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(54) **PRECIPITATION-HARDENED SOFT
MAGNETIC FERRITIC STAINLESS STEELS**

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(75) Inventors: **Tsunemi Takiguchi**, Shibata-gun (JP);
Takashi Ebata, Shibata-gun (JP)

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Correspondence Address:

BURR & BROWN
PO BOX 7068
SYRACUSE, NY 13261-7068 (US)

(57) **ABSTRACT**

(73) Assignee: **Tohoku Steel Co., Ltd.**, Shibata-gun (JP)

A precipitation-hardened soft magnetic ferritic stainless steel comprises C: not more than 0.2 mass %, Si: 0.01-3.0 mass %, Mn: not more than 0.5 mass %, S: not more than 0.3 mass %, Cr: 12.0-19.0 mass %, Ni: 1.0-4.0 mass % and Al: 0.2-4.0 mass % and further contains at least one of Ti: less than 0.5 mass % and Zr: less than 0.3 mass % and the remainder being inevitable impurities and Fe, and has substantially a microstructure of a ferrite phase after a solution treatment and an aging treatment.

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PRECIPITATION-HARDENED SOFT MAGNETIC FERRITIC STAINLESS STEELS

BACKGROUND OF THE INVENTION

[0001] 1. Field of the Invention

[0002] This invention relates to a precipitation-hardened soft magnetic ferritic stainless steel, and more particularly to a precipitation-hardened soft magnetic ferritic stainless steel having not only excellent magnetic properties and corrosion resistance but also a high hardness, which contributes to an improvement of a durability such as a wear resistance, a resistance to a buckling and the like in a movable part of a magnetic circuit apparatus, and a good cold workability. Especially, it is preferable to use such a ferritic stainless steel as a magnetic core material for various electromagnetic valves, an electronic control fuel injection device and others.

[0003] 2. Description of Related Art

[0004] As the magnetic core for the electromagnetic valve, the electronic control fuel injection device and the like, the soft magnetic ferritic stainless steels are practically and frequently used from demands to the magnetic properties and the corrosion resistance. And now, when the parts made of the soft magnetic ferritic stainless steel are used in a sliding portion or an impacting portion of the apparatus in operation, it often becomes a problem that the deformation through wearing or buckling causes not only the change of a size but also the deterioration of magnetic circuit properties and airtightness to bring about the deterioration of a control accuracy. As a countermeasure for such a problem, it is attempted to attain the increase of the strength and the decrease of the wear by subjecting the sliding portion or the impacting portion to a surface hardening treatment such as a Cr plating, a nitriding treatment or the like.

[0005] However, such a countermeasure is not preferable because it brings about the deterioration of the magnetic properties as an important characteristic for the soft magnetic material and the increase of the production cost of the apparatus.

[0006] Recently, it is frequently demanded to abolish a step of handling harmful substances such as chromium and the like, for example, a plating step in view of the environmental problems, so that it is desired to develop soft magnetic materials having a good mechanical durability, particularly a high hardness (not less than 270 HV) while ensuring excellent magnetic properties without passing through the above step.

[0007] As an attempt for increasing the hardness of the ferritic stainless steel itself without deteriorating the magnetic properties, there are found many cases that the hardness is somewhat increased by solid-solution strengthening with an alloying element (about 170-220 HV), but it is not known to develop a highly soft magnetic material having a remarkably high hardness of not less than 270 HV up to the present time.

SUMMARY OF THE INVENTION

[0008] It is, therefore, an object of the invention to provide a precipitation-hardened soft magnetic ferritic stainless steel having not only excellent magnetic properties and corrosion resistance required as a magnetic core material for various

electromagnetic valves, electronic control fuel injection devices and others but also a good cold workability and a high hardness contributing to the improvement of the durability such as the wear resistance, the resistance to buckling and the like.

[0009] Although various precipitation-hardened stainless steels as represented by 17-4 PH steel are known up to now, almost all of them are a single system consisting of a martensite single phase or an austenite single phase as a base of the steel structure, or a dual-phase system including a ferrite phase. There are extremely few cases of studying and developing a precipitation-hardened soft magnetic ferritic stainless steel of a single system consisting of a ferrite single phase. Particularly, there is not found a case of developing the ferritic stainless steel having excellent soft magnetic properties except the descriptions of Japanese Patents 1194892 and 1832191.

[0010] The above Japanese Patent 1194892 is an epoch-making invention getting a head start on the precipitation-hardened soft magnetic ferritic stainless steel and discloses conditions for stabilizing the ferrite phase in detail. And also, the above Japanese Patent 1832191 is an invention further improving an appearance luster of the material.

[0011] In both the patents, the hardness after the solution treatment and the aging treatment has a very high value of not less than 400 HV as a single phase material of the soft magnetic ferrite, but there are problems that the magnetic properties do not reach to the level required when using in recent electronic control apparatuses and further the cold workability is deteriorated due to the excessively high hardness to cause troubles in the mass productivity and the like.

[0012] To solve the above problems, the inventors have made examinations with respect to a chemical composition in the steel. As a result, the inventors have obtained an extremely effective knowledge for the achievement of the object that the aging precipitation of intermetallic compounds of Ni and Al added together to the steel (a part of Ti and Zr added is considered to be also included in the compound) is a main hardening factor of the precipitation-hardened soft magnetic ferritic stainless steel, and hence the hardness after the aging treatment can be rendered into a sufficiently practical value of about 300-400 HV without deteriorating the cold workability before the aging treatment and the soft magnetic properties are more superior to those disclosed in the above patents.

[0013] The invention is based on the above knowledge and the gist thereof is as follows.

[0014] (1) A precipitation-hardened soft magnetic ferritic stainless steel characterized by comprising C: not more than 0.2 mass %, Si: 0.01-3.0 mass %, Mn: not more than 0.5 mass %, S: not more than 0.3 mass %, Cr: 12.0-19.0 mass %, Ni: 1.0-4.0 mass % and Al: 0.2-4.0 mass % and further containing at least one of Ti: less than 0.5 mass % and Zr: less than 0.3 mass %, and the remainder being inevitable impurities and Fe, and having substantially a microstructure of a ferrite phase after a solution treatment and an aging treatment (first invention).

[0015] (2) A precipitation-hardened soft magnetic ferritic stainless steel characterized by comprising C:

not more than 0.2 mass %, Si: 0.01-3.0 mass %, Mn: not more than 0.5 mass %, S: not more than 0.3 mass %, Cr: 12.0-19.0 mass %, Ni: 1.0-4.0 mass % and Al: 0.2-4.0 mass % and further containing at least one of Ti: less than 0.5 mass % and Zr: less than 0.3 mass % and at least one of Nb: not more than 1.0 mass %, Mo: not more than 4.0 mass %, Cu: not more than 2.0 mass %, B: not more than 0.01 mass % and REM: not more than 0.1 mass %, and the remainder being inevitable impurities and Fe, and having substantially a microstructure of a ferrite phase after a solution treatment and an aging treatment (second invention).

DETAILED DESCRIPTION OF THE INVENTION

[0016] In the invention, the reason of limiting the chemical composition in the steel to the above range will be explained below. Moreover, mass % in the chemical composition of the steel represents simply as “%”.

[0017] C: not more than 0.2%

[0018] C is an austenite stabilizing element obstructing the formation of steel microstructure based on the ferrite phase and also adversely affecting the magnetic properties. To this end, the C content is desirable to be decreased as far as possible and is limited to not more than 0.2% in view of the fixation as a carbide or a carbosulfide by Ti, Zr and Nb and the productivity.

[0019] Si: 0.01-3.0%

[0020] Si is not only a useful element as a deoxidizing agent in the stainless steel but also a ferrite stabilizing element, and effectively contributes to the increase of the maximum magnetic permeability and the decrease of the coercive force among the magnetic properties, and is also a useful element for increasing the specific resistance to improve the response in a high-frequency zone, and is large in the effect of increasing the hardness of the ferrite phase. In order to develop the effect, Si content is required to be not less than 0.01%. However, when the Si content exceeds 3.0%, the cold workability is obstructed to bring about the lowering of the productivity. Therefore, the Si content is limited to 0.01-3.0%.

[0021] Mn: not more than 0.5%

[0022] Mn is a useful element as a deoxidizing agent in the stainless steel and has effects of fixing S as a sulfide and further improving the machinability. However, since Mn is an austenite stabilizing element, when Mn is excessively added in an amount exceeding 0.5%, the ferrite phase is destabilized and further the magnetic properties and the corrosion resistance are deteriorated, so that the Mn content is limited to not more than 0.5%. Moreover, the lower limit of the Mn content is not especially limited, but is preferable to be 0.05% in order to remarkably develop the above effects.

[0023] S: not more than 0.3%

[0024] Since S tends to deteriorate the magnetic properties likewise C, it is desirable to decrease S content as far as possible. Considering a point that S can prevent the deterioration of the magnetic properties to a some extent through the fixation effect with Mn, Ti and Zr, the S content is limited to not more than 0.3%. Moreover, since S is also an element for improving the machinability, in case of the stainless steel requiring the machinability, the S content is preferable to be not less than 0.02%.

[0025] Cr: 12.0-19.0%

[0026] Cr is one of major components in the ferritic stainless steel according to the invention and is an element stabilizing the ferrite phase and also effectively improving the corrosion resistance and increasing the specific resistance. However, when Cr content is less than 12.0%, these effects are poor, while when Cr is added in an amount exceeding 19.0%, the magnetic properties are adversely affected. Therefore, the Cr content is limited to 12.0-19.0%.

[0027] Ni: 1.0-4.0%

[0028] Ni is an element having an effect that it is precipitated in steel as an intermetallic compound together with Al after the solution treatment and the aging treatment to increasing the hardness. In order to develop such an effect, Ni content is required to be not less than 1.0%. However, the excess addition of Ni is apt to easily induce the formation of the martensite phase or the austenite phase during the solution treatment, the upper limit of the Ni content is 4.0% as a limit forming substantially the ferrite single-phase in view of the ferrite stabilizing effect of the other adding elements.

[0029] Al: 0.2-4.0%

[0030] Al is precipitated in the steel as an intermetallic compound together with Ni to increase the hardness and is an element useful as a deoxidizing agent and also has a ferrite stabilizing action. Moreover, after the solution treatment and the aging treatment, Al added in an amount larger than the amount forming the intermetallic compound with Ni has actions for increasing the maximum magnetic permeability, and lowering the coercive force, and further contributing to the increase of the specific resistance to improve the response in a high-frequency zone likewise Si. To this end, Al content is limited to not less than 0.2% in view of the Ni content. However, the excess addition of Al exceeding 4.0% not only needs a special refining process but also obstructs the cold workability, the upper limit of Al content is 4.0%.

[0031] At least one of Ti: less than 0.5% and Zr: less than 0.3% Since Ti and Zr are elements effective for fixing C and S to enhance the magnetic properties and the corrosion resistance, it is required to contain at least one of Ti and Zr in the invention. Also, it is considered that a part of Ti and Zr contributes to the increase of the hardness by solid-soluting into the intermetallic compounds of Ni and Al after

the solution treatment and the aging treatment. The Ti content of not less than 0.5% and/or the Zr content of not less than 0.3% contribute to the increase of the hardness, but obstruct the cold workability to lower the productivity, so that the Ti content is limited to less than 0.5% and the Zr content is limited to less than 0.3%. Moreover, in order to develop the effect of enhancing the magnetic properties and the corrosion resistance, it is preferable that the Ti content is not less than 0.1% and the Zr content is not less than 0.01%.

[0032] In the invention, at least one of Nb: not more than 1.0%, Mo: not more than 4.0%, Cu: not more than 2.0%, B: not more than 0.01% and REM: not more than 0.1% can be contained, if necessary, in addition to the above components.

[0033] Nb: not more than 1.0%

[0034] Nb is an element effective for fixing C to enhance the magnetic properties and the corrosion resistance. However, the excess addition of Nb exceeding 1.0% rather obstructs the magnetic properties and the cold workability, so that the Nb content is limited to not more than 1.0%.

[0035] Mo: not more than 4.0%

[0036] Mo is a ferrite stabilizing element and is an element effective for improving the corrosion resistance. However, the excess addition of Mo exceeding 4.0% obstructs the cold workability and lowers the productivity, so that the Mo content is limited to not more than 4.0%.

[0037] Cu: not more than 2.0%

[0038] Cu is an element effective for improving the corrosion resistance and also contributes to the age hardening. However, the excess addition of Cu exceeding 2.0% brings about the embrittlement, and complicates the cold working such as cold drawing, straightening or the like, and lowers the productivity, so that the Cu content is limited to not more than 2.0%.

[0039] B: not more than 0.01%, REM: not more than 0.1%

[0040] Both B and REM contribute to improve the cold workability, but when B and REM exceed 0.01% and 0.1%, respectively, they rather become a factor obstructing the cold workability. Therefore, the B content and REM content are limited to not more than 0.01% and not more than 0.1%, respectively.

[0041] An embodiment of the process for producing the precipitation-hardened soft magnetic ferritic stainless steel according to the invention will be explained below.

[0042] At first, a raw material of steel having the above chemical composition is melted and refined in, for example, a vacuum induction furnace, and shaped into an ingot, which is bloomed at 1000-1100° C. and heated to 1000-1100° C. and hot rolled to form a member having a shape of wire, rod or plate.

[0043] Then, the member is annealed at 750-1100° C. and subjected to cold drawing and straightening at a reduction of area of 5-25% in case of the wire member or to a cold straightening in case of the rod or plate member.

[0044] Thereafter, the precipitation-hardened soft magnetic ferritic stainless steel according to the invention can be manufactured by subjecting to a solution treatment wherein the member is heated to 1000-1100° C., held at this temperature for 1-2 hours and quenched with a forced air cooling fan, water spray or the like, and subjecting to a straightening, and subjecting to an age hardening treatment wherein the member is heated and held at a temperature of 500-600° C. for 2-3 hours and air-cooled or slowly cooled with nitrogen gas or the like.

[0045] Moreover, the age hardening treatment may be performed after the parts are worked at a state subjected to the solution treatment and the straightening. Alternatively, after the parts are worked at a state subjected to the cold straightening, the solution treatment of heating under vacuum or in an atmosphere furnace and quenching with nitrogen gas or the like, and the age hardening treatment may be performed.

[0046] The following examples are given in illustration of the invention and are not intended as limitations thereof.

[0047] Each of various steel raw materials having a chemical composition shown in Table 1 and a weight of 7 kg is melted in an Ar gas stream and poured into a mold to form an ingot of 80 mm in diameter. Next, the ingot is subjected to a hot forging at 1000-1050° C. into a rod of 24 mm in diameter, which is further subjected to a hot swaging at 1000-1050° C. into a rod of 18 mm in diameter and annealed at 900° C. and then subjected to a cold drawing to form a rod of 17 mm in diameter for use in various tests. With respect to the thus obtained rods, the hardness, magnetic properties, corrosion resistance and cold workability are examined to obtain results as shown in Table 2. Moreover, the magnetic properties are measured by using a B-H loop tracer after a ling specimen having an outer diameter of 10 mm, an inner diameter of 4.5 mm and a thickness of 5 mm is prepared from the rod and subjected to a solution treatment by heating in a vacuum furnace at 1050° C. for 1 hour and quenching with nitrogen gas and subsequently to an aging treatment at 550° C. for 2 hours. Further, the hardness is measured by using the same specimen. The corrosion resistance is evaluated by observing a degree of rust formed on a surface of a specimen after an aqueous solution of 5% NaCl is sprayed at 35° C. for 48 hours onto the specimen made by subjecting a rod having a diameter of 15 mm and a length of 100 mm to the same heat treatment as in the specimen for the evaluation of the magnetic properties and polishing with 800 emery paper. Moreover, the evaluation of the corrosion resistance is conducted by two stages of "O" representing a case that the rust is not formed or it is locally and thinly formed on a corner portion of a tip of the rod and "X" representing a case that the rust formation is clear observed. And also, the cold workability is evaluated by presence or absence of the occurrence of defects such as pull crack, breakage and the like in the cold drawing for the preparation of the rod to be tested, and more concretely evaluated by two stages of "O" representing a case that the cold drawing can easily be performed without causing the defects and "X" representing a case that the defects are caused and it is difficult to conduct a mass production process including the cold working.

TABLE 1

| | Sample No. | other components | | | | | | | | | | |
|---------------------|------------|------------------|------|------|-------|-------|-------|------|------|------|-------|--------------------------|
| | | C | Si | Mn | P | S | Cr | Ni | Al | Ti | Zr | |
| Example | 1 | 0.012 | 0.97 | 0.19 | 0.006 | 0.012 | 14.27 | 2.74 | 0.98 | 0.17 | — | |
| | 2 | 0.131 | 2.34 | 0.14 | 0.005 | 0.210 | 18.24 | 2.76 | 0.91 | 0.08 | 0.180 | |
| | 3 | 0.005 | 0.03 | 0.38 | 0.006 | 0.008 | 12.40 | 3.44 | 3.15 | 0.38 | — | |
| | 4 | 0.011 | 0.99 | 0.20 | 0.007 | 0.013 | 14.21 | 2.72 | 0.97 | 0.18 | — | Mo: 2.8 Cu: 1.76 B:0.001 |
| | 5 | 0.150 | 2.64 | 0.15 | 0.006 | 0.230 | 18.34 | 2.78 | 0.88 | 0.46 | 0.110 | Mo: 0.08 B: 0.03 |
| | 6 | 0.007 | 0.02 | 0.36 | 0.006 | 0.004 | 12.40 | 3.55 | 3.20 | 0.06 | — | Nb: 0.72 REM: 0.06 |
| | 7 | 0.014 | 0.98 | 0.21 | 0.005 | 0.014 | 14.65 | 2.81 | 0.96 | — | 0.080 | |
| Comparative Example | 8 | 0.015 | 0.84 | 0.23 | 0.005 | 0.13 | 10.20 | 3.34 | 0.87 | 0.12 | — | Mo: 1.18 Cu: 0.34 |
| | 9 | 0.013 | 0.98 | 0.17 | 0.006 | 0.017 | 16.23 | 5.11 | 1.18 | 0.16 | — | No: 1.86 |
| | 10 | 0.008 | 1.56 | 0.19 | 0.006 | 0.018 | 14.70 | 0.47 | 0.16 | 0.14 | — | No: 1.13 |
| | 11 | 0.011 | 0.95 | 0.18 | 0.005 | 0.012 | 14.30 | 2.73 | 0.99 | — | — | |
| | 12 | 0.012 | 1.01 | 0.18 | 0.004 | 0.014 | 13.80 | 2.71 | 0.98 | 0.19 | — | Cu: 2.60 |

[0048]

TABLE 2

| Sample No. | During cold | | | | | | | | | | | | |
|---------------------|--------------|--------------------------|----------------|---------------------------|-----------------|------|--|----------------|---------------------------|------|------|-----------------------|----------------------|
| | working Cold | After solution treatment | | | | | After solution treatment and aging treatment | | | | | | |
| | | workability | Hardness (HV5) | Magnetic flux density (T) | | | Coercive force (A/cm) | Hardness (HV5) | Magnetic flux density (T) | | | Coercive force (A/cm) | Corrosion resistance |
| | | | B ₂ | B ₅ | B ₂₅ | | B ₂ | B ₅ | B ₂₅ | | | | |
| Example | 1 | ○ | 203 | 0.76 | 1.02 | 1.27 | 0.59 | 343 | 0.73 | 0.99 | 1.26 | 0.61 | ○ |
| | 2 | ○ | 238 | 0.49 | 0.93 | 1.19 | 1.05 | 371 | 0.47 | 0.92 | 1.19 | 1.07 | ○ |
| | 3 | ○ | 221 | 0.59 | 1.01 | 1.23 | 0.83 | 384 | 0.61 | 1.02 | 1.23 | 0.81 | ○ |
| | 4 | ○ | 234 | 0.43 | 0.86 | 1.19 | 0.98 | 363 | 0.42 | 0.84 | 1.18 | 1.00 | ○ |
| | 5 | ○ | 241 | 0.48 | 0.93 | 1.19 | 1.06 | 375 | 0.47 | 0.93 | 1.19 | 1.08 | ○ |
| | 6 | ○ | 243 | 0.38 | 0.99 | 1.22 | 1.03 | 391 | 0.38 | 0.81 | 1.20 | 1.05 | ○ |
| | 7 | ○ | 211 | 0.74 | 1.03 | 1.27 | 0.63 | 348 | 0.71 | 1.01 | 1.27 | 0.65 | ○ |
| Comparative Example | 8 | ○ | 254 | 0.14 | 0.42 | 0.73 | 3.13 | 307 | 0.12 | 0.38 | 0.71 | 3.45 | X |
| | 9 | X | 338 | 0.04 | 0.14 | 0.61 | 4.24 | 411 | 0.03 | 0.15 | 0.65 | 4.27 | ○ |
| | 10 | ○ | 205 | 0.79 | 1.06 | 1.26 | 0.56 | 241 | 0.78 | 1.04 | 1.25 | 0.55 | ○ |
| | 11 | ○ | 234 | 0.09 | 0.34 | 0.88 | 2.28 | 342 | 0.07 | 0.33 | 0.87 | 2.32 | ○ |
| | 12 | X | 238 | 0.64 | 0.93 | 1.22 | 0.78 | 353 | 0.55 | 0.90 | 1.22 | 0.86 | ○ |

[0049] As seen from the results shown in Table 2, all of Sample Nos. 1-7 of the examples are excellent in the corrosion resistance and the cold workability, and have a hardness of not less than 340 HV5 after the aging treatment, and the magnetic properties have substantially no difference before and after the aging treatment and show excellent values as a soft magnetic material.

[0050] On the other hand, Sample No. 8 of the comparative example is low in the Cr content and Sample No. 9 of the comparative example is too large in the Ni content, so that they are largely influenced by the austenite stabilizing element and the value of the magnetic flux density is less than 1 T at B₂₅ and the coercive force is high, which are poor in the magnetic properties as a soft magnetic material. Sample No. 10 of the comparative example is excellent in the magnetic properties but the hardness even after the aging treatment is far below 300 HV5 because the amounts of Ni and Al added are too small. Sample No. 11 of the comparative example is poor in the magnetic properties because the elements such as Ti, Zr and the like for strongly fixing C and S are not added into steel. Sample No. 12 of the comparative example is excellent in the hardness and the magnetic properties, but is poor in the cold workability because the amount of Cu added is too high, and the breakage and the

pull crack frequently occur in the cold drawing for the preparation of the test steel, and the yield in the preparation of the test steel is very low.

[0051] According to the invention, there can be provided precipitation-hardened soft magnetic ferritic stainless steels having not only excellent magnetic properties and corrosion resistance but also a good cold workability and a high hardness contributing to improve the durability such as wear resistance, resistance to buckling and the like. When such stainless steels are used as a magnetic core material for various electromagnetic valves, electronic control fuel injection devices and the like, the improvement of the durability and the reduction of the production cost are attained and the environmental protection is good, so that the invention greatly contributes to the industrial circles.

What is claimed is:

1. A precipitation-hardened soft magnetic ferritic stainless steel characterized by comprising C: not more than 0.2 mass %, Si: 0.01-3.0 mass %, Mn: not more than 0.5 mass %, S: not more than 0.3 mass %, Cr: 12.0-19.0 mass %, Ni: 1.0-4.0 mass % and Al: 0.2-4.0 mass % and further containing at least one of Ti: less than 0.5 mass % and Zr: less than 0.3 mass %, and the remainder being inevitable impurities and

Fe, and having substantially a microstructure of a ferrite phase after a solution treatment and an aging treatment.

2. A precipitation-hardened soft magnetic ferritic stainless steel characterized by comprising C: not more than 0.2 mass %, Si: 0.01-3.0 mass %, Mn: not more than 0.5 mass %, S: not more than 0.3 mass %, Cr: 12.0-19.0 mass %, Ni: 1.0-4.0 mass % and Al: 0.2-4.0 mass % and further containing at least one of Ti: less than 0.5 mass % and Zr: less than 0.3

mass % and at least one of Nb: not more than 1.0 mass %, Mo: not more than 4.0 mass %, Cu: not more than 2.0 mass %, B: not more than 0.01 mass % and REM: not more than 0.1 mass %, and the remainder being inevitable impurities and Fe, and having substantially a microstructure of a ferrite phase after a solution treatment and an aging treatment.

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