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

(11) **EP 2 055 797 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
06.05.2009 Bulletin 2009/19

(21) Application number: **07792874.5**

(22) Date of filing: **22.08.2007**

(51) Int Cl.:
C22C 38/00 $^{(2006.01)}$
C21D 8/12 $^{(2006.01)}$
C22C 19/03 $^{(2006.01)}$
H01F 1/147 $^{(2006.01)}$

(86) International application number:
PCT/JP2007/066284

(87) International publication number:
WO 2008/023734 (28.02.2008 Gazette 2008/09)

(84) Designated Contracting States:
AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC MT NL PL PT RO SE SI SK TR
Designated Extension States:
AL BA HR MK RS

(30) Priority: **23.08.2006 JP 2006226410**

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(54) IRON-BASED ALLOY AND PROCESS FOR PRODUCING THE SAME

(57) It is an object of the present invention to provide a ferromagnetic Fe-based alloy having a large reversible strain obtained by application and removal of a magnetic field gradient.

The Fe-based alloy contains one or two or more types selected from Al: 0.01 to 11%, Si: 0.01 to 7% and Cr: 0.01 to 26%, or Al: 0.01 to 11%, Si: 0.01 to 7%, Cr: 0.01 to 26% and Ni: 35 to 50%. A twin crystal interface is introduced by working the Fe-based alloy at a working rate: 10% or more. An area ratio of the twin crystal interface to a crystal grain boundary is 0.2 or more. One or two or more types of Ti: 0.01 to 5%, V: 0.01 to 10%, Mn: 0.01 to 5%, Co: 0.01 to 30%, Ni: 0.01 to 10%, Cu: 0.01 to 5%, Zr: 0.01 to 5%, Nb: 0.01 to 5%, Mo: 0.01 to 5%, Hf: 0.01 to 5%, Ta: 0.01 to 5%, W: 0.01 to 5%, B: 0.001 to 1%, C: 0.001 to 1%, P: 0.001 to 1% and S: 0.001 to 1% may be added to the Fe-based alloy if needed.

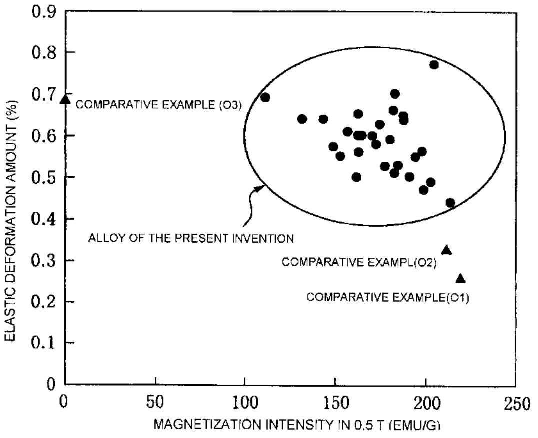

FIGURE 1

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Description

Technical Field

[0001] The present invention relates to a ferromagnetic Fe-based alloy having a large reversible strain obtained by application and removal of a magnetic field gradient, the Fe-based alloy capable of being displaced, and a method for producing the same.

Background Art

[0002] Attentions have been focused on a titanium alloy as a material having a low Young's modulus and exhibiting high elastic deformability. The titanium alloy is used for an artificial tooth root, an artificial bone and a glass frame or the like. For example, it is known that a titanium alloy containing a IVa group or Va group element is a material having a low Young's modulus and exhibiting high elastic deformability (Patent Documents 1 and 2).

[0003] Patent Documents 1 and 2 describe the deformation behavior of the titanium alloy to external stress. Examples of external factors which cause a deformation include a temperature and a magnetic field in addition to the stress.

A shape-memory alloy displacably controlled by a temperature is known, and has a dimension change of a level of several %. A shape memory effect is a phenomenon in which an original shape of a deformed material is restored using martensitic reverse transformation produced when the deformed material is heated at a certain temperature or more. When the shape memory effect is used, the shape-memory alloy can be used as a thermally driven actuator. However, the shape-memory alloy requires temperature control and further has a poor response since the shape change of the shape-memory alloy in being cooled is rate-controlled by thermal diffusion.

[0004] Attentions have been also focused on a ferromagnetic shape-memory alloy an actuator material. The ferromagnetic shape-memory alloy, which has a dimension change of several % exceeding that of a conventional magnetrostriction material when an external magnetic field is applied to the ferromagnetic shape-memory alloy, also eliminate a low response as a fault of a thermally driven shape-memory alloy. Examples of the ferromagnetic shape-memory alloys include an Ni-Mn-Ga based material. As the ferromagnetic shape-memory alloy, an actuator material having a shape change caused by applying a magnetic field has been known (Patent Document 3). However, the Ni-Mn-Ga based material has inferior ductility, and it is difficult to apply a complicated and precise shape required for machine parts to the Ni-Mn-Ga based alloy.

[0005]

Patent Document 1: Japanese Patent Application Laid-Open No. 2002-332531
Patent Document 2: Japanese Patent Application Laid-Open No. 2002-249836
Patent Document 3: U.S. Pat. No. 5,958,154

Disclosure of the Invention

Problem to be solved by the Invention

[0006] The present inventors have researched and examined various ferromagnetic materials capable of being magnetically driven while maintaining high elastic deformability, the materials having good ductility, in view of the faults of the conventional titanium alloy or Ni-Mn-Ga based alloy. As a result, the inventors found that a ferromagnetic Fe-based alloy having a large reversible strain exhibited by application and removal of a magnetic field gradient is obtained by the suitable selection of alloy components and compositions, and the proper management of producing conditions, using Fe which is an inexpensive material as a base.

It is an object of the present invention to provide an Fe-based ferromagnetic alloy having a large reversible strain obtained by application and removal of a magnetic field gradient and good ductility base on these findings, the Fe-based alloy having a proper amount of one or two or more types of Al, Si, Cr and Ni added.

Means for solving problem

[0007] An Fe-based alloy of the present invention contains one or two or more types selected from Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass and Cr: 0.01 to 26% by mass. The Fe-based alloy can further contain one or two or more types selected from Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Mn: 0.01 to 5% by mass, Co: 0.01 to 30% by mass, Ni: 0.01 to 10% by mass, Cu: 0.01 to 5% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass, W: 0.01 to 5% by mass, B: 0.001 to 1% by mass, C: 0.001 to 1% by mass, P: 0.001 to 1% by mass and S: 0.001 to 1% by mass.

[0008] An Fe-based alloy of the present invention can contain one or two or more types selected from Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass, Cr: 0.01 to 26% by mass and Ni: 35 to 50% by mass. The Fe-based alloy can further contain one or two or more types selected from Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Mn: 0.01 to 5% by mass, Co: 0.01 to 30% by mass, Cu: 0.01 to 5% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass, W: 0.01 to 5% by mass, B: 0.001 to 1% by mass, C: 0.001 to 1% by mass, P: 0.001 to 1% by mass and S: 0.001 to 1% by mass.

[0009] This Fe-based alloy, which is ferromagnetic at least at an ordinary temperature, has an existing deformed twin crystal generated by working.

The existing amount of the twin crystal is adjusted to 0.2 or more as an area ratio of a twin crystal interface to an area of a crystal grain boundary (hereinafter, merely referred to as "an area ratio of a twin crystal interface"). A metal structure having the existing twin crystal is formed by solution-treating an Fe-based alloy having a predetermined composition at 600 to 1350°C and then working the Fe-based alloy at a working rate: 10% or more. Furthermore, the Fe-based alloy may be aging-treated at 200 to 800°C.

Effect of the Invention

[0010] The present inventors have added various alloy elements to Fe which is a ferromagnetic element in order to provide a material having a large reversible strain obtained by application and removal of a magnetic field gradient, the material displacably controlled. The present inventors have researched and examined the relationship between a composition and a working rate, and an elastic deformation amount and magnetic property. As a result, there could be obtained a ferromagnetic alloy having high elastic deformation, the alloy having the large reversible strain obtained by the application and removal of the magnetic field gradient by the Fe-based alloy containing a proper amount of Al, Si, Cr and Ni and good ductility.

Best Mode for Carrying Out the Invention

[0011] An Fe-based alloy of the present invention, which has a metal structure having a twin crystal, is reversibly deformed. This is guessed as follows. It has been known that a ferromagnetic material receives a force corresponding to a magnetic field gradient according to the relational expression of $F=-M\ (dH/dx)$ to be displaced. That is, a force F obtained by a certain magnetic field gradient dH/dx is proportional to a magnetization intensity M. The larger the force F applied to a material is, the larger the obtained deformation amount is, and thereby, the magnetization intensity M is preferably larger. The deformation amount caused by a magnetic field is reduced when stress required for deforming the material is high, and thereby a Young' s modulus is desirably low. However, when the elastic deformability of the material is small, a strain is allowed to remain by removing the magnetic field gradient. Therefore, large elastic deformability is required in order to obtain a large reversible strain by the application and removal of the magnetic field gradient.

[0012] α Fe having a b.c.c. structure is a ferromagnetic element having a large magnetic moment. However, pure Fe, which is plastically deformed immediately, has a small elastic deformation amount. Various alloy elements are added into Fe, and the obtained Fe-based alloy is cold-worked. The magnetic property and elastic deformation amount of the Fe-based alloy are researched. As a result, when Al, Si, Cr and Ni or the like are added into Fe, the Fe-based alloy can be confirmed to have an enhanced elastic deformation amount while exhibiting high magnetic property. When a displacement control element using the magnetic field gradient is considered, strong magnetization ability to a comparatively low magnetic field is preferably shown. When the magnetization curve of an Fe alloy of the present invention is measured, the Fe alloy has a magnetization intensity of 100 emu/g or more to an external magnetic field of 0.5 tesla (hereinafter, referred to as T).

[0013] On the other hand, a result of researching the relationship between cold working and elastic deformation behavior showed the followings. An elastic limit strain of a metal material such as annealed Fe is usually about 0.3%. However, when the metal material is cold-worked, the metal material is work-hardened to suppress slip deformation to increase a hardness and a tension strength and heighten a yield stress and an elastic limit. In the Fe alloy of the present invention, a strain of 0.4% or more exceeding a usual elastic deformation amount to bending deformation of 1% is restored, for example. Fig. 1 collectively shows the relationship between the magnetization intensity to the external magnetic field of 0. 5 T and the elastic deformation amount to the bending deformation of 1%. Any of alloys of the present invention has a magnetization intensity of 100 emu/g or more and an elastic deformation amount of 0.4% or more. Such properties can be applied in a wide temperature range of a liquid nitrogen temperature (-196°C) to 400°C.

[0014] The Fe alloy of the present invention has a comparatively small Young's modulus and exhibits a large elastic deformation amount. However, examples of each of factors thereof include ΔE effect and reversible movement of the twin crystal.

The Young's modulus, which is a property value involved in an interatomic cohesive force, is believed to be difficult to be controlled in working or heat treatment. However, in the ferromagnetic material, ΔE effect reducing the Young's modulus is caused by the rotation of the magnetic moment when the stress is applied.

It has been known that a deformed twin crystal existing in large quantity in the worked structure moves reversibly to deformation and unloading after being deformed. The reversible move phenomenon of the twin crystal exhibits shows a larger elastic deformation amount than that of a material having no twin crystal. As a result, a large elastic deformation amount is obtained.

The existing amount of the twin crystal can be represented as an area ratio of an interface from the ratio of the lengths a twin crystal interface and crystal grain boundary by measuring the length of the twin crystal interface and the length of the crystal grain boundary based on a metal structure observed by an optical microscope or the like.

Herein, a difference between high elastic deformation which is obtained in the present invention and superelasticity in shape-memory alloy will be described. In the twin crystal obtained in the present invention, the relation of the crystallographic direction of two areas bordering on the twin crystal interface merely becomes a twin crystal relation by working. On the other hand, in the superelasticity, stress-induced martensitic transformation accompanied by a crystal structure change to a martensitic phase from a mother phase is generated by the stress. In such a point, a clear difference exists in both the high elastic deformation and the superelasticity.

[0015] The Fe-based alloy of the present invention is based on an Fe alloy containing one or two or more types selected from Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass, Cr: 0.01 to 26% by mass or Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass, Cr: 0.01 to 26% by mass and Ni: 35 to 50% by mass.

Al, Si, Cr and Ni have effects for increasing the elastic deformation amount after being cold-worked and permeability while having a high magnetization intensity. The addition of Al, Si or Cr of 0.01% by mass ormore attains the effects remarkably. However, the excess addition causes remarkable deterioration of workability or magnetic property, and thereby Al: 11% by mass, Si: 7% by mass and Cr: 26% by mass are set as the upper limit. The addition of Ni of 35% by mass or more has effects for increasing an elastic deformation amount after being cold-worked while having a high magnetization intensity.

However, the excess addition causes remarkable deterioration of workability or magnetic property, and thereby Ni: 50% by mass is set as the upper limit.

[0016] Ti, V, Zr, Nb, Mo, Hf, Ta and W are components effective for forming a carbide and a sulfide or the like to miniaturize a crystal grain to enhance a toughness. The excess addition thereof causes remarkable deterioration of the magnetic property, and thereby the content thereof is selected in the range of Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass and W: 0.01 to 5% by mass in being added.

Mn is a component effective for acting as a deoxidizing agent, and generating a sulfide to enhance machinability. However, the excess addition thereof causes remarkable deterioration of the magnetic property, and thereby the content thereof is selected in the range of Mn: 0.01 to 5% by mass in being added.

Cu is a component effective for enhancing weatherability. However, the excess addition thereof causes remarkable deterioration of the magnetic property, and thereby the content thereof is selected in the range of Cu: 0.01 to 5% by mass in being added.

[0017] Co is a component effective for raising a Curie temperature. The excess addition thereof causes deterioration of ductility, and thereby the content thereof is selected in the range of Co: 0.01 to 30% by mass in being added.

Ni is a component effective for enhancing a corrosion resistance even when the amount of Ni is less than 35% by mass, and thereby Ni can be added as an optional component in a range in which remarkable deterioration of the magnetic property is not caused. In this case, the content thereof is preferably selected in the range of Ni: 0.01 to 10% by mass.

B, C and P are components effective for miniaturizing the crystal grain. However, the excess addition thereof causes remarkable deterioration of ductility. Consequently, when B, C and P are added, the content thereof is selected in the range of B: 0.001 to 1% by mass, C: 0.001 to 1% by mass and P: 0.001 to 1% by mass.

S is a component effective for enhancing machinability. However, the excess addition thereof causes deterioration of workability. Consequently, when S is added, the content thereof is selected in the range of S: 0.001 to 1% by mass.

[0018] After the Fe-based alloy having a composition adjusted to a predetermined value is melted, the melted alloy is cast, forged and hot-rolled. The melted alloy is formed into a plate material, a wire material and a pipe material or the like which have an obj ective size by working such as cold-rolling and drawing. The cold-worked Fe-based alloy is solution-treated at a temperature: 600 to 1350°C to remove a strain introduced in a process until cold working to homogenize the alloy. Since a recrystallization temperature or more required, a solution temperature is made to be 600°C or more. Also, since a melting point temperature or less (specifically, 1350°C or less) is sufficiently required, the solution temperature is preferably set to the range of 700 to 1100°C. The solution temperature is made to be 0.1 hours or more since diffusion for recrystallization and solution is required. The solution temperature of 6 hours or less is required in order to prevent remarkable oxidization of the alloy, and the solution temperature is preferably set to the range of 0.2 to 2 hours.

[0019] The solution-treated Fe-based alloy may be heat-treated at 200 to 600°C if needed. This heat treatment has an effect of the tempering of hard and brittle martensite. A temperature of 200°C or more is required in order to obtain this effect. However, the Fe-based alloymay transform into a martensite phase again during cooling at a temperature exceeding 600°C, and thereby the temperature is set to 600°C or less. This heat treatment time is made to be 0.01 hours or more since diffusion required for tempering is required. The heat treatment time of 24 or less hours is required since the heat treatment for a long time reduces the elastic deformability. Preferably, the heat treatment time is set to the range of 0.1 to 4 hours.

[0020] The solution-treated Fe-based alloy is subjected to rolling, forging, bending and reducing works or the like at room temperature or a temperature of 700°C or less. The working at the room temperature or the temperature of 700°C or less is effective for increasing the amount of the twin crystal and an elastic region. However, hot working which may cause dynamic recrystallization is not preferable. Usually, in view of defining working in a temperature region of $0.6T_M$ (T_M: melting point) or more as hot working, a working temperature is set to 0.6 T_M or less, specifically, 700°C or less. A working rate of 10% or more is required since a ratio of the area of the twin crystal interface to that of the crystal grain boundary is 0.2 or more. The working rate of 95% or less is required in order to avoid large burden to equipment.

The influence of the twin crystal on the enhancement in the elastic deformability becomes remarkable when a ratio of the area of the twin crystal interface to that of the crystal grain boundary is made to be 0.2 or more in the whole metal structure.

[0021] The Fe-based alloy may be solution-treated at 600°C to 1350°C for 0.1 to 6 hours, subjected to working of 10% or more at room temperature or a temperature of 700°C or less, and then ageing-treated at 200°C to 800°C for 0.1 to 24 hours. When the Fe-based alloy is ageing-treated, the strength of the Fe-based alloy can be adjusted by a strain aging effect or restoration/recrystallization. Therefore, an aging temperature of 200°C or more is required in order to promote at least atomic short distance diffusion, however, a sufficient elastic strain is not obtained at a high temperature heat exceeding 800°C. The aging time needs to be 0.1 hours or more since diffusion for generating the strain aging effect and restoration/recrystallization is required. The aging time needs to be 24 hours or less in order to prevent the reduction of an elastic strain. The aging time is preferably set to the range of 0.2 to 6 hours.

[0022] Examples of magnetic drive actuators include a piston type pump. The principle of the piston type pump using the magnetic drive actuator is that the volume of a chamber used in order to feed a fluid, usually liquid is changed by the shape change of magnetic field gradient induction of an actuator element. The motion of a piston is generated by wide range shape change of the actuator element. A magnetic field generation source may be placed outside the chamber.

Example 1

[0023] Fe-based alloys having compositions of Table 1 were melted, cast, hot-rolled and cold-rolled to a plate thickness: 0.5 mm. Further, the Fe-based alloys were solution-treated at 1000°C for 60 minutes. For alloy designs in Table 1, alloys A1 to A5 are based on an Fe-Al-based alloy; alloys S1 to S4 based on an Fe-Si-based alloy; alloys C1 to C4 based on an Fe-Cr-based alloy; and alloys N1 to N4 based on an Fe-Ni-based alloy. Alloys A5, A6, S5, S 6, C5, C6, N5 and N6 are obtained by combining a plurality of fundamental Fe-based alloys.

[0024]

[Table 1]

Table 1: Prepared Fe-based alloy

alloy No.	alloy component, content (% by mass)					alloy No.	alloy component, content (% by mass)				
	Al	Si	Cr	Ni	Fe		Al	Si	Cr	Ni	Fe
A1	2	-	-	-	balance	C1	-	-	5	-	balance
A2	5	-	-	-	balance	C2	-	-	12	-	balance
A3	7	-	-	-	balance	C3	-	-	18	-	balance
A4	10	-	-	-	balance	C4	-	-	22	-	balance
A5	5	3	-	-	balance	C5	-	-	12	45	balance
A6	5	-	12	-	balance	C6	2	-	12	-	balance
S1	-	0.5	-	-	balance	N1	-	-	-	36	balance
S2	-	1.5	-	-	balance	N2	-	-	-	40	balance
S3	-	3	-	-	balance	N3	-	-	-	45	balance
S4	-	6	-	-	balance	N4	-	-	-	50	balance

(continued)

Table 1: Prepared Fe-based alloy											
alloy No.	alloy component, content (% by mass)					alloy No.	alloy component, content (% by mass)				
	Al	Si	Cr	Ni	Fe		Al	Si	Cr	Ni	Fe
S5	-	3	12	-	balance	N5	2	-	-	45	balance
S6	-	3	-	45	balance	N6	-	0.5	12	45	balance

[0025] Table 2 shows results obtained by investigating the elastic deformation amount and magnetization intensity of each of the solution-treated Fe-based alloys at room temperature when the Fe-based alloy is subjected to cold-rolling of 40% at room temperature.

The elastic deformation amount was made to be a shape strain amount restored by applying a bending strain amount of 1% in a three-point bending test and then unloading the amount. The magnetization intensity is obtained by applying a magnetic field of 0.5 T using a vibrating sample magnetometer. The area ratio of a twin crystal interface was determined based on the average value of crystal grain boundaries and twin crystal interfaces obtained from optical microscope photographs of five views.

[0026] As shown in Table 2, even in any alloy of Fe-Al-, Fe-Si-, Fe-Cr- and Fe-Ni-based alloys, the area ratio of the twin crystal interfaces is 0.6 or more. The area ratio of the twin crystal interface tends to increase according to the weight increase of Al, Si, Cr and Ni. For example, the Fe-Al-based alloy A2 of Al: 5% by mass has a large number of existing deformed twin crystals (Fig. 2).

[0027] The elastic deformation amount also tends to increase when the area ratio of the twin crystal interface is larger. As shown in the stress-strain diagrammatic view (Fig. 3) of the alloy A2, the elastic deformation amount of 0.55% to the strain application of 1% is shown in being unloaded. Even in the other alloys, the elastic deformation amount of 0.4% or more is obtained. The alloy A2 also has a characteristic that a stress-strain diagrammatic view is more linear than that of a hyperelastic material.

[0028] The magnetization intensity is reduced with the increase in an addition element. However, any Fe-based alloy has a high magnetization intensity of 100 emu/g or more. On the other hand, Comparative Examples O1 (Fe) and 02 (Fe-Co) have a large magnetization intensity, however, have hardly existing twin crystals. Comparative Examples O1 (Fe) and 02 (Fe-Co) have an elastic deformation amount lower than the material of the present invention. Comparative Example 03 (SUS316L) exhibits a high area ratio of a twin crystal interface and a high elastic deformation amount. However, the magnetization intensity in 0.5 T is about 0.

[0029]

[Table 2]

Table 2: Area ratio of twin crystal interface, elastic deformation amount and magnetization intensity of cold-rolled material (cold-rolling rate: 40%)							
alloy No.	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	alloy No.	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
A1	0.76	0.47	198.1	C1	0.65	0.51	182.3
A2	0.79	0.55	193.6	C2	0.70	0.53	177.0
A3	0.83	0.64	187.2	C3	0.78	0.58	171.4
A4	0.90	0.70	182.0	C4	0.81	0.60	164.7
A5	1.38	0.58	172.4	C5	1.07	0.57	148.5
A6	0.86	0.57	162.3	C6	0.84	0.56	162.3
S1	0.88	0.44	214.1	N1	1.22	0.69	111.4
S2	1.01	0.49	201.9	N2	1.41	0.64	143.1
S3	1.87	0.56	197.2	N3	1.94	0.63	174.5
S4	2.04	0.66	181.3	N4	2.13	0.61	156.8

(continued)

Table 2: Area ratio of twin crystal interface, elastic deformation amount and magnetization intensity of cold-rolled material (cold-rolling rate: 40%)

alloy No.	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	alloy No.	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
S5	1.98	0.50	161.4	N5	2.06	0.64	159.4
S6	2.46	0.61	187.6	N6	2.38	0.64	131.0
O1	-0	0.26	218.6				
O2	0.10	0.33	211.2				
O3	1.04	0.69	-0				

O1 to O3: Comparative Examples
O1: Fe,
O2: Fe-5% by mass Co,
O3: SUS316L

Example 2

[0030] Alloys A2, S3, C2 and N3 of Table 1, which were selected as a Fe-Al-based, Fe-Si-based, Fe-Cr-based and Fe-Ni-based alloys, were cold-worked and aging-treated after being solution-treated.
The relationship between producing conditions and property values is shown in Table 3. In test No.1, cold rolling was not carried out after being solution-treated, and twin crystals did not exist. Test No.2 is obtained by applying cold-rolling of 40% to the test No.1, and the elastic deformation amount was also large. Test No.3 was rolled at a cold working rate of 80%, and the area ratio of the twin crystal interface and the elastic deformation amount increased with the increase in the working rate. However, the magnetization intensity had no change and magnetic property was well maintained.

[0031] Test Nos. 7 to 12 are aging-treated after being solution-treated and cold-rolled. In the test Nos.7-8and10-11, the area ratio of the twin crystal interface is 0.2 or more, and the suitable elastic deformation amount was obtained. However, in the test Nos. 9 and 12, an aging temperature was high, and the material was annealed to reduce the elastic deformation amount. In any case, the magnetic property was good.
The above results show that the elastic deformation amount can be adjusted by suitable aging treatment.
The solution temperature was changed in test Nos. 4 to 6. In the test No.4 and 5, the area ratio of the twin crystal interface, the elastic deformation amount and the magnetization intensity were good. However, in the test No. 6, the solution temperature was high, and thereby a liquid phase appeared to partially melt the material.

[0032]

[Table 3]

Table 3: Influence of producing condition on physical properties

test No.	alloy No.	solution-treatme nt		cold working rate (%)	aging treatment		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
		(°C)	(minutes)		(°C)	(times)			
1	A2	1000	60	0	no aging treatment		0	0.25	192.3
2	A2	1000	60	40	no aging treatment		0.79	0.55	193.6
3	A2	1000	60	80	no aging treatment		1.24	0.63	194.2
4	S3	1000	60	40	no aging treatment		1.87	0.56	197.2

(continued)

Table 3: Influence of producing condition on physical properties

test No.	alloy No.	solution-treatme nt		cold working rate (%)	aging treatment		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
		(°C)	(minutes)		(°C)	(times)			
5	S3	1200	60	40	no aging treatment		2.04	0.54	197.8
6	S3	1500	60	40	partially melted sample				
7	C2	1000	60	40	500	2	0.59	0.46	177.1
8	C2	1000	60	40	600	2	0.21	0.43	177.2
9	C2	1000	60	40	900	2	0	0.32	177.5
10	N3	1000	60	40	500	2	1.65	0.66	174.5
11	N3	1000	60	40	600	2	0.46	0.55	174.7
12	N3	1000	60	40	900	2	0	0.37	175.0

Example 3

[0033] Alloys A3, S2, C3 and N3 of Table 1 respectively have a Fe-Al-based, Fe-Si-based, Fe-Cr-based and Fe-Ni-based fundamental compositions. Various Fe-based alloys were prepared by adding a third component of claim 2 or 4. The Fe-based alloys were cast, hot-rolled and cold-rolled to a plate thickness: 0.5 mm in the same manner as in Example 1 after being melted. The Fe-based alloys were cold-rolled and aging-treated after being solution-treated.
Table 4 (Fe-Al-based), Table 5 (Fe-Si-based), Table 6 (Fe-Cr-based) and Table 7 (Fe-Ni-based) show results obtained by measuring the elastic deformation amount and magnetization intensity of each of the obtained Fe-based alloys.

[0034] As shown in search results of Tables 4 to 7, each of Fe-based alloys having enhanced magnetism, a corrosion resistance, strength and ductility or the like obtained adding a third element exhibited an area ratio of a twin crystal interface of 0.6 or more. The Fe-based alloy had an elastic deformation amount of 0. 4% or more to the strain application of 1%. Also, the Fe-based alloys had a high magnetization intensity of 100 emu/g or more to the magnetic field application of 0.5 T. Furthermore, the elastic deformation amount could be adjusted by aging-treating after cold-rolling.

[0035]

[Table 4]

Table 4: Influence of addition of third component on physical properties of Fe-7% by mass Al alloy

test No.	amount of third component to be added (% by mass)	cold-rolled material (working rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
A-1	Ti: 2	0.91	0.66	169.4	0.77	0.58	169.5
A-2	V: 3	0.93	0.67	166.2	0.78	0.59	166.4
A-3	Mn: 1	0.84	0.64	176.1	0.69	0.57	176.1
A-4	Co: 8	1.02	0.68	190.5	0.87	0.61	190.6
A-5	Ni: 2	0.84	0.63	174.5	0.71	0.56	174.8
A-6	Cu: 2	0.85	0.64	175.8	0.73	0.57	175.9
A-7	Zr: 1	0.87	0.65	173.9	0.75	0.58	174.0
A-8	Nb: 1	0.86	0.66	177.2	0.73	0.60	177.3

(continued)

Table 4: Influence of addition of third component on physical properties of Fe-7% by mass Al alloy							
test No.	amount of third component to be added (% by mass)	cold-rolled material (working rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
A-9	Mo: 2	0.83	0.64	176.3	0.70	0.56	176.5
A-10	Hf: 1	0.89	0.67	175.1	0.76	0.60	175.4
A-11	Ta: 3	0.99	0.70	171.4	0.82	0.62	171.6
A-12	W: 2	0.95	0.69	176.5	0.80	0.61	176.8
A-13	B: 0.05	0.87	0.66	171.7	0.75	0.60	171.9
A-14	C: 0.05	0.82	0.67	180.8	0.72	0.61	181.0
A-15	P: 0.05	0.85	0.66	170.8	0.74	0.59	171.0
A-16	S: 0.05	0.86	0.65	172.6	0.78	0.56	172.6
A-17	V: 2 Nb: 1	0.93	0.67	159.0	0.81	0.57	159.1
A-18	Ni: 2 Mo: 1 B: 0.05	0.90	0.68	156.2	0.79	0.59	156.6

[0036]

[Table 5]

Table 5: Influence of addition of third component on physical properties of Fe-1.5% by mass Si alloy							
test No.	amount of third component to be added (% by mass)	cold-rolled material (working rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
S-1	Ti: 2	1.07	0.50	183.4	0.91	0.43	183.5
S-2	V: 3	1.06	0.51	182.3	0.88	0.45	182.3
S-3	Mn: 1	1.02	0.49	189.7	0.83	0.47	189.7
S-4	Co: 8	1.16	0.56	202.5	0.99	0.48	202.7
S-5	Ni: 2	1.06	0.49	187.6	0.90	0.47	187.6
S-6	Cu: 2	1.04	0.50	187.9	0.86	0.43	188.0
S-7	Zr: 1	1.08	0.50	188.0	0.92	0.42	188.1
S-8	Nb: 1	1.03	0.49	191.2	0.84	0.41	191.3
S-9	Mo: 2	1.07	0.51	190.9	0.89	0.45	191.0
S-10	Hf: 1	1.05	0.50	189.1	0.85	0.43	189.4
S-11	Ta: 3	1.12	0.55	183.4	0.97	0.49	183.4
S-12	W: 2	1.17	0.53	188.7	1.01	0.46	188.8

(continued)

Table 5: Influence of addition of third component on physical properties of Fe-1.5% by mass Si alloy

test No.	amount of third component to be added (% by mass)	cold-rolled material (working rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
S-13	B: 0.05	1.04	0.51	184.8	0.82	0.43	185.1
S-14	C: 0.05	0.98	0.54	192.1	0.79	0.47	192.3
S-15	P: 0.05	1.01	0.51	186.1	0.81	0.42	186.2
S-16	S: 0.05	1.10	0.52	185.0	0.93	0.43	185.3
S-17	V: 2 Nb: 1	1.12	0.53	174.6	0.95	0.41	174.7
S-18	Ni: 2 Mo: 1 B: 0.05	1.15	0.55	172.1	0.94	0.44	172.2

[0037]

[Table 6]

Table 6: Influence of addition of third component on physical properties of Fe-18% by mass Cr alloy

test No.	amount of third component to be added (% by mass)	cold-rolled material (working rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
C-1	Ti: 2	0.83	0.59	156.2	0.71	0.53	156.5
C-2	V: 3	0.88	0.62	153.8	0.75	0.52	153.9
C-3	Mn: 1	0.80	0.59	160.5	0.69	0.57	160.7
C-4	Co: 8	0.91	0.63	174.3	0.77	0.56	174.6
C-5	Ni: 2	0.79	0.58	156.9	0.68	0.55	157.1
C-6	Cu: 2	0.81	0.59	155.4	0.70	0.52	155.6
C-7	Zr: 1	0.82	0.58	157.4	0.72	0.50	157.5
C-8	Nb: 1	0.85	0.59	162.1	0.74	0.51	162.2
C-9	Mo: 2	0.95	0.61	160.0	0.83	0.54	160.1
C-10	Hf: 1	0.83	0.59	159.2	0.73	0.53	159.2
C-11	Ta: 3	0.99	0.64	155.8	0.85	0.57	156.0
C-12	W: 2	1.02	0.63	161.3	0.88	0.56	161.4
C-13	B: 0.05	0.82	0.60	152.4	0.71	0.52	152.5
C-14	C: 0.05	0.81	0.64	165.6	0.67	0.58	165.7
C-15	P: 0.05	0.86	0.61	153.2	0.75	0.54	153.4
C-16	S: 0.05	0.79	0.59	152.9	0.69	0.50	152.9

(continued)

Table 6: Influence of addition of third component on physical properties of Fe-18% by mass Cr alloy

test No.	amount of third component to be added (% by mass)	cold-rolled material (working rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
C-17	V: 2 Nb: 1	0.87	0.62	144.1	0.74	0.52	144.3
C-18	Ni: 2 Mo: 1 B: 0.05	0.92	0.64	141.7	0.80	0.53	141.8

[0038]

[Table 7]

Table 7: Influence of addition of third component on physical properties of Fe-45% by mass Ni alloy

test No.	amount of third component to be added (% by mass)	cold-rolled material (workinq rate: 40%)			aging-treated material (500°C times 2 hours)		
		area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
N-1	Ti: 2	2.05	0.65	158.9	1.70	0.67	158.9
N-2	V: 3	2.13	0.67	156.2	1.72	0.68	156.3
N-3	Mn: 1	1.99	0.64	163.6	1.63	0.67	163.7
N-4	Co: 8	2.25	0.68	175.1	1.81	0.70	175.1
N-5	Cu: 2	1.95	0.63	159.9	1.64	0.64	156.2
N-6	Zr: 1	2.01	0.65	165.7	1.74	0.66	166.0
N-7	Nb: 1	2.09	0.66	163.2	1.79	0.68	163.4
N-8	Mo: 2	2.00	0.64	162.8	1.67	0.65	162.9
N-9	Hf: 1	1.98	0.69	157.4	1.63	0.71	157.5
N-10	Ta: 3	2.04	0.65	166.0	1.70	0.66	166.2
N-11	W: 2	2.02	0.64	159.7	1.72	0.64	159.0
N-12	B: 0.05	1.97	0.63	158.6	1.67	0.64	158.7
N-13	C: 0.05	1.95	0.68	168.4	1.66	0.70	168.5
N-14	P: 0.05	1.99	0.64	160.1	1.71	0.65	160.4
N-15	S: 0.05	1.96	0.66	147.3	1.65	0.67	147.4
N-16	V: 2 Nb: 1	2.11	0.65	168.9	1.84	0.65	169.1
N-17	Mn: 2 Mo: 1 B: 0.05	2.12	0.65	140.0	1.80	0.66	140.9

Example 4

[0039] The alloy A2 of Table 1, which was selected, was cast, hot-rolled, cold-rolled to a plate thickness: 0.5 mm, further solution-treated at 1000°C for 60 minutes, and finally cold-rolled at a depressing rate: 20%.
For the obtained Fe-based alloy, the area ratio of the twin crystal interface, the elastic deformation amount and the magnetization intensity were determined at each of temperatures of -50°C, 25°C, 100°C and 200°C. The elastic deformation amount was made to be a shape strain amount restored by applying a strain amount of 1% in a tensile test at each of the temperatures and unloading the amount. The area ratio of the twin crystal interface and the magnetization intensity were determined in the same manner as in Example 1 at each of the temperatures.

[0040] As shown in the search results of Table 8, the area ratio of the twin crystal interface and the elastic deformation amount showed large values as before even at 200°C without heavily depending on the change of a test temperature. The deformation stress of a shape-memory alloy is greatly changed to the temperature. For example, the temperature dependence of the apparent yield stress of a Ti-Ni shape-memory alloy is about 5 MPa/°C. However, as shown in a stress-strain diagrammatic view (Fig. 4), the change of stress of the Fe alloy of the present invention to the temperature is small. The change of the present invention, which is about 0.5 MPa/°C, is about 1/10 of that of the Ti-Ni alloy. Therefore, the Fe alloy of the present invention is also suitable for the use in a wide temperature range from room temperature or less to high temperature. Since the Fe alloy has a sufficiently high Curie temperature, the Fe alloy exhibited a high magnetization intensity even at 200°C.

[0041]

[Table 8]

Table 8: Influence of test temperature on physical properties

test No.	test temperature (°C)	area ratio of twin crystal interface	elastic deformation amount (%)	magnetization intensity (emu/g)
1	-50	0.80	0.59	188.3
2	25	0.79	0.58	187.2
3	100	0.76	0.57	185.4
4	200	0.75	0.57	182.9

Example 5

[0042] The alloys A2 and S3 of Table 1 and an alloy O1 (Fe) as Comparative Example were selected, cast, hot-rolled and cold-rolled to a plate thickness: 0.83 mm. Furthermore, they were solution-treated at 1000°C for 60 minutes, and finally cold-rolled at a depressing rate: 40%.
A magnetic field gradient was applied to the obtained Fe-based alloy in an electromagnetic coil to apply an initial displacement of 2.8 mm. Then, the elastic deformation amount and restoration rate of the Fe-based alloy when the magnetic field was removed were determined. Herein, the restoration rate (%) is defined by the formula: (elastic deformation amount/initial displacement) times 100.

[0043] As shown in the search results of Table 9, in the alloys A2 and S3, a strain did not remain after the removal of the magnetic field gradient, and the perfect restoration rate was obtained. The same result was also obtained even in the other alloys of the present invention such as the Fe-Al-based, Fe-Si-based, Fe-Cr-based and Fe-Ni-based alloys. The magnitude of the restoration rate depended on the elastic deformation amount in the bending test greatly. In Comparative Example O1 having a small elastic deformation amount, the given initial displacement was not completely restored to reduce the restoration rate.

[0044]

[Table9]

Table 9: Elastic deformation amount produced in accordance with application and removal of magnetic field gradient, and restoration rate

alloy No.	elastic deformation amount (mm)	restoration rate (%)
A2	2.8	100
S3	2.8	100
O1	2.4	84

Industrial Applicability

[0045] As described above, a proper amount of Al, Si, Cr and Ni or the like is added into Fe, and the obtained Fe-based alloy is rolled. Thereby, the large reversible strain is obtained by the application and removal of the magnetic field gradient to obtain the ferromagnetic Fe-based alloy displacably controlled. By using this property, functional materials useful as the magnetic drive actuator and a sensor or the like are provided.

Brief Description of the drawings

[0046]

Fig. 1 is a magnetization intensity-elastic deformation amount view of alloys of the present invention in 0.5 T;
Fig. 2 is a microphotograph of an Fe-5% by mass Al alloy having a metal structure having dispersed deformed twin crystals;
Fig. 3 is a stress-strain diagrammatic view of an Fe-5% by mass Al alloy; and
Fig. 4 is a stress-strain diagrammatic view according to a test temperature of an Fe-7% by mass Al alloy.

Claims

1. An Fe-based alloy displaced in accordance with application and removal of a magnetic field gradient, the Fe-based alloy comprising one or two or more types selected from Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass and Cr: 0.01 to 26% by mass, the balance including Fe and unavoidable impurities, an area ratio of a twin crystal interface to a crystal grain boundary being 0.2 or more.

2. The Fe-based alloy according to claim 1, further comprising one or two or more types selected from Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Mn: 0.01 to 5% by mass, Co: 0.01 to 30% by mass, Ni: 0.01 to 10% by mass, Cu: 0.01 to 5% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass, W: 0.01 to 5% by mass, B: 0.001 to 1% by mass, C: 0.001 to 1% by mass, P: 0.001 to 1% by mass and S: 0.001 to 1% by mass.

3. An Fe-based alloy displaced in accordance with application and removal of a magnetic field gradient, the Fe-based alloy comprising one or two or more types selected from Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass, Cr: 0.01 to 26% by mass and Ni: 35 to 50% by mass, the balance including Fe and unavoidable impurities, an area ratio of a twin crystal interface to a crystal grain boundary being 0.2 or more.

4. The Fe-based alloy according to claim 3, further comprising one or two or more types selected from Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Mn: 0.01 to 5% by mass, Co: 0.01 to 30% by mass, Cu: 0.01 to 5% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass, W: 0.01 to 5% by mass, B: 0.001 to 1% by mass, C: 0.001 to 1% by mass, P: 0.001 to 1% by mass and S: 0.001 to 1% by mass.

5. The Fe-based alloy according to any one of claims 1 to 4, wherein the area ratio of the twin crystal interface to the crystal grain boundary being 3.0 or less.

6. The Fe-based alloy according to claim 5, wherein the Fe-based alloy has a magnetization intensity of 100 emu/g or more in 0.5 tesla (T).

7. A method for producing an Fe-based alloy displacably controlled in accordance with application and removal of a magnetic field gradient, the method comprising:

   solution-treating the Fe-based alloy at a temperature range of 600 to 1350°C for 0.1 to 6 hours, the Fe-based alloy comprising one or two or more types selected from Al: 0.01 to 11% by mass, Si: 0.01 to 7% by mass and Cr: 0.01 to 26% by mass, the balance including Fe and unavoidable impurities, an area ratio of a twin crystal interface to a crystal grain boundary being 0.2 or more; and
   working the Fe-based alloy at a working rate: 10% or more.

8. The method for producing the Fe-based alloy according to claim 7, wherein the Fe-based alloy further comprises

one or two or more types selected from Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Mn: 0.01 to 5% by mass, Co: 0.01 to 30% by mass, Ni: 0.01 to 10% by mass, Cu: 0.01 to 5% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass, W: 0.01 to 5% by mass, B: 0.001 to 1% by mass, C: 0.001 to 1% by mass, P: 0.001 to 1% by mass and S: 0.001 to 1% by mass.

9. A method for producing an Fe-based alloy displacably controlled in accordance with application and removal of a magnetic field gradient, the method comprising:

solution-treating the Fe-based alloy at a temperature range of 600 to 1350°C for 0.1 to 6 hours, the Fe-based alloy comprising one or two or more types selected from A1: 0.01 to 11% by mass, Si: 0.01 to 7% by mass, Cr: 0.01 to 26% by mass and Ni : 35 to 50% by mass, the balance including Fe and unavoidable impurities, an area ratio of a twin crystal interface to a crystal grain boundary being 0.2 or more; and
working the Fe-based alloy at a working rate: 10% or more.

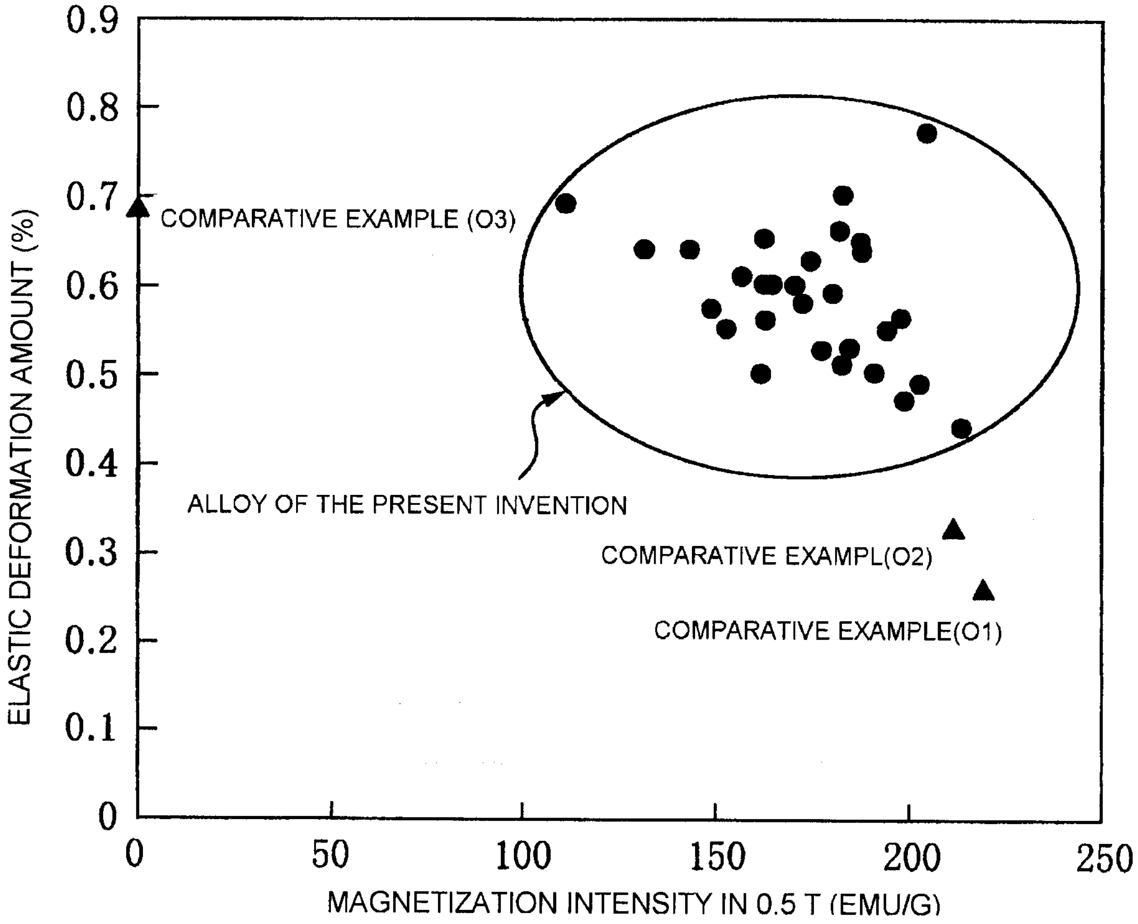
10. The method for producing the Fe-based alloy according to claim 9, wherein the Fe-based alloy further comprises one or two or more types selected from Ti: 0.01 to 5% by mass, V: 0.01 to 10% by mass, Mn: 0.01 to 5% by mass, Co: 0.01 to 30% by mass, Cu: 0.01 to 5% by mass, Zr: 0.01 to 5% by mass, Nb: 0.01 to 5% by mass, Mo: 0.01 to 5% by mass, Hf: 0.01 to 5% by mass, Ta: 0.01 to 5% by mass, W: 0. 01 to 5% by mass, B: 0.001 to 1% by mass, C: 0.001 to 1% by mass, P: 0.001 to 1% by mass and S: 0.001 to 1% by mass.

11. The method for producing the Fe-based alloy according to any one of claims 7 to 10, wherein the Fe-based alloy is worked at 700°C or less.

12. The method for producing the Fe-based alloy according to any one of claims 7 to 11, wherein the Fe-based alloy is worked at a working rate of 95% or less.

13. The method for producing the Fe-based alloy according to any one of claims 7 to 12, wherein the Fe-based alloy is aging-treated at a temperature range of 200 to 800°C for 0.1 to 24 hours after the Fe-based alloy is worked.

14. The method for producing the Fe-based alloy according to any one of claims 7 to 13, wherein the area ratio of the twin crystal interface to the crystal grain boundary is made to be 0.2 or more and 3.0 or less.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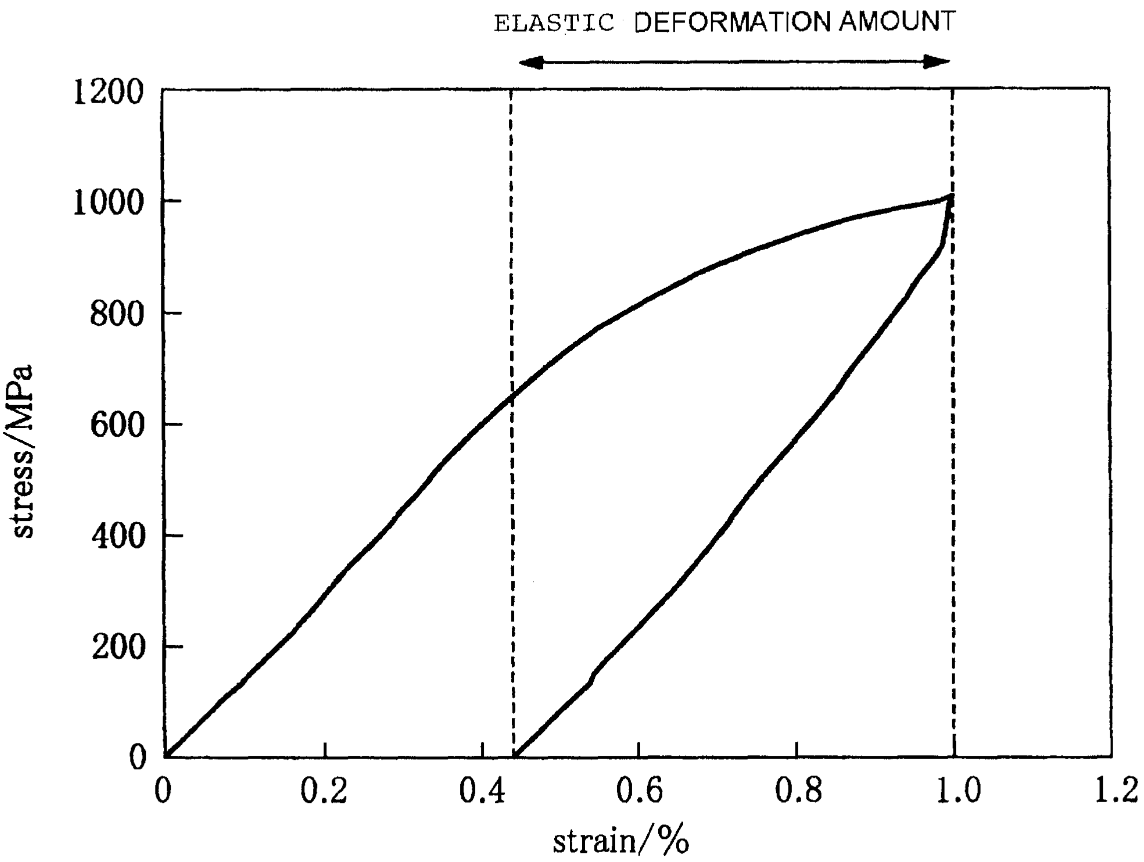
0.8
0.7
0.6
0.5
0.4
0.3
0.2
0.1
0
ELASTIC DEFORMATION AMOUNT (%)
0
50
100
150
200
250
MAGNETIZATION INTENSITY IN 0.5 T (EMU/G)
COMPARATIVE EXAMPLE (O3)
ALLOY OF THE PRESENT INVENTION
COMPARATIVE EXAMPL(O2)
COMPARATIVE EXAMPLE(O1)

FIGURE 1

FIGURE 2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1000
800
600
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0.4
0.6
0.8
1.0
1.2
strain/%

FIGURE 3

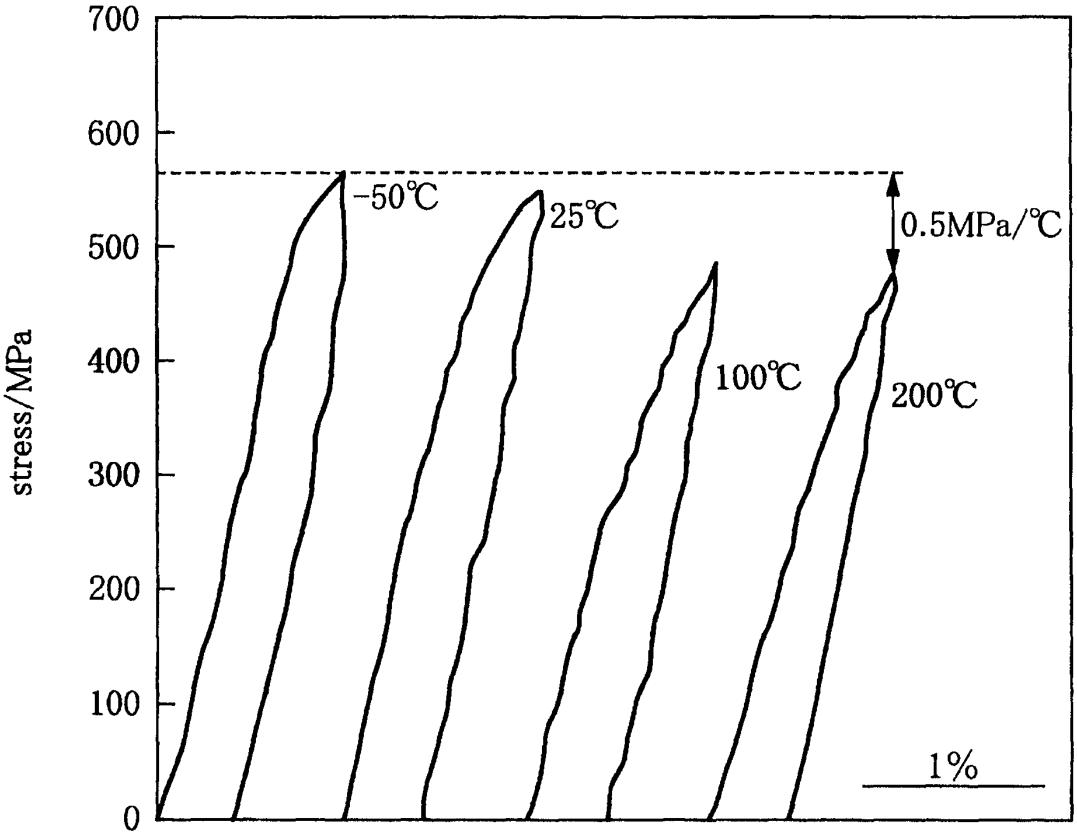

FIGURE 4

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/066284

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D8/12*(2006.01)i, *C22C19/03*(2006.01)i, *H01F1/147*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-38/60, C21D8/12, C22C19/03, H01F1/147

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)
JSTPlus(JDream2)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y	JP 56-31348 B2 (The Research Institute for Electric and Magnetic Materials), 21 July, 1981 (21.07.81), Claims 4, 5 & DE 2630141 A & GB 1558621 A & US 4244754 A	1-14 1-14
Y	JP 4-63243 A (Mitsui Engineering & Shipbuilding Co., Ltd., Satoshi WATANABE), 28 February, 1992 (28.02.92), Field of industrial application (Family: none)	1-14

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

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Date of the actual completion of the international search 13 November, 2007 (13.11.07)	Date of mailing of the international search report 20 November, 2007 (20.11.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2007)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/066284

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 4-63245 A (Mitsui Engineering & Shipbuilding Co., Ltd., Satoshi WATANABE), 28 February, 1992 (28.02.92), Field of industrial application (Family: none)	1-14
A	JP 2004-52109 A (Kiyohito ISHIDA, National Institute of Advanced Industrial Science and Technology), 19 February, 2004 (19.02.04), (Family: none)	1-14
A	JP 11-269611 A (Yasufumi FURUYA, Tadao WATANABE, Kanto Tokushu Seiko Kabushiki Kaisha), 05 October, 1999 (05.10.99), & WO 99/49092 A1 & EP 1069200 A	1-14
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- JP 2002249836 A **[0005]**
- US 5958154 A **[0005]**