A novel iron-base soft magnetic alloy having excellent soft magnetism, particularly a low coercive force and a high permeability in a high-frequency range, and low iron loss. This alloy is produced by adding a given amount of aluminum and preferably further given amounts of elements such as niobium to an Fe-Si-B alloy to give an amorphous alloy, forming the alloy into thin belt, powder, thin film; etc., and heat treating the resulting alloy, thus giving an alloy composed of at least 30% of a crystalline portion and the balance of an amorphous portion.
### Title: IRON-BASE SOFT MAGNETIC ALLOY

#### Abstract

A novel iron-base soft magnetic alloy having excellent soft magnetism, particularly a low coercive force and a high permeability in a high-frequency range, and low iron loss. This alloy is produced by adding a given amount of aluminum and preferably further given amounts of elements such as niobium to an Fe-Si-B alloy to give an amorphous alloy, forming the alloy into thin belt, powder, thin film, etc., and heat treating the resulting alloy, thus giving an alloy composed of at least 30% of a crystalline portion and the balance of an amorphous portion.
Fe-base soft magnetic alloy

Technical Field

The present invention relates to an Fe-base soft magnetic alloy and, in particular, to an alloy having excellent soft magnetic properties.

Background of the Invention

Fe-base amorphous magnetic alloys having a high saturation magnetic flux density are known to be used as magnetic core materials for 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 high saturation magnetostriction and core loss and a low permeability.

A method of producing an Fe-base amorphous alloy has been reported recently in which a thin Fe-base amorphous ribbon formed by rapidly quenching an alloy composition melt is heat-treated to generate fine crystalline particles having a particle size of about 100 Å or so. The Fe-base amorphous alloy thus produced exhibits better soft magnetic properties than any other conventional Fe-base amorphous alloys (Japanese Patent Application Laid-Open No. 64-79342, Japanese Patent Application Laid-Open No. Hei1-156452, U.S.P. 4,881,989). The reported Fe-base amorphous alloy has a basic composition of FeSiB and additionally contains high melting point metals such as Cu, Nb,
etc., in which the alloy structure has been finely crystallized to obtain fine crystalline particles having a particle size of about 100 Å or so. Accordingly, the Fe-base amorphous alloy has become possible to have a lowered saturation magnetostriction, though conventional Fe-base amorphous alloys were difficult to have it. As a result, the reported Fe-base amorphous alloy is said to have improved soft magnetic properties, especially improved frequency characteristics of magnetic permeability.

However, when Cu is added to the alloy, Cu tends to gather by itself to cause heterogeneity of the alloy. Thereby, there can be such drawback as difficulty of forming a thin film by a single roll method or sticking of Cu to the nozzle which brings on a change in the composition of the alloy.

On the other hand, regarding Cu-free fine crystalline soft magnetic alloys, Fe-Ta-C alloys have been reported (Hasegawa, et al., Journal of Applied Magnetics, Society of Japan, 14, 313, 1990). However, these alloys could not be said sufficient in view of the practicability (economical efficiency) thereof.

One object of the present invention is to provide a novel Fe-base soft magnetic alloy, which is a soft magnetic material substitutable for the above-mentioned conventional soft magnetic materials and which has an extremely low saturation magnetostriction with having excellent high frequency magnetic properties, in particular, having a high permeability and a low iron loss in a high frequency region.

Another object of the present invention is to provide a Fe-base soft magnetic alloy which is a metal-metalloid alloy
having a relatively low melting point and which can be produced by the use of any conventional device for producing ordinary magnetic materials.

Disclosure 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 Al to an Fe-base Fe-Si-B 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 other particular metal(s), especially Nb, to such an Fe-base Fe-Si-B-Al soft magnetic alloy is effective for obtaining excellent soft magnetic properties of the resulting alloy. The present invention is based on these findings.

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

\[(\text{Fe}_{1-xM_x})_{100-a-b-c-d}\text{Si}_{a}\text{Al}_{b}\text{B}_{c}\text{M'}_{d}\]

where M is Co and/or Ni;
M' is at least one element selected from the group consisting of Nb, Mo, Zr, W, Ta, Hf, Ti, V, Cr, Mn, Y, Pd, Ru, Ga, Ge, C and P;
x is an atomic ratio;
a, b, c and d each are an atomic %; and
x, a, b, c and d each satisfy \(0 \leq x \leq 0.15\), \(0 \leq a \leq 24\), \(2 < b \leq 15\), \(4 \leq c \leq 20\), and \(0 \leq d \leq 10\). In particular, at least 30 % of the alloy structure is desired to be occupied by a crystalline phase (fine crystalline particles), and the crystalline phase is
desired to be composed of an iron solid solution having a bcc structure. M' is preferably Nb.

Brief Description of the Drawings

Fig. 1 is a graph showing a relationship between the crystallization temperature of an Fe-base soft magnetic alloy and the Al content therein.

Fig. 2 is a graph showing a relationship between the coercive force (Hc) of an Fe-base soft magnetic alloy and the composition thereof.

Fig. 3 is a graph showing a relationship between the saturation magnetization (Ms) of an Fe-base soft magnetic alloy and the composition thereof.

Fig. 4 is a graph showing X-ray diffraction patterns of the Fe-base soft magnetic amorphous alloy, and the crystalline alloy of the present invention.

Fig. 5 is a graph showing the temperature dependence of the magnetic flux density and the coercive force of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 6 is a graph showing the temperature dependence of the effective magnetic permeability of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 7 is a graph showing the temperature dependence of the iron loss of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 8 is a graph showing the temperature dependence of the crystal particle size and the lattice constant of a bcc
crystal of an Fe-base soft magnetic alloy of the present invention.

Fig. 9 is a graph showing the temperature dependence of the saturation magnetostriction of an Fe-base soft magnetic alloy of the present invention.

Fig. 10 is a graph showing the frequency characteristic of the effective magnetic permeability of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 11 is a graph showing the frequency characteristic of the iron loss of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 12 is a graph showing the magnetic flux density dependence of the iron loss of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 13 is a graph showing the frequency characteristic of the effective magnetic permeability of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 14 is a graph showing the frequency characteristic of the iron loss of a magnetic core of an Fe-base soft magnetic alloy of the present invention.

Fig. 15 is a graph showing B-H loop of an Fe-base soft magnetic alloy of the present invention before heat-treatment.

Fig. 16 is a graph showing B-H loop of an Fe-base soft magnetic alloy of the present invention after heat-treatment.

Fig. 17 is a graph showing X-ray diffraction patterns of the Fe-base soft magnetic amorphous alloy, and the crystalline alloy of the present invention.
Description of Preferred Embodiments of the Invention

The Fe-base soft magnetic alloys of the present invention contain less than 0.5, preferably less than 0.1 atomic % copper (Cu) and more preferably are entirely free of copper in view of magnetic properties.

In the Fe-base soft magnetic alloy of the present invention, Fe may be substituted by Co and/or Ni in the range of up to 0.15 for the value x. Since Co and Ni have a negative interaction parameter relative to Fe, it is believed that they are substituted for Fe in the bcc structure lattice by dissolving in the Fe-major bcc solid solution formed during the heat treatment of the alloy of the present invention. Accordingly, it is believed that a magnetostriction constant and a magnetocrystalline anisotropy constant of the bcc solid solution would be reduced. Since the alloy of the present invention where the Ni (and/or Co) content (x) is 0 ≤ x ≤ 0.02, particularly x = 0, i.e. including no Ni nor Co, has a high permeability, it is preferably applied to such a use that requires a high permeability, as (material for magnetic core of) a common mode choke coil, an inductor for filters, transformers for signals and so on.

On the other hand, in case that the Ni (and/or Co) content (x) is 0.02 ≤ x ≤ 0.15, such effect is obtained that the magnetostriction constant and a magnetocrystalline anisotropy constant of the alloy are reduced as noted previously, accompanied with the effect that the alloy has a high permeability. Further, a magnetocrystalline anisotropy is
sufficiently induced in the alloy by heat treatment in a magnetic field. Accordingly, the alloy is preferably applied to such a use as (material for magnetic core of) common-mode choke coil, an inductance coil for filters, transformers for signals, a high frequency transformer, a magnetic amplifier and so on. In this case, the Ni (and/or Co) content (x) is preferably 0.02 ≤ x ≤ 0.15, and more preferably 0.03 ≤ x ≤ 0.1.

Al is an essential element of constituting the alloy of the present invention, and addition of a determined amount (more than 2 and not more than 15 atomic %) of Al to the alloy causes enlargement of the temperature difference (∆T) between the crystallization temperature (TX₁) of the soft magnetic crystals having a small magnetocrystalline anisotropy (Fe-base bcc solid solution) and the crystallization temperature (TX₂) of the crystals of interfering with the soft magnetic property (for example, Fe-B crystals) to thereby inhibit formation of Fe-B crystals in heat-treatment of the alloy composition and lead the resulting alloy to having sufficient soft magnetic properties by heat-treatment at a relatively low temperature. Fig. 1 shows the relationship between the crystallization temperature of an Fe-base soft magnetic alloy to which Al is added and the Al content atomic % in the alloy. From Fig. 1, it is noted that increase of the Al content in the alloy causes simple decrease of TX₁ while TX₂ is relatively unchanged irrespective of the variation of the Al content, so that the increase of the Al content in the alloy thereby causes increase of the temperature difference (∆T) between TX₁ and TX₂.

In the present invention, the Al content (b) in the alloy
is more than 2 atomic % and not more than 15 atomic %, preferably from 2.5 atomic % to 15 atomic % and more preferably from 3 to 12 atomic %. Determination of the Al content in the range 3 to 12 atomic % causes a high permeability and a low core loss. In case that the Ni/Co content \( (x) \) is \( 0 \leq x < 0.02 \), especially \( x = 0 \), the Al content \( (b) \) is preferably from 6 to 12 atomic %, more preferably from 6 to 10 atomic %, and most preferably from 7 to 10 atomic %.

Since Al, similar to Ni (Co), has a negative interaction parameter relative to Fe, it is believed that addition of Al results in its dissolution in the Fe-major solid solution, that is, dissolution in the way to be substituted for the Fe atom in the \( \alpha \)-Fe crystal structure and stabilization of the bcc crystal. Thereby an environment of easy self-crystallization in the alloy during heat-treatment yields. Accordingly, since crystal grains having a small magnetocrystalline anisotropy are selectively formed in the alloy by addition of Al thereto, as mentioned above, it is believed that the alloy would have an excellent soft magnetic properties because of such morphology.

Si and B are elements which make the Fe-base soft magnetic alloy of the present invention amorphous in the initial stage (before heat-treatment). The Si content in the alloy of the present invention is from 0 to 24 atomic %, preferably from 6 to 18 atomic %, and more preferably from 10 to 16 atomic %. Determination of the Si content in the said range preferably causes improvement of the ability of formation of amorphous in the initial stage (before the heat-treatment).

The B content \( (c) \) in the alloy of the present invention
is from 4 to 20 atomic %, preferably from 6 to 15 atomic %, and more preferably from 10 to 14 atomic %. Within the determined range of B, a sufficient temperature difference between the crystallization temperatures (TX₁ and TX₂) can be obtained and the alloy may be made amorphous with ease. The ability of formation of amorphous changes according to whether the content of B is more or less than 9 atomic %. In the range of the content of B being 9.5-15 atomic %, particularly 10-14 atomic %, the amorphous alloy including Al is provided an excellent ability of amorphous formation and uniformalized crystal grains are obtained after heat treatment.

The basic composition of the Fe-base soft magnetic alloy of the present invention is composed of the above-mentioned Fe (M), B, Si and Al. In order to improve the corrosion-resistance and the magnetic properties of the alloy of the present invention, other element(s) M' may be added to the alloy. As M' is mentioned at least one, i.e. one or more of the elements selected from the group consisting of Nb, Mo, Zr, W, Ta, Hf, Ti, V, Cr, Mn, Y, Pd, Ru, Ga, Ge, C and P. Addition of the M' elements is effective for improving the ability of the base composition of Fe-Si-Al-B alloy of forming the amorphous phase of the alloy.

The Nb, W, Ta, Zr, Hf, Ti and Mo elements are particularly effective to prevent crystallization of the Fe-B crystalline which hampers the soft magnetic properties of the alloy or to elevate it's crystallization temperature, whereby it improves the soft magnetic properties of the alloy. Further, addition of these elements to the alloy makes the crystal grain
fine. The V, Cr, Mn, Y and Ru elements are particularly effective in improving the anti-corrosion properties of the alloy. The C, Ge, P and Ga elements are particularly effective in the process of forming the amorphous alloy. One more of the foregoing elements can be added. As these elements M', preferred are Nb, Ta, W, Mn, Mo and V. Above all, Nb is most preferred. Addition of Nb results in an extreme improvement of the soft magnetic properties, especially the coercive force, permeability and core loss of the alloy. The content of the M' element(s) is from 1 to 10 atomic %, preferably from 1 to 8 atomic %, more preferably from 1 to 6 atomic %. Addition of the M' element(s) to the alloy of the present invention in such an amount as falling within the determined range forms in the alloy compound(s) of the added element(s) which may retard deterioration of the amorphous phase-forming ability and the magnetic properties of the alloy.

Incidentally, alloy further containing inevitable impurities such as N, S, O etc., is also comprised in the alloy composition of the present invention.

The Fe-base soft magnetic alloy according to the present invention has an alloy structure, at least 30 % of which consists of crystal (fine crystalline particles), with the balance of the structure being an amorphous phase. 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 60 %, more preferably 80 % or more of the alloy structure consists of the fine crystalline
particles in view of magnetic properties.

The crystalline particles of the alloy of the present invention has a bcc structure, where Fe as a main component and Si, B, Al (occasionally Ni and/or Co) are 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, 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 of the like. Briefly, on the basis of the standard value of the X-ray diffraction intensity of 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. Apart from this, it may also be determined from the ratio of the X-ray diffraction intensity of the diffracted X-rays to be proportional to crystallization of the alloy to the X-ray diffraction intensity by the halo effect which is specific to the amorphous phase to be decreased with progress of crystallization of the alloy.

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

In general, the Fe-base soft magnetic alloy of the
present invention may be produced by a rapid melt-quenching method of forming an amorphous metal from a melt of the above-mentioned composition. For instance, an amorphous alloy is first formed in the form of a ribbon, powder or thin film by a single roll method, cavitation method, sputtering method or vapor deposition method, 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.

Generally, a rapid-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 H₂ or in oxidizing gas atmosphere such as air, after fully de-aired into vacuum. 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 400 to 700°C, and more preferably from 520 to 680°C. The heat-treatment time is desired to be from 0.1 to 10 hours, preferably from 1 to 5 hours. The heat-treatment may be effected either in the absence or presence of a magnetic field.

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.
Examples 1-9

A quenched ribbon sample having a width of about 1.0-5 mm and a thickness of about 14-20 μm was formed from a melt containing Fe, Si, Al, B and (Nb) in an argon gas atmosphere of one atmosphere pressure by a single roll method. The sample was then heat-treated for about one hour in the presence of a nitrogen gas and argon gas in the absence of a magnetic field.

Other samples were formed in the same manner as above, except that the composition of Fe, Si, Al, B and Nb was varied as shown in Table 1, and these were heat-treated at an optimum temperature (°C) for about one hour and then cooled in a nitrogen stream. The coercive force Hc (mOe) and the saturation magnetization Ms (emu/g) of the heat-treated samples were measured. In addition, the saturation magnetostriction constant λs (×10⁻⁶) of each sample was measured by a strain gage method. The composition of the alloy was determined by IPC analysis.

The iron loss of each of the thus heat-treated coiled magnetic core samples was determined from an area as surrounded by the alternating current hysteresis loop measured with a digital oscilloscope under the condition of a frequency of 100 kHz and a maximum magnetic flux density of 0.1 T. The permeability (μ) of each of them was determined by measuring the inductance L with an LCR meter under the condition of a frequency of 100 kHz and an exciting magnetic field of 5 mOe. The results obtained are also shown in Table 1 below.

As comparative samples, Fe₇₅Si₁₅B₁₂ (Comparative Example 1, commercial product) and FeCuSiBNb (Comparative Example 2, Cu-containing Fe-base soft magnetic alloy described in Japanese
2074805

Patent Application Laid-Open No. 64-79342) were prepared, and the coercive force, saturation magnetization, iron loss and permeability of these samples were also shown in Table 1 below.

<table>
<thead>
<tr>
<th>Example</th>
<th>Composition</th>
<th>Hc mOe</th>
<th>Ms emu/g</th>
<th>$\lambda s \times 10^{-6}$</th>
<th>Iron Loss W/kg</th>
<th>$\mu$</th>
<th>Particle Size Å</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Fe$<em>{73}$Si$</em>{8}$Al$_{13}$B$_9$</td>
<td>95</td>
<td>165</td>
<td>6.2</td>
<td>100</td>
<td>1000</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>Fe$<em>{71}$Si$</em>{10}$Al$_{13}$B$_9$</td>
<td>85</td>
<td>136</td>
<td>5.6</td>
<td>80</td>
<td>1500</td>
<td>—</td>
</tr>
<tr>
<td>3</td>
<td>Fe$<em>{67}$Si$</em>{12}$Al$_{12}$B$_9$</td>
<td>50</td>
<td>110</td>
<td>3.0</td>
<td>65</td>
<td>2000</td>
<td>—</td>
</tr>
<tr>
<td>4</td>
<td>Fe$<em>{66}$Si$</em>{14}$Al$_{8}$B$_9$</td>
<td>38</td>
<td>110</td>
<td>2.0</td>
<td>40</td>
<td>4000</td>
<td>340</td>
</tr>
<tr>
<td>5</td>
<td>Fe$<em>{68}$Si$</em>{12}$Al$_{8}$B$_9$</td>
<td>75</td>
<td>110</td>
<td>2.2</td>
<td>45</td>
<td>2800</td>
<td>—</td>
</tr>
<tr>
<td>6</td>
<td>Fe$<em>{67}$Si$</em>{12}$Al$_{8}$B$_9$</td>
<td>95</td>
<td>99</td>
<td>1.5</td>
<td>70</td>
<td>1700</td>
<td>—</td>
</tr>
<tr>
<td>7</td>
<td>Fe$<em>{66}$Si$</em>{14}$Al$_{8}$B$_9$Nb$_1$</td>
<td>10</td>
<td>96</td>
<td>1.2</td>
<td>25</td>
<td>5400</td>
<td>300</td>
</tr>
<tr>
<td>8</td>
<td>Fe$<em>{67}$Si$</em>{14}$Al$_{8}$B$_9$Nb$_2$</td>
<td>15</td>
<td>92</td>
<td>1.0</td>
<td>18</td>
<td>7200</td>
<td>—</td>
</tr>
<tr>
<td>9</td>
<td>Fe$<em>{66}$Si$</em>{14}$Al$_{8}$B$_9$Nb$_3$</td>
<td>15</td>
<td>88</td>
<td>0.6</td>
<td>10</td>
<td>20000</td>
<td>140</td>
</tr>
<tr>
<td>Comp. Example 1</td>
<td>Fe$_{78}$Si$<em>9$B$</em>{13}$</td>
<td>50</td>
<td>167</td>
<td>27</td>
<td>40</td>
<td>6000</td>
<td>—</td>
</tr>
<tr>
<td>2</td>
<td>Fe$<em>{73.5}$Si$</em>{13.5}$B$_9$Cu$_3$Nb$_3$</td>
<td>15</td>
<td>140</td>
<td>2.3</td>
<td>15</td>
<td>17000</td>
<td>—</td>
</tr>
</tbody>
</table>

As is obvious from the results in Table 1 above, the sample of Example 7 containing Nb as M' had a much lower coercive force value than the other FeSiB samples. The value of the coercive force of the sample of Example 7 is almost same as that of the sample of Comparative Example 2 (15 mOe). The samples of Examples 3 and 4 had magnetic properties, with the exception of permeability and saturation magnetization, comparable or superior to those of FeSiB amorphous alloys of comparative Examples 1 and
2.

The sample of Example 9 had superior magnetic properties as to permeability, iron loss and magnetostriction than those of Comparative Example 1 and 2.

Fig. 2 is a graph showing the composition dependence of the coercive force Hc of various Fe-Si-Al-B alloy samples, in which the compositions as surrounded by the line gave a good soft magnetic characteristic of having a coercive force of not more than 100 mOe.

Fig. 3 is a graph showing the composition dependence of the saturation magnetization Ms of various Fe-Si-Al-B alloy samples, in which a sample (Fe_{73}Si_{13}Al_{13}B_{9}) having a high saturation magnetization of 165 emu/g was obtained from the composition range having a coercive force Hc of not higher than 100 mOe.

Of these samples, the sample of Example 4 (Fe_{63}Al_{13}Si_{14}B_{9}) and the sample of Example 7 (Fe_{63}Al_{13}Si_{14}B_{9}Nb_{1}) having a smaller coercive force than the conventional FeSiB amorphous alloy sample (Comparative Example 1) were measured with respect to the crystal constant a (Å), the crystal particle size D (Å), the first crystallization temperature TX_{1} (°C) and the second crystallization temperature TX_{2} (°C). The data measured are shown in Table 2 below.
Table 2

<table>
<thead>
<tr>
<th></th>
<th>T_{X1} (°C)</th>
<th>T_{X2} (°C)</th>
<th>D (Å)</th>
<th>a (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Examle 4</td>
<td>475</td>
<td>560</td>
<td>340</td>
<td>2.86</td>
</tr>
<tr>
<td>7</td>
<td>485</td>
<td>610</td>
<td>300</td>
<td>2.85</td>
</tr>
<tr>
<td>Comp. Example 1</td>
<td>493</td>
<td>523</td>
<td>-</td>
<td>-</td>
</tr>
</tbody>
</table>

The Table 2 data show that the ΔT value for the Examples 4 and 7 of the present invention are significantly larger than that of the Comparative Example 2. From the data shown in Table 2 above, it has been confirmed that the alloys of the present invention had crystalline particles of bcc solid solution, having a particle size of approximately 300 Å and consisting mainly of iron, as formed by crystallization to be conducted by heat-treatment.

The first crystallization temperature T_{X1} is a temperature at which the Fe-base soft magnetic alloy samples may be produced by the use of a conventional heat-treatment device. Regarding the relationship between the first crystallization temperature T_{X1} and the second crystallization temperature T_{X2} of these samples, the difference between the two temperatures T_{X1} and T_{X2} was 95°C in the sample of Example 4 and was 125°C in the sample of Example 7, and in the comparative Example 2 was 30°C. From the data, it is understood that formation of crystals interfering with the soft magnetic property of the alloys may well be retarded by selection of the adequate heat-treatment temperature.

The alloy of Example 9 (Fe_{68}Si_{14}Al_{16}Nb_{8}B_{6}), which has
especially excellent characteristics of high permeability, low iron loss and low magnetostriction, was investigated and examined in more detail, and the results of the examination are mentioned below.

Precisely, the alloy was formed into a ribbon sample having a width of 2.8 mm and a thickness of 17 μm by a single roll method. X-ray diffraction image of the ribbon sample was obtained, immediately after quenched or after heat-treated in a nitrogen gas atmosphere at 580°C for one hour. Fig. 4 shows the X-ray diffraction curves obtained, in which (a) indicates the quenched sample and shows a halo pattern which is specific to an amorphous alloy, and (b) indicates the heat-treated sample and shows a diffraction peak of specific bcc crystals. Specifically, the pattern (b) gives a peak indicating regular lattice reflection of DO₃ structure in the low angle region.

The ribbon sample of the alloy of Example 9 (Fe₆₆Si₁₄Al₆Nb₅B₁₀) was formed into a coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 2.8 mm, which was then heat-treated in a nitrogen atmosphere for one hour. The heat-treatment temperature dependence of the magnetic flux density B₁₀ (T) and the coercive force Hc (mOe) of the coiled magnetic core sample under an applied magnetic field of 100 e was examined, which is shown in Fig. 5. As is obvious from Fig. 5, the magnetic flux density B₁₀ is approximately 0.7 T in the heat-treatment temperature range of from 550°C to 670°C. Regarding the coercive force Hc, it has the minimum value of 12 mOe at 580°C and increases with elevation of the heat-treatment temperature.
Fig. 6 and Fig. 7 each show the heat-treatment temperature dependence of the effective magnetic permeability $\mu_e$ of the coiled magnetic core sample at various frequency and that of the iron loss (100 KHz, 0.1T) of the same, respectively. From Fig. 6, it is noted that the effective magnetic permeability $\mu_e$ has the maximum value at 580°C in a low frequency region (10 KHz or less) and then gradually decreases with elevation of the heat-treatment temperature in the same region. On the other hand, it is further noted that in a high frequency region (100 KHz or more), the temperature of giving the maximum value of the effective magnetic permeability is shifted to a high temperature side with elevation of the frequency. From Fig. 7, it is noted that the iron loss is satisfactorily low or is almost 10 W/g or so in the heat-treatment temperature range of from 580°C to 670°C.

Regarding the alloy of Example 9 as heat-treated for one hour in a nitrogen gas atmosphere, Fig. 8 shows the heat-treatment temperature dependence of the crystal particle size $D_{110}$ (Å) as derived from the half-value width of the (110) diffraction intensity peak of bcc crystal of the alloy by the use of a Sheller's formula and the heat-treatment temperature dependence of the lattice constant $a$ (Å) as obtained from the (110) diffraction peak of the bcc crystal of the same. As is obvious from Fig. 8, the crystal particle size is always almost 140 Å or so, irrespective of elevation of the heat-treatment temperature. On the other hand, however, it is noted that the lattice constant gradually decreases with elevation of the heat-treatment temperature.
Fig. 9 shows the heat-treatment temperature dependence of the saturation magnetostriction constant $\lambda_s (x 10^{-6})$ of the alloy of Example 9 as heat-treated in a nitrogen gas atmosphere for one hour. As is obvious from Fig. 9, the saturation magnetostriction gradually decreases with elevation of the heat-treatment temperature. In particular, it is noted that the alloy sample shows an almost zero magnetostriction in a heat-treatment temperature range of 600°C or higher.

A coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 2.8 mm was made of the alloy of example 9 of the present invention, which was heat-treated at 580°C or 600°C. Fig. 10 shows the frequency characteristic of the effective magnetic permeability $\mu_e$ of each of the two heat-treated coiled magnetic core samples. It also shows the frequency characteristic of the effective magnetic permeability of alloys of Comparative Example 1 and Comparative Example 2 and a typical Mn-Zn ferrite. From Fig. 10, it is noted that the alloy of the present invention has a larger magnetic permeability value than the conventional amorphous alloy (Comparative Example 1) and Mn-Zn ferrite. In addition, in comparison with the fine crystalline soft magnetic alloy having a good frequency characteristic (Comparative Example 2), it is noted that the alloy of the present invention has a higher effective magnetic permeability in a high frequency region of 100 KHz or more. From the data, it is understood that the alloy of the present invention is a novel fine crystalline soft magnetic alloy having excellent magnetic characteristics in a high frequency region.
Fig. 11 and Fig. 12 each show the frequency dependence (characteristic) and the magnetic flux density dependence, respectively, of the iron loss (W/g) of the Example 9 (580°C) coiled magnetic core sample as above. These also show the frequency dependence and the magnetic flux density dependence, respectively, of the iron loss of alloys of Comparative Example 1 and Comparative Example 2 and a typical Mn-Zn ferrite. Regarding the frequency dependence of the iron loss of each sample which is shown in Fig. 11, it is noted that the alloy of the present invention has a smaller iron loss than conventional amorphous alloy, Mn-Zn ferrite and fine crystalline soft magnetic alloy in a frequency range of from 10 KHz to 700 KHz. Regarding the magnetic flux density dependence of the iron loss of each sample which is shown in Fig. 12, it is noted that the alloy of Example 9 (580°C) has a smaller iron loss than conventional amorphous alloy, Mn-Zn ferrite and fine crystalline soft magnetic alloy in a magnetic flux density range of from 0.1 T to 0.5 T. These results show that the alloy of the present invention has an excellent magnetic properties compared to the conventional alloy.

Examples 10-25

A amorphous ribbon having a width of about 1.3 mm and a thickness of about 18 μm was formed from a melt containing Fe, Si, Al, B and Nb in an argon gas atmosphere of one atmosphere pressure by a single roll method. The ribbon of the alloy was formed into a coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 1.3 mm. After the coiled core was optimum heat-treated in the absence of
a magnetic field, the coercive force $H_c$ (mOe), the saturation magnetostriction constant $\lambda_s$ ($\times 10^{-6}$), the effective permeability ($\mu$) (a frequency of 100 KHz, an exciting magnetic field of 5mOe) and the iron loss (a frequency of 100 KHz, a maximum magnetic flux density of 0.1T) of each core were measured. The composition of the samples and the results obtained are shown in Table 3 below.

<table>
<thead>
<tr>
<th>Example</th>
<th>Coercive Force (mOe)</th>
<th>Saturation Magnetization ($\times 10^{-6}$)</th>
<th>Permeability (100KHz.5mOe)</th>
<th>Iron Loss (W/kg) (100KHz.0.1T)</th>
<th>Particle Size ($\AA$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>46</td>
<td>1.8</td>
<td>4000</td>
<td>52</td>
<td>160</td>
</tr>
<tr>
<td>11</td>
<td>36</td>
<td>1.5</td>
<td>3400</td>
<td>50</td>
<td>155</td>
</tr>
<tr>
<td>12</td>
<td>26</td>
<td>0.6</td>
<td>5600</td>
<td>30</td>
<td>145</td>
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<tr>
<td>13</td>
<td>22</td>
<td>0.5</td>
<td>3100</td>
<td>50</td>
<td>135</td>
</tr>
<tr>
<td>14</td>
<td>46</td>
<td>1.0</td>
<td>5400</td>
<td>30</td>
<td>160</td>
</tr>
<tr>
<td>15</td>
<td>30</td>
<td>1.1</td>
<td>8300</td>
<td>17</td>
<td>150</td>
</tr>
<tr>
<td>16</td>
<td>28</td>
<td>0.5</td>
<td>8600</td>
<td>20</td>
<td>145</td>
</tr>
<tr>
<td>17</td>
<td>16</td>
<td>0.2</td>
<td>8000</td>
<td>22</td>
<td>130</td>
</tr>
<tr>
<td>18</td>
<td>25</td>
<td>0.5</td>
<td>8600</td>
<td>22</td>
<td>160</td>
</tr>
<tr>
<td>19</td>
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<td>20</td>
<td>40</td>
<td>$\sim$0</td>
<td>8000</td>
<td>17</td>
<td>155</td>
</tr>
<tr>
<td>21</td>
<td>28</td>
<td>0.3</td>
<td>4400</td>
<td>28</td>
<td>165</td>
</tr>
<tr>
<td>22</td>
<td>26</td>
<td>0.1</td>
<td>9400</td>
<td>16</td>
<td>150</td>
</tr>
<tr>
<td>23</td>
<td>40</td>
<td>$\sim$0.2</td>
<td>4300</td>
<td>30</td>
<td>155</td>
</tr>
<tr>
<td>24</td>
<td>28</td>
<td>0.4</td>
<td>4400</td>
<td>28</td>
<td>160</td>
</tr>
<tr>
<td>25</td>
<td>42</td>
<td>$\sim$0.8</td>
<td>2200</td>
<td>50</td>
<td>165</td>
</tr>
</tbody>
</table>
Example 10  Fe_{6.9}Si_{12}Al_{7}Nb_{3}B_{9}
Example 11  Fe_{6.9}Si_{12}Al_{8}Nb_{3}B_{9}
Example 12  Fe_{6.7}Si_{12}Al_{9}Nb_{3}B_{9}
Example 13  Fe_{6.6}Si_{12}Al_{10}Nb_{3}B_{9}
Example 14  Fe_{6.6}Si_{12}Al_{1}Nb_{3}B_{9}
Example 15  Fe_{6.5}Si_{12}Al_{1}Nb_{3}B_{9}
Example 16  Fe_{6.4}Si_{12}Al_{3}Nb_{3}B_{9}
Example 17  Fe_{6.3}Si_{12}Al_{10}Nb_{3}B_{9}
Example 18  Fe_{6.6}Si_{12}Al_{1}Nb_{3}B_{9}
Example 19  Fe_{6.4}Si_{12}Al_{10}Nb_{3}B_{9}
Example 20  Fe_{6.2}Si_{12}Al_{10}Nb_{3}B_{9}
Example 21  Fe_{6.1}Si_{12}Al_{10}Nb_{3}B_{9}
Example 22  Fe_{6.0}Si_{12}Al_{10}Nb_{3}B_{9}
Example 23  Fe_{6.4}Si_{12}Al_{10}Nb_{3}B_{9}
Example 24  Fe_{6.4}Si_{12}Al_{10}Nb_{3}B_{9}
Example 25  Fe_{6.4}Si_{12}Al_{10}Nb_{3}B_{9}

As is obvious from the results in Table 3 above, the alloy of the example 10-25 including no Ni shows very low magnetostriction in the range of 7-10 atomic % of the Al content.

Examples 26-39 Comparative Example 3

A amorphous ribbon having a width of about 2.8 mm and a thickness of about 18 μm was formed by the same process of example 10 and the ribbon of the alloy was formed into a coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 2.8 mm. After the coiled core was optimum heat-treated in the absence of a magnetic field, the effective permeability (μ) (a frequency of 100 KHz, an exciting magnetic field of 5mOe) and the iron loss (a frequency of 100 KHz, a maximum magnetic flux density of 0.1T) of each core were measured. The composition of the samples and the results
obtained are shown in Table 4 below.

Table 4

<table>
<thead>
<tr>
<th>Example</th>
<th>Composition (atom%)</th>
<th>Permeability $\mu$ (100KHz, 5mOe)</th>
<th>Iron Loss (W/kg) (100KHz, 0.1T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>26</td>
<td>Fe$<em>{65.8}$Si$</em>{14}$Al$_6$Nb$<em>6$B$</em>{8.5}$</td>
<td>14000</td>
<td>12</td>
</tr>
<tr>
<td>27</td>
<td>Fe$<em>{65}$Si$</em>{14}$Al$_6$Nb$<em>6$B$</em>{8.5}$</td>
<td>19000</td>
<td>9</td>
</tr>
<tr>
<td>28</td>
<td>Fe$<em>{65}$Si$</em>{18}$Al$<em>7$Nb$<em>6$B$</em>{8.5}$B$</em>{10}$</td>
<td>20000</td>
<td>10</td>
</tr>
<tr>
<td>29</td>
<td>Fe$<em>{64}$Si$</em>{14}$Al$_8$Nb$<em>6$B$</em>{10}$</td>
<td>17000</td>
<td>10</td>
</tr>
<tr>
<td>30</td>
<td>Fe$<em>{64}$Si$</em>{18}$Al$_7$Nb$<em>6$B$</em>{11}$</td>
<td>12000</td>
<td>12</td>
</tr>
<tr>
<td>31</td>
<td>Fe$<em>{65}$Si$</em>{14}$Al$_6$Nb$<em>6$B$</em>{9.5}$</td>
<td>16000</td>
<td>14</td>
</tr>
<tr>
<td>32</td>
<td>Fe$<em>{68}$Si$</em>{12}$Al$_6$Nb$<em>6$B$</em>{10}$</td>
<td>7000</td>
<td>22</td>
</tr>
<tr>
<td>33</td>
<td>Fe$<em>{67}$Si$</em>{13}$Al$_6$Nb$<em>6$B$</em>{10}$</td>
<td>12000</td>
<td>16</td>
</tr>
<tr>
<td>34</td>
<td>Fe$<em>{63.7}$Si$</em>{13}$Al$_{12}$Nb$<em>6$B$</em>{3}$</td>
<td>14000</td>
<td>9</td>
</tr>
<tr>
<td>35</td>
<td>Fe$<em>{6}$Si$</em>{13}$Al$_{12}$Nb$<em>6$B$</em>{10}$</td>
<td>10000</td>
<td>16</td>
</tr>
<tr>
<td>36</td>
<td>Fe$<em>{68.8}$Si$</em>{13}$Al$_7$Nb$<em>6$B$</em>{12}$</td>
<td>9000</td>
<td>18</td>
</tr>
<tr>
<td>37</td>
<td>Fe$<em>{68}$Si$</em>{12}$Al$_7$Nb$<em>6$B$</em>{14}$</td>
<td>7800</td>
<td>20</td>
</tr>
<tr>
<td>38</td>
<td>Fe$<em>{6}$Si$</em>{16}$Al$_6$Nb$<em>6$B$</em>{10}$</td>
<td>5000</td>
<td>34</td>
</tr>
<tr>
<td>39</td>
<td>Fe$<em>{6}$Si$</em>{18}$Al$_{10}$Nb$<em>6$B$</em>{10}$</td>
<td>4200</td>
<td>46</td>
</tr>
</tbody>
</table>

As is obvious from the results in Table 4 above, the alloy including more than 9 atomic % of B shows a low iron loss and a high permeability.

Examples 40-59

A amorphous ribbon having a width of about 1.3 mm and a thickness of about 18 $\mu$m was formed from a melt containing Fe, Si, Al, B, and M' in an argon gas atmosphere of one atmosphere pressure by a single roll method. The ribbon of the alloy was
formed into a coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 1.3 mm. After the coiled core was optimum heat-treated in the absence of a magnetic field, the coercive force $H_c$ (mOe), the permeability ($\mu$) (a frequency of 100 KHz, an exciting magnetic field of 5mOe) and the iron loss (a frequency of 100 KHz, a maximum magnetic flux density of 0.1T) of each core were measured. The composition of the samples and the results obtained are shown in Table 5 below.

Table 5

<table>
<thead>
<tr>
<th>Example</th>
<th>Coercive Force (mOe)</th>
<th>Permeability (100KHz, 5mOe)</th>
<th>Iron Loss (W/kg) (100KHz, 0.1T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>26</td>
<td>13800</td>
<td>15</td>
</tr>
<tr>
<td>41</td>
<td>56</td>
<td>13200</td>
<td>12</td>
</tr>
<tr>
<td>42</td>
<td>18</td>
<td>4000</td>
<td>40</td>
</tr>
<tr>
<td>43</td>
<td>22</td>
<td>5000</td>
<td>30</td>
</tr>
<tr>
<td>44</td>
<td>28</td>
<td>6000</td>
<td>24</td>
</tr>
<tr>
<td>45</td>
<td>20</td>
<td>14000</td>
<td>15</td>
</tr>
<tr>
<td>46</td>
<td>50</td>
<td>4200</td>
<td>40</td>
</tr>
<tr>
<td>47</td>
<td>22</td>
<td>11000</td>
<td>18</td>
</tr>
<tr>
<td>48</td>
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<tr>
<td>49</td>
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<td>5000</td>
<td>26</td>
</tr>
<tr>
<td>50</td>
<td>20</td>
<td>12000</td>
<td>18</td>
</tr>
<tr>
<td>51</td>
<td>28</td>
<td>8000</td>
<td>24</td>
</tr>
<tr>
<td>52</td>
<td>28</td>
<td>8200</td>
<td>22</td>
</tr>
<tr>
<td>53</td>
<td>32</td>
<td>11000</td>
<td>18</td>
</tr>
<tr>
<td>54</td>
<td>26</td>
<td>9000</td>
<td>20</td>
</tr>
<tr>
<td>55</td>
<td>26</td>
<td>8000</td>
<td>28</td>
</tr>
<tr>
<td>56</td>
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<td>8000</td>
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</tr>
<tr>
<td>57</td>
<td>28</td>
<td>7000</td>
<td>30</td>
</tr>
<tr>
<td>58</td>
<td>46</td>
<td>6000</td>
<td>26</td>
</tr>
<tr>
<td>59</td>
<td>42</td>
<td>5200</td>
<td>42</td>
</tr>
</tbody>
</table>
Example 40  Fe₆₆Si₁₄Al₈Mo₈B₉
41  Fe₆₆Si₁₄Al₈Ta₈B₉
42  Fe₆₆Si₁₄Al₈Cr₈B₉
43  Fe₆₆Si₁₄Al₈V₈B₉
44  Fe₆₆Si₁₄Al₈Ti₈B₉
45  Fe₆₆Si₁₄Al₈W₃B₉
46  Fe₆₆Si₁₄Al₈Mn₈B₉
47  Fe₆₆Si₁₄Al₈Hf₈B₉
48  Fe₆₆Si₁₄Al₈Zr₈B₉
49  Fe₆₆Si₁₄Al₈Y₈B₉
50  Fe₆₄Si₁₄Al₈Nb₆Mo₂B₁₀
51  Fe₆₂Si₁₃Al₆Nb₃Ta₂B₁₂
52  Fe₆₂Si₁₃Al₆Nb₃Zr₁B₁₂
53  Fe₆₂Si₁₃Al₆Mo₆W₂B₁₀
54  Fe₆₂Si₁₃Al₇Nb₄Pd₃B₁₀
55  Fe₆₂Si₁₃Al₆Nb₄Ru₄B₁₀
56  Fe₆₂Si₁₄Al₄Ga₄Nb₄B₁₀
57  Fe₆₂Si₁₄Al₆Ge₆Nb₄B₁₀
58  Fe₆₂Si₁₄Al₆Zr₆B₉C₄
59  Fe₆₂Si₁₄Al₆Zr₄B₁₀P₃

As is obvious from the results in Table 5 above, both amorphous alloys including an other element than Nb as M'(examples 40-49, 53, 53 and 59) and alloys including the element together with Nb show excellent magnetic characteristics.

Examples 60-66

A amorphous ribbon having a width of about 1.3 mm and a thickness of about 18 μm was formed by the same process of example 10 and the ribbon of the alloy was formed into a coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 1.3 mm. After the coiled core
was optimum heat-treated in the absence of a magnetic field, the effective permeability ($\mu$) (a frequency of 100 KHz, an exciting magnetic field of 5mOe) and the iron loss (a frequency of 100 KHz, a maximum magnetic flux density of 0.1T) of each core were measured. The composition of the samples and the results obtained are shown in Table 6 below.

Table 6

<table>
<thead>
<tr>
<th>Example</th>
<th>Composition (atom%)</th>
<th>Permeability $\mu$ (100KHz)</th>
<th>Iron Loss(W/kg) (100KHz, 0.1T)</th>
</tr>
</thead>
<tbody>
<tr>
<td>60</td>
<td>Fe$_7$Si$_8$Al$_5$Nb$_6$B$_6$</td>
<td>3400</td>
<td>40</td>
</tr>
<tr>
<td>61</td>
<td>Fe$_7$Si$_8$Al$_5$Nb$_6$B$_6$</td>
<td>4600</td>
<td>37</td>
</tr>
<tr>
<td>62</td>
<td>Fe$_7$Si$_8$Al$_5$Nb$_6$B$_6$</td>
<td>2600</td>
<td>46</td>
</tr>
<tr>
<td>63</td>
<td>Fe$_7$Si$_9$Al$_5$Nb$_6$B$_6$</td>
<td>2000</td>
<td>58</td>
</tr>
<tr>
<td>64</td>
<td>Fe$_7$Si$_9$Al$_5$Nb$_4$B$_1$</td>
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<td>32</td>
</tr>
<tr>
<td>65</td>
<td>Fe$_6$Si$_8$Al$_5$Nb$_4$B$_12$</td>
<td>5000</td>
<td>36</td>
</tr>
<tr>
<td>66</td>
<td>Fe$_6$Si$_8$Al$_5$Nb$_6$B$_1$</td>
<td>1000</td>
<td>100</td>
</tr>
</tbody>
</table>

Examples 67-81

A amorphous ribbon having a width of about 2.8 mm and a thickness of about 18 $\mu$m was formed by the same process of example 10 and the ribbon of the alloy was formed into a coiled magnetic core having an inner diameter of 15 mm, an outer diameter of 19 mm and a height of 2.8 mm. After the coiled core was optimum heat-treated in the absence of a magnetic field, the effective permeability ($\mu$) (a frequency of 100 KHz, an exciting magnetic field of 5mOe) and the iron loss (a frequency of 100
2074805

KHz, a maximum magnetic flux density of 0.1T) of each core were measured. The composition of the samples and the results obtained are shown in Table 7 below.

<table>
<thead>
<tr>
<th>Example</th>
<th>Before Heat-treatment</th>
<th>After Heat-treatment</th>
<th>Particle Size</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Permeability (100KHz, 5mOe)</td>
<td>Iron Loss (W/Kg) (100KHz, 0.1T)</td>
<td>Permeability (100KHz, 5mOe)</td>
</tr>
<tr>
<td>67</td>
<td>9000</td>
<td>20</td>
<td>10000</td>
</tr>
<tr>
<td>68</td>
<td>13000</td>
<td>13</td>
<td>14000</td>
</tr>
<tr>
<td>69</td>
<td>13000</td>
<td>12</td>
<td>10000</td>
</tr>
<tr>
<td>70</td>
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<td>12</td>
<td>9000</td>
</tr>
<tr>
<td>71</td>
<td>6000</td>
<td>30</td>
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</tr>
<tr>
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<td>25</td>
<td>9000</td>
</tr>
<tr>
<td>73</td>
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<td>8600</td>
</tr>
<tr>
<td>81</td>
<td>8600</td>
<td>20</td>
<td>8800</td>
</tr>
</tbody>
</table>
Example 67  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
68  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
69  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
70  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
71  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
72  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
73  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
74  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
75  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
76  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
77  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
78  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
79  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
80  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}
81  Fe_{68}Ni_{14}Si_{14}Al_{14}Nb_{13}B_{12}

As is obvious from the results in Table 7 above, the alloy of these examples shows an excellent value of an iron loss as well as a permeability.

Further, the frequency dependence of the effect permeability ($\mu$) and the iron loss of the Example 69 (O) which was heat-treated in the absence of a magnetic field was measured. At the same time, the frequency dependence of the effect permeability ($\mu$) and the iron loss of the Example 69 (●) which was heat-treated in the presence of a magnetic field was measured. The results obtained are shown in Figs. 13 and 14. B-H loops in the exciting magnetic field (Hm) of 100 e, 10 e and 0.10 e are also illustrated in Figs. 15 and 16.
As is obvious from Fig. 13, the alloy of the present invention showed a high permeability in the high frequency range of 100 kHz or more by heat-treating in the presence of a magnetic field. Particularly in the range of 200 kHz or more, the alloy of the present invention showed higher permeability than that (Δ) of the ribbon (a comparative example 2, a width of 5 mm and a thickness of 18 μm) of a soft magnetic alloy having a good frequency characteristic which was heat-treated in the presence of a magnetic field.

As is obvious from Fig. 14, the iron loss of the alloy of the present invention was sharply reduced by heat-treating in the presence of a magnetic field. The value of the iron loss is lower than that (Δ) of the ribbon (a comparative example 2, a width of 5 mm and a thickness of 18 μm) which was heat-treated in the presence of a magnetic field.

Further, as is obvious from comparison of B-H loop of the pre-heat-treated alloy and that of the heat-treated alloy, the alloy of the present invention showed excellent soft magnetic properties by heat-treatment in the presence of a magnetic field. X-ray diffraction image of Example 69 which was heat-treated for one hour in a nitrogen atmosphere is shown in Fig. 17.

Examples 82-86

A amorphous ribbon (Fe-Co-Si-Al-Nb-B) having a width of about 2.8 mm and a thickness of about 18 μm was formed by the same process of example 10 and the ribbon of the alloy was formed into a coiled magnetic core having an inner diameter of 15
mm, an outer diameter of 19 mm and a height of 2.8 mm. After the coiled core was optimum heat-treated in the absence of a magnetic field, further heat-treated in the presence of a magnetic field. The permeability ($\mu$) (a frequency of 100 KHz, an exciting magnetic field of 5mOe) and the iron loss (a frequency of 100 KHz, a maximum magnetic flux density of 0.1T) of both pre-heat-treated core and a heat-treated core in a magnetic field were measured. The composition of the alloy and the results obtained are shown in Table 8 below.

Table 8

<table>
<thead>
<tr>
<th></th>
<th>Before Heat-treatment In the Presence of a Magnetic Field</th>
<th>After Heat-treatment</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron Loss (W/Kg) (100KHz, 0.1T)</td>
<td>Permeability (100KHz, 5mOe)</td>
<td>Iron Loss (W/Kg) (100KHz, 0.1T)</td>
</tr>
<tr>
<td>Example 82</td>
<td>18</td>
<td>11000</td>
</tr>
<tr>
<td>83</td>
<td>16</td>
<td>7100</td>
</tr>
<tr>
<td>84</td>
<td>28</td>
<td>3900</td>
</tr>
<tr>
<td>85</td>
<td>57</td>
<td>2800</td>
</tr>
<tr>
<td>86</td>
<td>30</td>
<td>5100</td>
</tr>
</tbody>
</table>

Example 82 $\text{Fe}_{66}\text{Co}_{1.6}\text{Si}_{1.4}\text{Al}_{6.4}\text{Nb}_{5}\text{B}_9$
83 $\text{Fe}_{66}\text{Co}_{3.2}\text{Si}_{1.4}\text{Al}_{6.4}\text{Nb}_{5}\text{B}_9$
84 $\text{Fe}_{66}\text{Co}_{4}\text{Si}_{1.4}\text{Al}_{4}\text{Nb}_{5}\text{B}_9$
85 $\text{Fe}_{66}\text{Co}_{2.8}\text{Si}_{1.1.2}\text{Al}_{8}\text{Nb}_{5}\text{B}_9$
86 $\text{Fe}_{66}\text{Co}_{6.8}\text{Si}_{5.4}\text{Al}_{8}\text{Nb}_{5}\text{B}_9$

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As is obvious from the results in Table 8 above, the alloy including Co instead of Ni shows as low iron loss as that including Ni, whereas some examples having Co show a lower permeability than the latter.

The content of crystal (fine crystalline particles) is 60% or more in the alloy of the all examples above.

Capability of Exploitation in Industry

As is obvious from the results in the above-mentioned examples, the present invention provides a novel Fe-base soft magnetic alloy as prepared by adding Al to an Fe-Si-B alloy composition, and the alloy has excellent soft magnetic properties. In addition, since the Fe-base soft magnetic alloy of the present invention has a large temperature difference between the crystallization temperature of crystals of showing a good soft magnetic property and the crystallization temperature of crystals of interfering with a soft magnetic property, the range of the temperature of heat treatment is sufficiently wider than that of the conventional amorphous alloys.

The Fe-base soft magnetic alloy of the present invention shows a very low magnetostriction by adding Al thereto and at the same time substituting Ni (Co) for a part of Fe, whereby a magnetic core having a low iron loss can be obtained.

Furthermore, in accordance with the present invention, Nb or the like element may be added to an Fe-Si-Al-B alloy composition to give a novel Fe-base soft magnetic alloy having excellent soft magnetic properties, especially having an extremely low coercive force, low iron loss and low
magnetostriction as well as a high permeability in a high frequency region.

Since the alloy of the present invention possesses excellent properties as above-mentioned, it is useful for such applications as (material for magnetic core of) a high-frequency transformer, a common-mode choke coil, a magnetic amplifier, an inductor for filters, a transformer for signals, a magnetic head and so on.
THE EMBODIMENTS OF THE INVENTION IN WHICH AN EXCLUSIVE PROPERTY OR PRIVILEGE IS CLAIMED ARE DEFINED AS FOLLOWS:

1. An Fe-base soft magnetic alloy having a composition as represented by the general formula:

\[(Fe_{1-x}M_x)_{100-a-b-c-d}Si_{a}Al_{b}B_{c}M'd\]

where:

- M is at least one element selected from the group consisting of Co and Ni;
- M' is at least one element selected from the group consisting of Nb, Mo, Zr, W, Ta, Hf, Ti, V, Cr, Mn, Y, Pd, Ru, Ga, Ge, C and P;
- x is an atomic ratio;
- a, b, c and d each are an atomic %; and
- x, a, b, c and d each satisfy \(0 \leq x \leq 0.15, 0 \leq a \leq 24, 2 < b \leq 15, 4 \leq c \leq 20, \) and \(0 \leq d \leq 10;\)

wherein the alloy has a structure in which at least 60% thereof is a crystalline phase with the balance being an amorphous phase.

2. The Fe-base soft magnetic alloy as claimed in claim 1, in which 80% to substantially 100% of the alloy structure is occupied by the crystalline phase.

3. The Fe-base soft magnetic alloy as claimed in claim 1 or 2, in which the crystalline phase is bcc solid solution consisting mainly of iron.
4. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 3, in which $M'$ is Nb.

5. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 4, in which the content $(x)$ of $M$ is 0.

6. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 4, in which the content $(x)$ of $M$ is $0.02 \leq x \leq 0.15$.

7. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 4, in which the content $(x)$ of $M$ is $0.03 \leq x \leq 0.1$.

8. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 5, in which $M$ is Ni.

9. The Fe-base soft magnetic alloy as claimed in claim 6, in which $M$ is Ni.

10. The Fe-base soft magnetic alloy as claimed in claim 7, in which $M$ is Ni.

11. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 7, in which the content $(b)$ of Al is $2.5 \leq b \leq 15$.

12. The Fe-base soft magnetic alloy as claimed in any
one of claims 1 to 7, in which the content (b) of Al is $3 \leq b \leq 12$.

13. The Fe-base soft magnetic alloy as claimed in claim 8, in which the content (b) of Al is $3 \leq b \leq 10$.

14. The Fe-base soft magnetic alloy as claimed in claim 5, in which the content (b) of Al is $7 \leq b \leq 12$.

15. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 14, in which the content (c) of B is $6 \leq c \leq 15$.

16. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 14, in which the content (c) of B is $9.5 \leq c \leq 15$.

17. The Fe-base soft magnetic alloy as claimed in any one of claims 1 to 14, in which the content (c) of B is $10 \leq c \leq 14$.

18. An Fe-base soft magnetic alloy,

(i) having a composition represented by the formula:

$$(\text{Fe}_{1- \chi} \text{M}_\chi)_{100-a-b-c-d} \text{Si}_{a} \text{Al}_{b} \text{B}_{c} \text{M}^{\prime} d$$

(wherein $\text{M}$ is at least one element selected from the group consisting of Co and Ni;

$\text{M}^{\prime}$ is at least one element selected from the group consisting of Nb, Mo, Zr, W, Ta, Hf, Ti, V, Cr, Mn, Y, Pd,
Ru, Ga, Ge, C and P;

- \( x \) is an atomic ratio satisfying \( 0 \leq x \leq 0.15 \); and
- \( a, b, c \) and \( d \) are each an atomic % satisfying

\[
0 \leq a \leq 24, \quad 2 < b \leq 15, \quad 4 \leq c \leq 20, \quad \text{and} \quad 0 \leq d \leq 10
\]

and,

(ii) consisting of 30 to 100% of a crystalline phase

mode of fine crystalline particles having a bcc structure containing Fe as a main component and Si, B, Al and where

present Ni and Co dissolved therein, the particles having a

particle size of 50 to 1,000 Å and 70 to 0% of an amorphous

phase.

19. A process for producing the alloy as defined in

claim 18, which comprises:

- forming an amorphous metal alloy by a rapid metal-

  quenching method from a melt having the composition as

defined in claim 18, wherein the amorphous metal alloy is in

the form of a ribbon, powder or thin film, and

- heat-treating the thus-formed amorphous metal alloy at a

temperature of 200 to 800°C in vacuum or in an inert gas

atmosphere to such an extent that 30 to 100% of the alloy is

crystallized.

20. The Fe-base soft magnetic alloy as claimed in any

one of claims 1 to 18, wherein the content (a) of Si is

\( 6 \leq a \leq 18 \).

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Fig. 1

Crystallization Temperature (°C) vs. Al (atom%) for Fe₅₇Si₂₄-xAlₓB₉.
Fig. 3

Fe-Si-Al-B

Ms(emu/g)

Fe + B (at%)
Fig. 4

(a)

(b) b.c.c.

DO₃

(110) (200) (211) (220) (310)

(111) (311)
Fig. 5

Magnetic Flux Density

Coercive Force

Heat-treatment Temperature (°C)
Fig. 6

Effective Magnetic Permeability $\mu_e$

Heat-treatment Temperature (°C)
Fig. 7

Iron Loss (w/kg)

Heat-treatment Temperature (°C)

F=100KHz
Bm=0.1T
Fig. 8

Example 9

Crystal Particle Size

Lattice Constant

Heat-treatment Temperature (°C)
Fig. 9

Example 9

Saturation Magnetostriction $\lambda_s (\times 10^{-8})$

Heat-treatment Temperature ($^\circ C$)

As-C 500 600 700
Fig. 10

Comparative Example

Example 1

Example 2

Mn-Zn Ferrite

Effective Magnetic Permeability

Frequency (KHz)

Heat-treatment Temperature

580°C

600°C

Patent

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Fig. 12

- : Example
- : Comparative Example 2
○ : Comparative Example 1
△ : Mn-Zn Ferrite

Iron Loss (w/kg)

Magnetic Flux Density B(T)
Fig. 14

Comparative Example 2

Iron Loss (w/kg) vs. Frequency f (KHz)

Bm = 0.1T
Fig. 15

Before Heat-treatment

Hm=10 Oe
Hm=1 Oe
Hm=0.1 Oe

(H (Oe))
Fig. 16

After Heat-treatment

\[ Hm = 10 \text{ Oe} \]
\[ Hm = 1 \text{ Oe} \]
\[ Hm = 0.1 \text{ Oe} \]

\[ B \]

\[ H (\text{Oe}) \]