



⑫

## EUROPEAN PATENT APPLICATION

⑰ Application number : **93304762.3**

⑸ Int. Cl.<sup>5</sup> : **H01F 1/153, H01F 3/00**

⑳ Date of filing : **17.06.93**

⑳ Priority : **17.06.92 JP 158338/92**

④③ Date of publication of application :  
**22.12.93 Bulletin 93/51**

⑧④ Designated Contracting States :  
**DE FR GB IT NL**

⑦① Applicant : **MITSUI PETROCHEMICAL  
INDUSTRIES, LTD.**  
**2-5, Kasumigaseki 3-chome Chiyoda-ku  
Tokyo 100 (JP)**

⑦② Inventor : **Watanabe, Hiroshi, c/o Mitsui  
Petrochem. Ind. Ltd.**  
**580-32, Aza-Taku 2-go, Nagaura  
Sodegaura-shi, Chiba-ken (JP)**  
Inventor : **Hirota, Yoshihiko, c/o Mitsui  
Petrochem. Ind. Ltd.**  
**580-32, Aza-Taku 2-go, Nagaura  
Sodegaura-shi, Chiba-ken (JP)**

⑦④ Representative : **Cresswell, Thomas Anthony  
J.A. Kemp & Co. 14 South Square Gray's Inn  
London WC1R 5LX (GB)**

⑤④ **Fe-base soft magnetic alloy and process for making same.**

⑤⑦ A noble Fe-base soft magnetic alloy of formula  $Fe_{100-a-b-c-d}P_aM_bM'_cCu_d$  where M is at least one element selected from Zr, Hf, Nb, Mo, W, Ta, Ti, V, Cr, Mn, Y and Ce ; M' is at least one element selected from Si, Al, Ga, Ge, Ru, Co, Ni, Sn, Sb and Pd ; a, b, c and d each are an atomic % and satisfy the relations :  $0 < a \leq 25$ ,  $0 < b \leq 15$ ,  $0 \leq c \leq 20$ , and  $0 \leq d \leq 5$  having excellent soft magnetic properties, especially low magnetostriction and low iron loss is made by adding a determined amount of a specific element M, a determined amount of Cu is further added to the alloy and the quenched alloy composition is shaped and heat-treated to provide the Fe-base soft magnetic alloy.

## BACKGROUND OF THE INVENTION

## 1. Field of the Invention

5 The present invention relates to an Fe-base soft magnetic alloy and, in particular, to an alloy having excellent soft magnetic properties and a process for making it.

## 2. Description of the Related Art

10 Fe-base amorphous magnetic alloys having a high saturation magnetic flux density are known to be used as magnetic core materials for magnetic heads, high frequency transformers, saturable reactors, choke coils, etc. However, though Fe-base amorphous magnetic alloys are lower priced than Co-base ones, the former have the drawbacks of large core loss in high frequency region and a low permeability. In addition, its saturation magnetostriction is high.

15 An Fe-B system alloy is known as conventional Fe-system amorphous magnetic alloys. However, the alloys including B (boron) are high priced because the element B is expensive.

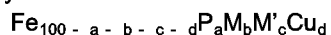
One object of the present invention is to provide a novel Fe-base soft magnetic alloy, which can be substituted for the above-mentioned conventional soft magnetic materials and has a low saturation magnetostriction and a low iron loss.

20 Another object of the present invention is to provide an Fe-base soft magnetic alloy which is lower priced.

## SUMMARY OF THE INVENTION

Intense researches and studies of various Fe-base soft magnetic alloys in view of the above objects have revealed that addition of specific element(s) M, particularly Zr, to an Fe-P system Fe-base soft magnetic alloy can provide an improved Fe-base Fe-Si-B-Al soft magnetic alloy having excellent soft magnetic characteristics, for example, having an extremely low saturation magnetostriction, and that addition of Cu to the Fe-P-M system Fe-base soft magnetic alloy is effective for obtaining excellent soft magnetic properties of the resulting alloy. The present invention is based on these findings.

30 Specifically, there is provided in accordance with the present invention an Fe-base soft magnetic alloy which has a composition represented by the formula:



where M is at least one element selected from the group consisting of Zr, Hf, Nb, Mo, W, Ta, Ti, V, Cr, Mn, Y and Ce;

35 M' is at least one element selected from the group consisting of Si, Al, Ga, Ge, Ru, Co, Ni, Sn, Sb and Pd; a, b, c and d each are an atomic % (atom %) and each satisfy  $0 < a \leq 25$ ,  $0 < b \leq 15$ ,  $0 \leq c \leq 20$ , and  $0 \leq d \leq 5$ . In particular, at least 30 % of the alloy structure is desired to be occupied by fine crystalline particles, and the crystalline particles are desired to be composed of bcc solid solution including mainly Fe.

## 40 DETAILED DESCRIPTION OF THE INVENTION

P (phosphorous) is an essential element of constituting the alloy of the present invention and addition of a determined amount of P (more than 0 atomic % and not more than 25 atomic %) enables to extend the range of formation of amorphous alloys after quenching without using an expensive element B (boron). Thereby, the cost of preparation of the alloy can be reduced.

45 The content (a) of P is more than 0 atomic % and not more than 25 atomic %, preferably from 1 to 15 atomic %, more preferably from 2 to 12 atomic %.

The element(s) M added to the Fe-base soft magnetic alloy of the present invention is supposed to prevent crystallization of the Fe-P system crystal which hampers soft magnetic properties of the alloy or to elevate its crystallization temperature. As M is mentioned at least one, i.e. one or more of the elements selected from the group consisting of Zr, Hf, Nb, Mo, W, Ta, Ti, V, Cr, Mn, Y and Ce. Particularly Zr is preferable. Addition of the element(s) M is further effective for making the crystal grain fine and for improving the ability of forming the amorphous phase of the alloy in the Fe-P system alloy.

50 The content (b) of the M element(s) is more than 0 atomic % and not more than 15 atomic %, preferably from 2 to 15 atomic %, more preferably from 3 to 12 atomic %.

55 The element(s) M' added to the Fe-base soft magnetic alloy of the present invention is one or more of the elements selected from the group consisting of Si, Al, Ga, Ge, Ru, Co, Ni, Sn, Sb and Pd. It is considered that these elements are dissolved in the Fe-major solid solution because they have a negative interaction para-

meter relative to Fe, that is, it is considered that the elements are dissolved as being substituted for Fe atom in the  $\alpha$ -Fe crystalline structure whereby stabilizes the bcc crystal. Thus, it is considered that the crystalline grain having a genuine magnetocrystalline anisotropy of bcc crystalline or low magnetostriction constant is formed to exhibit excellent soft magnetic properties.

The content (c) of the M' element(s) is from 0 atomic % to 20 atomic %, preferably from 1 to 15 atomic %.

Cu (copper) in the alloy of the present invention is effective for making the crystalline particles obtained by the heat-treatment of the amorphous fine. Further, it improves the magnetic properties of the alloy since the effective magnetic anisotropy energy becomes smaller than its genuine magnetocrystalline anisotropy energy as the particles become fine. However, the copper content should not be more than 5 atomic % with respect to the preparation of the alloy because the just quenched alloy tends to be brittle. Accordingly, the content (d) of Cu is from 0 to 5 atomic %, preferably from 0.5 to 3 atomic %.

Incidentally, alloy further containing inevitable impurities such as N, S, O etc., to the extent that these element do not deteriorate the properties of the alloy, is also included in the scope of the present invention.

The Fe-base soft magnetic alloy according to the present invention has an alloy structure, at least 30 % (30 % - 100 %) of which consists of (is composed of) fine crystalline particles, with the balance of the structure being an amorphous phase or other crystals than above-mentioned fine crystalline particles. The range of the ratio of the fine crystalline particles in the structure provides the alloy excellent (soft) magnetic properties. In the present invention, even if the crystalline particles occupy substantially 100 % of the structure, the alloy has yet sufficiently good magnetic properties. Preferably at least 50 %, more preferably 70 % or more of the alloy structure consists of (is composed of) the fine crystalline particles in view of magnetic properties.

The crystalline particles of the alloy of the present invention has mainly a bcc structure and it is considered that Fe as a main component and M, M' and a small amount of P are believed to be dissolved in.

It is preferred that the crystalline particles to be formed in the alloy of the present invention have a particle size of 1000 Å or less, preferably 500 Å or less, more preferably 50 to 300 Å. The particle size being 1000 Å or less, preferably 500 Å or less, more preferably 50 to 300 Å, provides the alloy of the present invention excellent magnetic properties.

The proportion of the crystalline grains to the total alloy structure in the alloy of the present invention may be determined experimentally by an X-ray diffraction method or the like. Briefly, on the basis of the standard value of the X-ray diffraction intensity of Fe-base crystal in the completely crystallized condition (saturated X-ray diffraction intensity condition), the proportion of the X-ray diffraction intensity of the magnetic alloy material sample to be examined to the standard value may be obtained experimentally.

The average size of the crystalline particles is determined from Scherrer's equation ( $t=0.9\lambda/\beta\cos\theta$ ) by using bcc peak reflection of the X-ray diffraction pattern (Element of X-ray Diffraction (Second Edition), pages 91-94, B.D. Cullity).

The Fe-base soft magnetic alloy of the present invention may be produced by a heat-treatment of an amorphous metal having a determined shape which is obtained by a common method of forming an amorphous metal. For instance, an amorphous alloy is first formed in the form of a ribbon, powder, fiber, or thin film by a melt quenching method such as a single roll method or double roll method, a thin film forming method such as a cavitation method, sputtering method or vapor deposition method, or a powder forming method such as mechanical alloying or the like. The resulting amorphous alloy is optionally shaped and worked into a desired shape, then it is heat-treated so that at least a part, preferably 30 % or more of the whole, of the sample is crystallized to obtain the alloy of the present invention.

The structure of the alloy after rapid-quenching is preferably amorphous but it may include partially crystal to the extent that the resulting alloy exhibits soft magnetic properties after heat-treatment.

Generally, a quenched alloy ribbon is formed by a single roll method, and this is shaped into a determined shape such as a coiled magnetic core and then heat-treated. The heat-treatment is effected in vacuum, in an inert gas atmosphere, such as an argon gas or nitrogen gas atmosphere, in reducing gas atmosphere such as H<sub>2</sub> or in oxidizing gas atmosphere such as air. Preferably, it is carried out in vacuum or in an inert gas atmosphere. The heat-treatment temperature is approximately from 200 to 800°C, preferably approximately from 300 to 700°C, and more preferably from 400 to 700 °C. The heat-treatment time is within 24 hours, preferably about from 0.5 to 5 hours. The heat-treatment may be effected either in the absence or presence of a magnetic field. Impressing of a magnetic field brings a magnetic anisotropy to the alloy.

By the heat treatment of the amorphous alloy being carried out in the aforementioned range of temperature and within the aforementioned time range, the soft magnetic alloy having excellent properties is obtained.

#### BRIEF DESCRIPTION OF THE DRAWING

Fig. 1 is a graph showing X-ray diffraction patterns of the Fe-base soft magnetic alloy of the present in-

vention after heat-treatment.

## EXAMPLES

5

Examples of the present invention are described hereinafter.

### Examples 1-3

10 A quenched ribbon (thin film) sample having a width of about 1.5 mm and a thickness of about 15-24  $\mu\text{m}$  was formed from a melt containing Fe, P, Zr, and (Cu) in an argon gas atmosphere of one atmosphere pressure by a single roll method. The sample was then heat-treated at the temperature shown by Table 1 for about one hour in the presence of a nitrogen gas and in the absence of a magnetic field.

15 The iron loss (Pc W/kg) of each of the samples was determined under the condition of a frequency of 100 kHz and a maximum magnetic flux density of 0.1 T. The permeability ( $\mu$ ) (1KHz) under the condition of a frequency of 1 kHz and a maximum exciting magnetic field of 5 mOe, the saturation magnetization Ms (emu/g) and the saturation magnetostriction constant  $\lambda_s$  ( $\times 10^{-6}$ ) of each samples were also determined. The composition of the alloy samples, the content of the fine crystalline particles in the alloy and the average particle size are shown in Table 1 below.

20

Table 1

	Composition of Alloy (atomic %)	Temperature of heat-treatment( $^{\circ}\text{C}$ )	Content of crystalline particle(%)	Particle size of Crystal ( $\text{\AA}$ )	
25	Exam.1	$\text{Fe}_{89}\text{Zr}_9\text{P}_2$	620	60 or more	-
	Exam.2	$\text{Fe}_{85}\text{Zr}_9\text{P}_6$	620	60 or more	-
	Exam.3	$\text{Fe}_{88}\text{Zr}_9\text{P}_2\text{Cu}_1$	620	60 or more	170
30	Comp. Exam.	$\text{Fe}_{78}\text{Si}_9\text{B}_{13}$	410	-	-

As shown by Table 1, the content of the fine crystalline particles is 60 % or more in all of the samples. The composition of the alloy was determined by IPC analysis.

The magnetic properties are shown in Table 2.

35 As comparative samples, a rapid quenched alloy of  $\text{Fe}_{78}\text{Si}_9\text{B}_{13}$  (Comparative Example, commercial product) was prepared as in the same condition as the example 1, and the iron loss, permeability, saturation magnetization and saturation magnetostriction of these samples were also shown in Table 2 below.

Table 2

	Iron Loss (Pc.CW/kg)	Permeability ( $\mu$ , 1kHz)	Saturation Magnetization (Ms,emu/g)	Saturation Magnetostriction ( $\times 10^{-6}$ )	
40	Exam.1	50	3400	-	-
	Exam.2	35	4700	-	-
45	Exam.3	30	8000	-	-0.6
	Comp. Exam.	40	5600	170	28

50 As is obvious from the results in Table 2 above, the iron loss and the permeability of the alloy samples of the present invention are almost the same as those of the sample of Comparative Example and the ally of the present invention is found to be sufficiently practical for the magnetic material substituted for the Fe-B amorphous soft magnetic alloy.

55 Fig. 1 shows the X-ray diffraction curves of the alloy of  $\text{Fe}_{88}\text{Zr}_9\text{P}_2\text{Cu}_1$  (atomic %)(Example 3) obtained by heat-treating the quenched alloy formed by a single roll method, at 620  $^{\circ}\text{C}$  in the presence of argon for one hour. As is obvious from the figure, the structure of the alloy obtained by heat-treatment has mainly bcc structure.

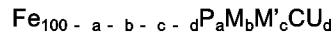
As is obvious from the results in the above-mentioned examples, the Fe-base soft magnetic alloy of the

present invention shows an excellent magnetic properties such as low ion loss, high permeability and low saturation magnestriction by adding specific element(s), particularly Zr together with Cu to Fe-P system alloy. Accordingly, the alloy of the present invention can be utilized widely for a magnetic head, high-frequency transformers, saturable reactors, choke coils and like as the magnetic material substituted for the Fe-B system soft magnetic alloy.

In addition, the Fe-base soft magnetic alloy of the present invention can be reduce the cost of the preparation of the alloy since it utilizes phosphor P instead of boron B.

**Claims**

1. An Fe-base soft magnetic alloy having a composition of formula:



where M is at least one element seleted from Zr, Hf, Nb, Mo, W, Ta, Ti, V, Cr, Mn, Y and Ce; M' is at least one element selected from Si, Al, Ga, Ge, Ru, Co, Ni, Sn, Sb and Pd;

a, b, c and d each are an atomic % and satisfy the relations:  $0 < a \leq 25$ ,  $0 < b \leq 15$ ,  $0 \leq c \leq 20$ , and  $0 \leq d \leq 5$ .

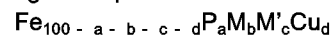
2. An alloy according to claim 1 in which at least 30% of the alloy structure is occupied by fine crystalline particles.

3. An alloy according to claim 2 in which the crystalline particle is a bcc solid solution including mainly iron.

4. An alloy according to any one of claims 1 to 3 in which the average size of the particles is not more than 100nm.

5. An alloy according to any one of claims 1 to 4 in which the saturation magnetostriction ( $\lambda_s$ ) of the alloy is from  $+10 \times 10^{-6}$  to  $-5 \times 10^{-6}$ .

6. A process for making an Fe-base soft magnetic alloy comprising forming a quenched alloy having a composition of formula



wherein M is at least one element selected from Zr, Hf, Nb, Mo, W, Ta, Ti, V, Cr, Mn, Y and Ce; M' is at least one element selected from Si, Al, Ga, Ge, Ru, Co, Ni, Sn, Sb and Pd; a, b, c and d each are an atomic % and each satisfy the relations

$0 < a \leq 25$ ,  $0 < b \leq 15$ ,  $0 \leq c \leq 20$ , and  $0 \leq d \leq 5$ ,

by a melt quenching method, a thin film forming method or a powder forming method and treating the quenched alloy by heat.

7. A process according to claim 6 in which the quenched alloy is maintained at the temperature from 350 °C to 700 °C for less than 24 hours during heat-treatment.

8. A process according to claim 6 or claim 7 for producing an alloy according to any one of claims 2 to 5.

9. A magnetic core consisting of an alloy according to any one of claims 1 to 5 or produced according to claim 6 or claim 7.

FIG. 1

