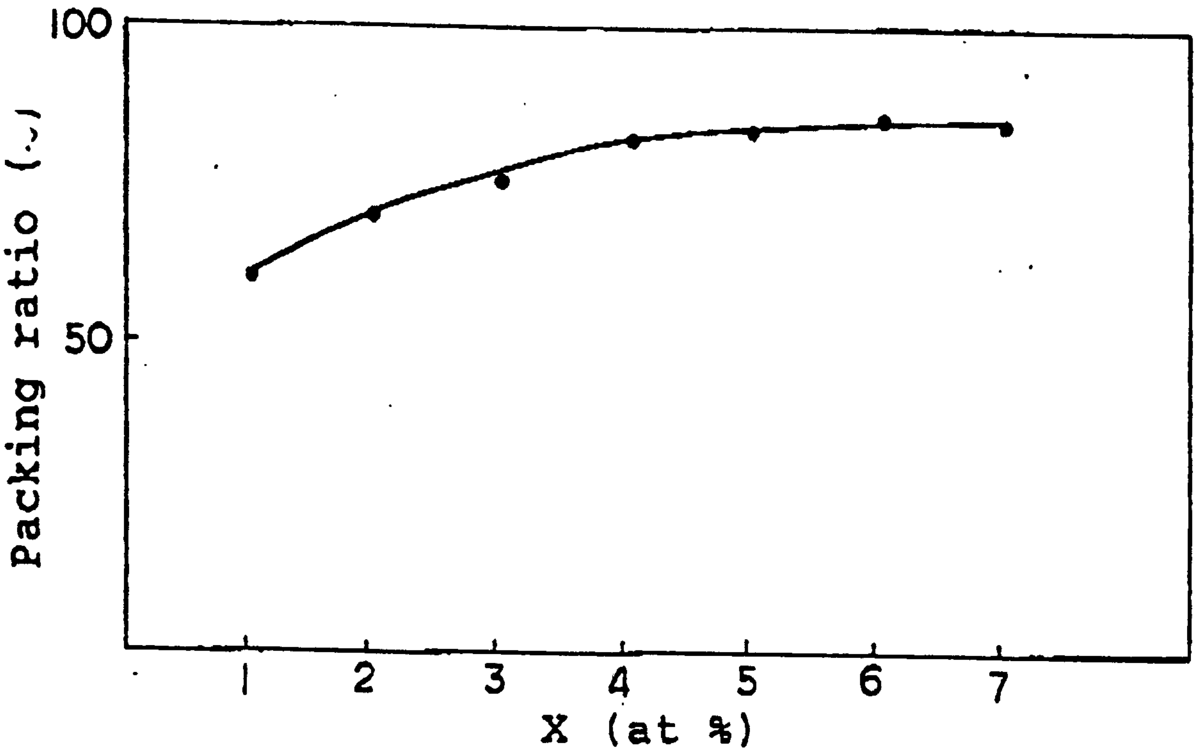


Fig. 2

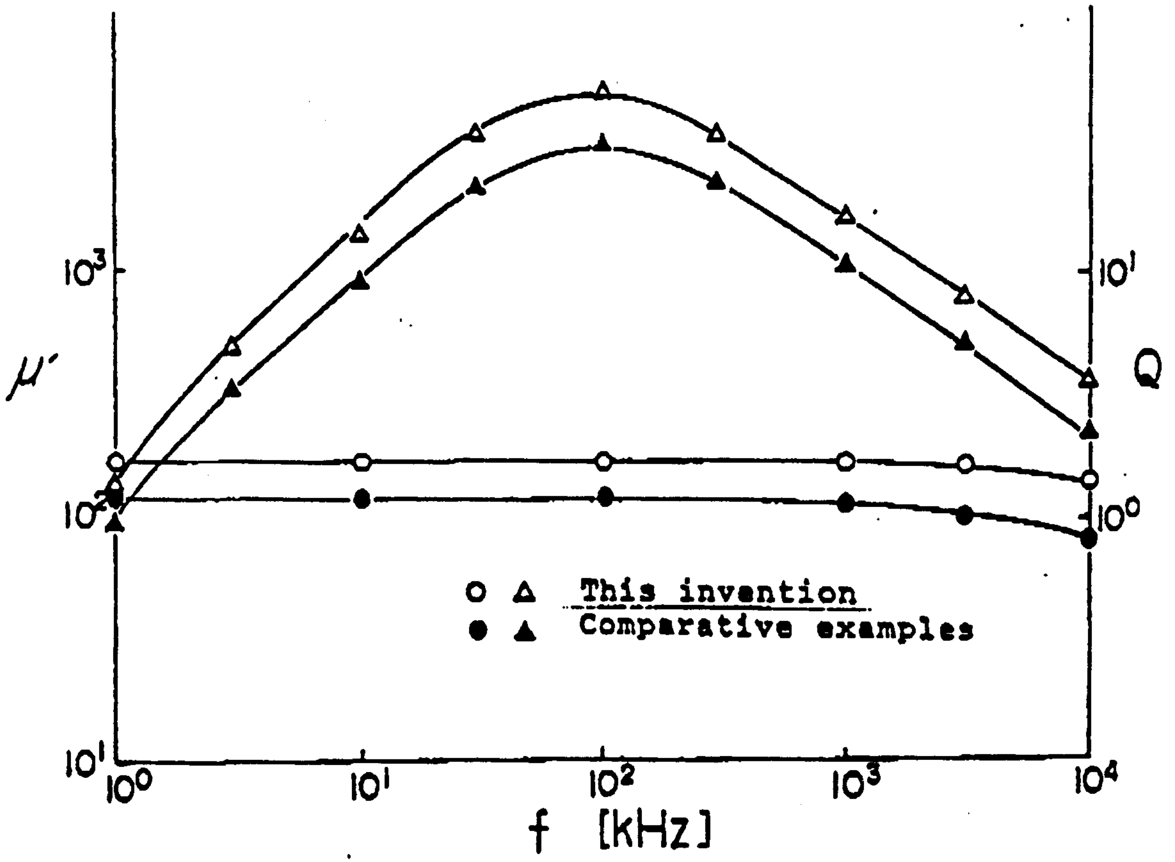

10^3
10^2
10^1
μ'
10^1
10^0
Q
10^0
10^1
10^2
10^3
10^4
f [kHz]
○ △ This invention
● ▲ Comparative examples

Fig. 3

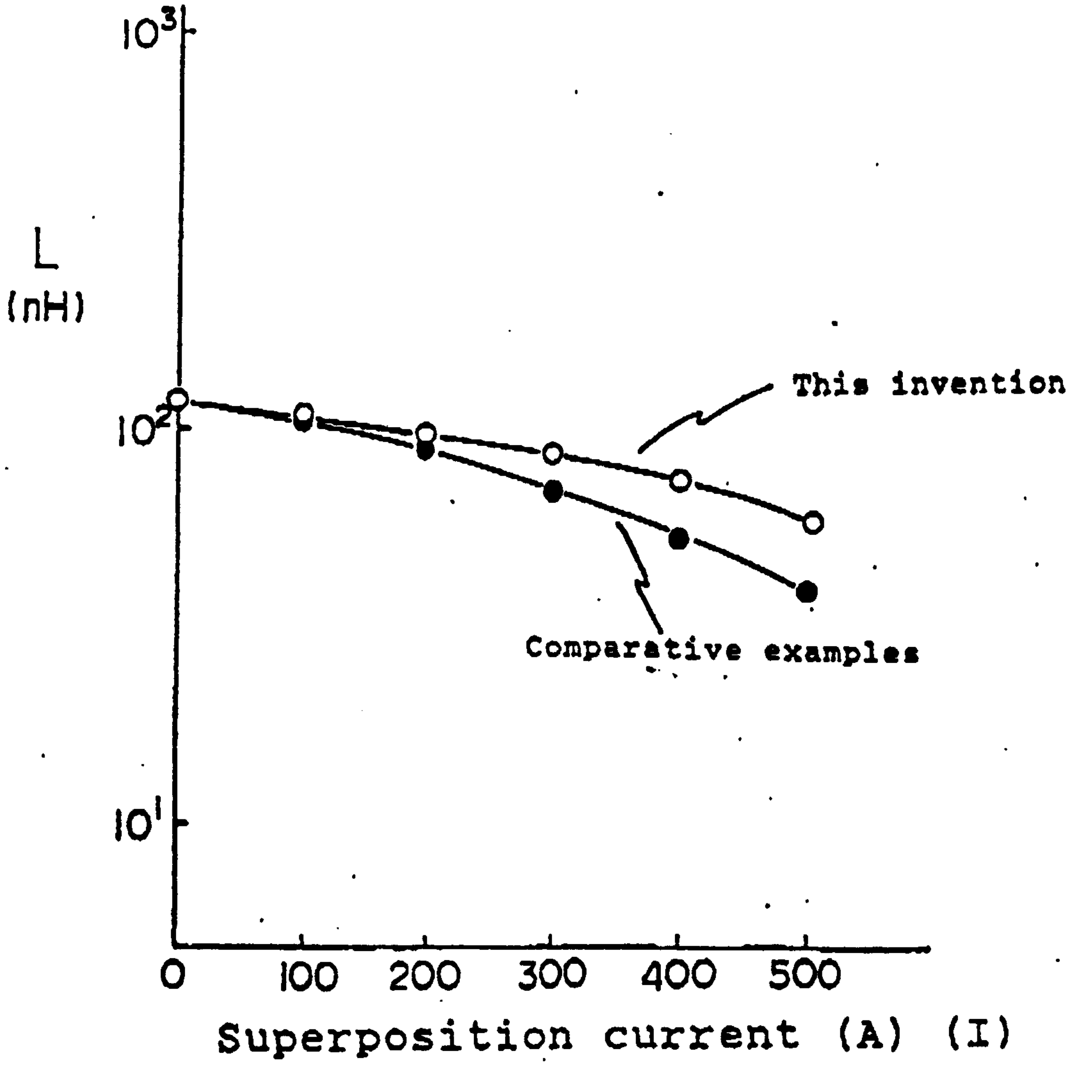

L
(nH)
10^3
10^2
10^1
0
100
200
300
400
500
Superposition current (A) (I)
This invention
Comparative examples

Fig. 4

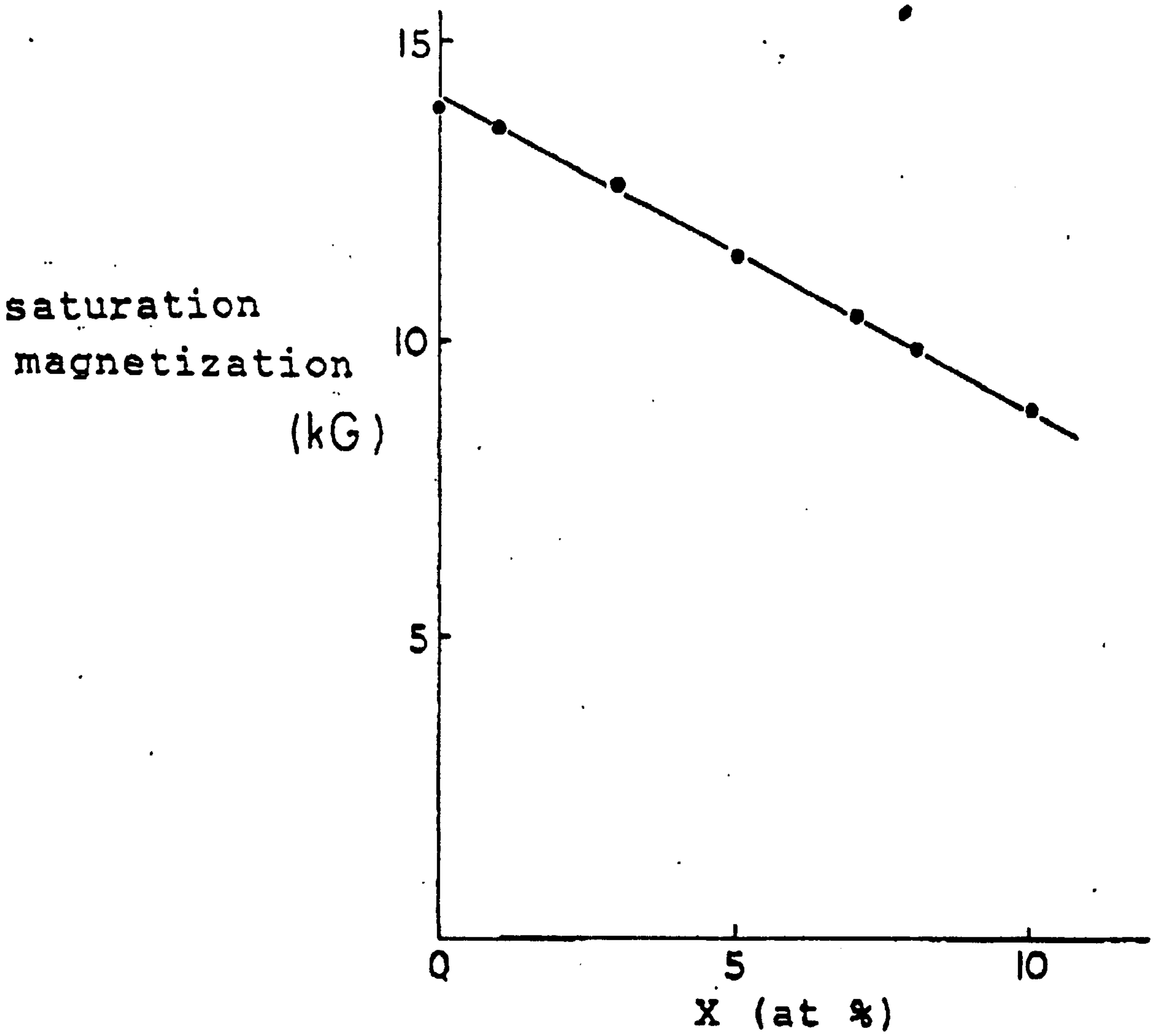


Fig. 5