

(19)



(11)

EP 1 788 105 A1

(12)

EUROPEAN PATENT APPLICATION

(43) Date of publication:

23.05.2007 Bulletin 2007/21

(51) Int Cl.:

C22C 38/34 ^(2006.01)

(21) Application number: **06021771.8**

(22) Date of filing: **17.10.2006**

(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 NL PL PT RO SE SI
SK TR**

Designated Extension States:

AL BA HR MK YU

(30) Priority: **18.11.2005 JP 2005334845**

(71) Applicant: **KABUSHIKI KAISHA KOBE SEIKO SHO**

**Kobe-shi,
Hyogo 651-8585 (JP)**

(72) Inventors:

- **Yoshihara, Nao**
Nada-ku
Kobe-shi
Hyogo 657-0863 (JP)
- **Koizumi, Fujiio**
Nada-ku
Kobe-shi
Hyogo 657-0863 (JP)

(74) Representative: **Müller-Boré & Partner**

Patentanwälte
Grafinger Strasse 2
81671 München (DE)

(54) **Spring steel wire rod excellent in pickling performance**

(57) A spring steel wire rod according to the present invention is a spring steel wire rod wherein: the spring steel wire rod contains C: 0.35% to 0.7% (by mass, the same is hereunder applied), Si: 1.5% to 2.50%, Mn: 0.05% to 1.0%, Cr: 0.05% to 1.9%, Cu: 0.05% to 0.7%, Ni: 0.15% to 0.8%, P: 0.02% or less (excluding 0%), S: 0.02% or less (excluding 0%); and the balance being Fe and unavoidable impurities, wherein the ratio of Si to Cu (Si/Cu) is in the range of 4 or more; and the difference

between the concentration of Cu in the surface layer and the concentration of Cu in the steel is 0.50% or less and the difference between the concentration of Ni in the surface layer and the concentration of Ni in the steel is 1.00% or less. The present invention makes it possible to improve pickling performance in a spring steel wire rod containing Si abundantly and further Cr, Cu, and Ni.

EP 1 788 105 A1

Description

[0001] The present invention relates to a spring steel wire rod excellent in pickling performance, and more specifically a technology for improving pickling performance of a spring steel wire rod containing Si abundantly and further Cr, Cu, and Ni. A spring steel wire rod according to the present invention is favorably used for: a valve spring used for the engine of an automobile or the like; a clutch spring; a brake spring; a suspension spring such as a stabilizer spring or a torsion bar spring; and other applications.

[0002] The chemical composition of a spring steel used for a valve spring, a suspension spring, or the like is stipulated in JIS G3565 to JIS G4801 for example and an appropriate steel type is used in accordance with the type of spring design. In recent years, as the size and weight of a spring reduce with the reduction of exhaust gas and fuel consumption, the design stress of the spring increases and it is desired to provide, for example, a spring steel wire rod which can realize a high strength of about 1,600 MPa or higher in terms of the tensile strength of a spring material wire (a quenched and tempered material). Further, in order to improve the durability in the air which is one of the important characteristics of a spring, the improvement of proof stress is also desired and a steel wire rod abundantly including Si and Cr as alloying elements which are capable of improving the proof stress by solid solution hardening tends to be used. In addition, in order to improve corrosion fatigue resistance which is another important characteristic of a spring, it is attempted to add Cu and Ni and thus improve corrosion resistance.

[0003] A spring is generally fabricated by heating a billet; subjecting the hot-rolled wire rod (the rolled wire rod) to filming treatment (surface coating treatment) by applying a lubricant to the surface if necessary; thereafter drawing the wire rod to a prescribed diameter; and applying forming (hot forming or cold forming). The heating is usually carried out in an oxidizing atmosphere and hence an oxidation layer comprising Fe oxide called "rolling scale" or "scale" is formed on the surface of a rolled wire rod. When a rolled wire rod bearing such scale is used for the fabrication of a spring, surface defects and the like appear, thus the quality deteriorates, and hence pickling treatment is applied before the drawing treatment in order to remove the scale.

[0004] Fig. 1 shows a photograph of a cross section of a rolled wire rod bearing scale on the surface of the steel containing Si abundantly and further Cr, Cu, and Ni, the photograph being taken with an Fe-SEM. The case corresponds to the case No. E-1 in the Example which will be described later. As shown in Fig. 1, the scale comprises, in order from the surface side, hematite (Fe_2O_3), magnetite (Fe_3O_4), wustite (FeO), and fayalite ($2\text{FeO} \cdot \text{SiO}_2$). Between the steel (the base steel) and the scale, subscale wherein Si and Cr condense is further formed.

[0005] Among those, fayalite is a low melting point oxide which is seen when a steel abundantly containing Si is used and is a material hard to exfoliate through ordinary pickling treatment. For example, when a steel containing Si and Cr is heated to a temperature exceeding the eutectic temperature of fayalite and wustite (about $1,170^\circ\text{C}$), a dense melt phase wherein those oxides are intricately interwound with each other is formed and then, when it is further heated to a temperature of $1,200^\circ\text{C}$ or higher, Cr intrudes into the aforementioned melt phase and the fayalite, condenses at the interface with the base steel, and forms a condensed layer (the detail will be described later). The Cr once condensed is very hard to remove through the succeeding processes and deteriorates pickling performance. When the pickling performance deteriorates, scale remains after pickling treatment, hence the adhesiveness with a lubricant applied on the surface (used for surface coating treatment) lowers, and wire breakage may undesirably occur during drawing. Even when wire breakage does not occur, cracks (crevices) may occur during drawing and breakage may occur during spring forming (cold coiling). Those problems are alleviated, for example, by prolonging the pickling treatment time and completely removing scale. In this case however, since the time of dipping in a pickling solution increases, the attack to the base steel by acid intensifies, the surface roughness lowers, and finally the durability comes to deteriorate even in the air. Further, since a part of hydrogen generated during the attack to the base steel by acid diffuses rapidly in the steel and is absorbed therein, the amount of stored hydrogen increases, that causes the embrittlement (hydrogen embrittlement) of the steel material, and wire breakage occurs during drawing in some cases.

[0006] Further, although it is not shown in Fig. 1, a layer wherein Cu and Ni are concentrated is also formed between the steel (the base steel) and the scale. The concentrated layer is seen when a steel contains Cu and Ni. It is known that: metals such as Cu and Ni which are nobler than iron are not oxidized by heating; hence such metals concentrate at the interface between scale and a base steel or in fayalite; and surface cracks caused by red shortness appear. For example, the melting point of Cu is about $1,080^\circ\text{C}$ and a steel material is usually heated to a temperature higher than the melting point of Cu (about $1,100^\circ\text{C}$ to $1,250^\circ\text{C}$ for example) before hot-rolled, and hence it is estimated that: Cu in a molten state (of a liquid phase) is formed at the interface between scale and the base steel; the Cu intrudes into grain boundaries of the base steel and concentrates; the steel material does not withstand shearing stress or tensile stress any more during hot rolling; and surface cracks caused by red shortness appear. Such a phenomenon is called liquid metal melt embrittlement and it is understood that the phenomenon resultantly deteriorates pickling performance.

[0007] Various methods are proposed in order to prevent: Cu from concentrating at a base steel interface; and surface cracks caused by red shortness from appearing.

[0008] For example, JP-A No. 297026/1994 describes a method for preventing surface cracks by: adding Si in a steel;

making Si exist in scale during the heating process preceding hot rolling; forming low melting point oxide liquid scale of an $\text{SiO}_2\text{-FeO}$ system; and thus taking the Cu molten liquid into the scale.

[0009] JP-A No. 223523/2004 describes a technology related to a method of heating a Cu containing steel material, the technology being proposed by the same applicants as those of JP-A No. 297026/1994. The patent application describes a method for controlling the temperature of a heating atmosphere and the oxygen concentration in the atmosphere with regard to the conditions of the heating before hot rolling as a method which makes it possible to prevent surface cracks caused by the concentration of Cu without such change of a steel composition as described in JP-A No. 297026/1994.

[0010] As stated above, although a spring steel wire rod containing Si abundantly and Cr, Cu, and Ni is used mostly in order to improve proof stress and corrosion fatigue resistance, there is concern that, in the case of such a spring steel wire rod, Cu concentrates at the interface between scale (particularly fayalite) and the base steel and hence pickling performance deteriorates.

[0011] However, a method for sufficiently improving the pickling performance of such a spring steel wire rod is not disclosed yet. JP-A No. 223523/2004 stated above describes a technology for preventing surface cracks caused by the concentration of Cu without the abundant addition of Si and by the technology the improvement of proof stress by the addition of Si cannot be obtained. Meanwhile, JP-A No. 297026/1994 stated above, as it is indicated in the section of "Prior Art" of JP-A No. 223523/2004 stated above which is proposed afterward, has the problems in that: a steel material to which Si is added has poor detachability of scale; the scale is hardly exfoliated and removed even when descaling with high-pressure water is applied before rolling; the surface properties deteriorate, for example scale remains and the surface of the steel material turns red; and, when a pickling process is applied thereafter, the scale hardly dissolves in the pickling process and hence the cost of the pickling process increases and the productivity lowers.

[0012] The present invention has been established in view of the above situation and the object thereof is to provide a spring steel wire rod having improved pickling performance in the case of a spring steel wire rod containing Si abundantly and further Cr, Cu, and Ni.

[0013] A spring steel wire rod according to the present invention which can solve the above problems is a spring steel wire rod wherein: the spring steel wire rod contains C: 0.35% to 0.7% (by mass, the same is hereunder applied unless otherwise specified), Si: 1.5% to 2.50%, Mn: 0.05% to 1.0%, Cr: 0.05% to 1.9%, Cu: 0.05% to 0.7%, Ni: 0.15% to 0.8%, P: 0.02% or less (excluding 0%), and S: 0.02% or less (excluding 0%), wherein the ratio of Si to Cu (Si/Cu) is in the range of 4.0 or more; and the difference between the concentration of Cu in the surface layer and the concentration of Cu in the steel is 0.50% or less and the difference between the concentration of Ni in the surface layer and the concentration of Ni in the steel is 1.00% or less.

[0014] In a preferable embodiment, a spring steel wire rod according to the present invention further contains at least one element selected from among the group comprising V: 0.07% to 0.4%, Ti: 0.01% to 0.1%, and Nb: 0.01% to 0.1%.

[0015] A spring according to the present invention which can solve the above problems is a spring fabricated from any one of the spring steel wire rods stipulated above.

[0016] A spring steel wire rod according to the present invention is excellent in pickling performance since the concentration of Cr and Ni in the surface layer thereof is considerably suppressed and the thickness of scale is very thin. When a spring is fabricated from a spring steel wire rod according to the present invention, a spring excellent in surface properties can be provided since the scale is easily exfoliated through a pickling process.

Fig. 1 is an Fe-SEM photograph showing a cross section of a rolled wire rod bearing scale.

Fig. 2 is a graph showing the relationship between a Cu concentration (%) and a distance from a surface.

Fig. 3 is a graph showing the relationship between a Ni concentration (%) and a distance from a surface.

[0017] The present inventors have earnestly studied in order to improve the pickling performance of a spring steel wire rod containing Si abundantly and further Cr, Cu, and Ni. As a result, as it will be explained later in detail, the present inventors have found that, by properly controlling particularly, (i) a descaling process preceding hot rolling, and (ii) a hot-rolling process, the concentration of Cu and Ni on the wire rod surface (particularly the concentration of Cu and Ni in fayalite) is suppressed; the difference between the concentration of Cu in the surface layer and the concentration of Cu in the steel (hereunder may be abbreviated to " ΔCu ") and the difference between the concentration of Ni in the surface layer and the concentration of Ni in the steel (hereunder may be abbreviated to " ΔNi ") are remarkably lowered; and thereby pickling performance outstandingly improves. And the present inventors have established the present invention.

[0018] Specifically, (i) water shower of a prescribed high pressure is applied in a descaling process preceding hot rolling. By so doing, Cu taken into fayalite is exfoliated and the amount of concentrated Cu in a surface layer can be reduced. Further, (ii) water shower of a prescribed high pressure is applied in a hot-rolling process. By so doing, the concentration of Cu in fayalite formed during hot rolling can be considerably suppressed.

[0019] The present invention is hereunder explained in detail.

[0020] As stated above, a spring steel wire rod according to the present invention is a spring steel wire rod wherein:

the spring steel wire rod comprises C: 0.35% to 0.7%, Si: 1.5% to 2.50%, Mn: 0.05% to 1.0%, Cr: 0.05% to 1.9%, Cu: 0.05% to 0.7%, Ni: 0.15% to 0.8%, P: 0.02% or less (excluding 0%), S: 0.02% or less (excluding 0%), and the balance consisting of Fe and unavoidable impurities; the ratio of Si to Cu (Si/Cu) is in the range of 4.0 or more; and the difference between the concentration of Cu in the surface layer and the concentration of Cu in the steel is 0.50% or less and the difference between the concentration of Ni in the surface layer and the concentration of Ni in the steel is 1.00% or less.

[0021] In the present specification, the term "steel wire rod" means a steel material (a rolled material) which is fabricated by heating and thereafter hot-rolling a billet into a linear shape, which is not yet subjected to pickling treatment.

[0022] Firstly, components in a steel are explained.

C: 0.35% to 0.7%

[0023] C is an element which contributes to the enhancement of strength (hardness) after being quenched and tempered and improves durability in the air. When a C content is less than 0.35%, the above functions cannot be effectively exhibited. On the other hand, when a C content exceeds 0.7%, toughness and ductility deteriorate, cracks tend to propagate and durability lowers, and thus corrosion resistance is also badly affected. A preferable C content is in the range of 0.39% to 0.54%.

Si: 1.5% to 2.50%

[0024] Si is an element which contributes to the enhancement of strength as a solid solution hardening element and also can improve proof stress. When a Si content is less than 1.5%, the strength of a matrix is insufficient. However, when a Si content exceeds 2.50%, the ratio of fayalite in scale increases and pickling performance deteriorates. A preferable Si content is in the range of 1.70% to 2.1%.

Mn: 0.05% to 1.0%

[0025] Mn is an element which enhances the hardenability of a steel. Mn is added by 0.05% or more in order to effectively exhibit such a function. When Mn is added in excess of 1.0% however, the hardenability increases, a super-cooled structure tends to form, and drawability deteriorates. Further, when an annealing process is applied after hot rolling before pickling treatment with the aim of softening a wire rod in the same way as "a spring forming process (c)" which will be described later, the cost unavoidably increases. A preferable Mn content is in the range of 0.12% to 0.8%. In the present invention, as stated later, measures such as the reduction of a S content, the addition of another sulfide-forming element such as Cu, and others are taken in order to prevent MnS which functions as the origin of fracture from forming.

Cr: 0.05% to 1.9%

[0026] Cr is an element which makes rust formed on a surface amorphous and dense under corrosive conditions, contributes to the improvement of corrosion resistance, and effectively affects the enhancement of hardenability like Mn. Cr is added by 0.05% or more in order to exhibit such functions. When a Cr content exceeds 1.9% however, a supercooled structure tends to form during cooling after rolling and drawability deteriorates. When an annealing process is applied after hot rolling before pickling treatment with the aim of softening a wire rod in the same way as "a spring forming process (c)" which will be described later, the cost unavoidably increases. A preferable Cr content is in the range of 0.15% to 1.75%.

Cu: 0.05% to 0.7%

[0027] Cu is an element which is electrochemically nobler than iron and has the function of improving corrosion resistance. Cu is added by 0.05% or more in order to effectively exhibit such a function. When a Cu content exceeds 0.7% however, the amount of Cu concentrated in a base steel surface layer, at the interface between a base steel and rolling scale, and in fayalite increases and pickling performance deteriorates. A preferable Cu content is in the range of 0.20% to 0.5%.

Ni: 0.15% to 0.8%

[0028] Ni has the functions of enhancing toughness after quenching and tempering, making rust forming on a surface amorphous and dense under corrosive conditions, and thus improving corrosion resistance. Further, Ni has also the function of suppressing ferrite decarburization occurring before and during rolling. Ni is added by 0.15% or more in order

to effectively exhibit such functions. When a Ni content exceeds 0.8% however, hardenability increases and a supercooled structure tends to form after rolling. In addition, the amount of retained austenite increases and spring hardness lowers. A preferable Ni content is in the range of 0.25% to 0.55%.

P: 0.02% or less (excluding 0%)

[0029] P segregates at prior austenite grain boundaries, embrittles the grain boundaries, and lowers resistance to delayed fracture. For that reason, a P content should be as small as possible. In the present invention, the upper limit of a P content is set at 0.02% in view of industrial production.

S: 0.02% or less (excluding 0%)

[0030] S segregates at prior austenite grain boundaries, embrittles the grain boundaries, and lowers resistance to delayed fracture. For that reason, a S content should be as small as possible. In the present invention, the upper limit of a S content is set at 0.02% in view of industrial production.

Ratio of Si to Cu (Si/Cu): 4.0 or more

[0031] In the present invention, not only the amounts of Si and Cu are regulated respectively but also the lower limit of a ratio Si/Cu is regulated. By the regulation, fayalite formed by the addition of Si and the amount of Cu concentrated at the interface between a base steel and scale by the addition of Cu are properly controlled, and hence the Cu concentration into the fayalite is suppressed and ΔCu lowers. As a result, pickling performance improves (refer to the after-mentioned Example). The upper limit of a ratio Si/Cu is set at 50 from the contents of Si and Cu described above. A preferable ratio Si/Cu is in the range of 4.5 to 35.

[0032] A spring steel wire rod according to the present invention contains the aforementioned components and the balance thereof consists of Fe and unavoidable impurities.

[0033] In the present invention, with the aim of further enhancing resistance to hydrogen embrittlement, it is preferable to further contain at least one element selected from among the group comprising V: 0.07% to 0.4%, Ti: 0.01% to 0.1%, and Nb: 0.01% to 0.1%. The elements are hereunder explained in detail.

V: 0.07% to 0.4%

[0034] V is an element which forms fine carbide and nitride and contributes to the improvement of resistance to hydrogen embrittlement. Further, V enhances fatigue resistance. In addition, V improves toughness and proof stress by, the crystal grain fractionizing effect and also contributes to the improvement of corrosion resistance and resistance to permanent set in fatigue. It is preferable to add V by 0.07% or more in order to effectively exhibit such functions. When V is added in excess of 0.4% however, the amount of carbide not dissolved in austenite increases during heating for hardening, sufficient strength and hardness cannot be obtained, the amount of retained austenite also increases, and the hardness of a spring lowers. A yet preferable V content is in the range of 0.1% to 0.2%.

Ti: 0.01% to 0.1%

[0035] Ti is an element which fractionizes prior austenite crystal grains after quenching and tempering and is effective in the improvement of resistance to hydrogen embrittlement. Further, Ti has the function of enhancing durability in the air. It is preferable to add Ti by 0.01% or more in order to effectively exhibit such functions. When Ti is added excessively however, coarse nitride tends to precipitate and durability in the air deteriorates. For that reason, it is preferable to set the upper limit of a Ti content at 0.1%. A yet preferable Ti content is in the range of 0.04% to 0.09%.

Nb: 0.01% to 0.1%

[0036] Nb is an element which forms fine precipitate comprising carbide, nitride, sulfide, and a composite compound thereof and thus contributes to the improvement of resistance to hydrogen embrittlement. Further, toughness and proof stress also improve by the crystal grain fractionizing effect. It is preferable to add Nb by 0.01% or more in order to effectively exhibit such functions. When Nb is added in excess of 0.1% however, the amount of carbide not dissolved in austenite increases during heating for hardening and an intended tensile strength cannot be obtained. A yet preferable Nb content is in the range of 0.02% to 0.05%.

[0037] The components in a steel according to the present invention have been explained above.

Difference between the Cu concentration in a surface layer and the Cu concentration in a steel (ΔCu): 0.50% or less

[0038] In the present invention, ΔCu is controlled to a low level of 0.50% or less. As stated above, although most of the scale (the primary scale) formed through heating can be removed through ordinary descaling treatment applied before hot rolling, the scale (the secondary scale) formed during hot rolling and during cooling after hot rolling, particularly in the case of such a steel containing Si and Cu in quantities as a steel according to the present invention, cannot be easily removed through ordinary descaling treatment, Fe diffuses in the scale, and thereby Cu precipitates at the interface between the scale (fayalite) and the base steel or in fayalite. As a result, pickling performance deteriorates. In the present invention, as it will be explained later in detail, since not only a descaling process preceding hot rolling but also a finish-rolling process is properly controlled, ΔCu can be controlled to a low level. The lower the value ΔCu is, the better. For example, a value ΔCu is preferably 0.45% or less, and yet preferably 0.40% or less.

[0039] Here, the method for measuring "a Cu concentration in a surface layer" is explained with reference to Fig. 2. Fig. 2 comprises the graphs obtained by using a specimen prepared as stated below and measuring a Cu content from a surface to the center of the interior by EPMA quantitative linear analysis under after-mentioned conditions; and shows the relationship between a Cu concentration (%) and a distance from the surface. Here with regard to Fe, the point where the Fe strength (cps) of X-ray comes to the maximum when the EPMA quantitative linear analysis is applied in the same way as stated above is defined as a base steel interface (an interface between scale and a base steel). The region between a surface and a base steel interface is defined as "a surface layer" and the maximum value of the Cu content in the surface layer is defined as "a Cu concentration in a surface layer." The state of such a surface layer varies also in accordance with components in a steel, fabrication conditions of a wire rod, and others but the surface layer contains at least fayalite.

EPMA measuring apparatus: An X-ray microanalyzer "JXA-8800 RL" made by JEOL Ltd. was used,

Specimen: prepared by embedding a steel material bearing scale into resin, mirror-finishing a cross section thereof perpendicular to the rolling direction with an abrasive, and thereafter applying vapor deposition of osmium in order to keep electric conductivity,

Accelerating voltage: 15 kV,

Irradiation current: 0.3 μA , and

Quantitative linear analysis: measured at 300 spots in total at distribution intervals of 1 μm .

Difference between the Ni concentration in a surface layer and the Ni concentration in a steel (ΔNi): 1.00% or less

[0040] In the present invention, ΔNi is also controlled to a low level of 1.00% or less. Ni is an element which contributes to the improvement of corrosion resistance like Cu as stated above and is the same as Cu also in the fact that Ni precipitates at the interface between scale (fayalite) and a base steel or in fayalite in a heating process and a hot-rolling process. As a result, pickling performance deteriorates. In the present invention therefore, it is necessary to suppress the concentration of Ni in the same way as Cu. The lower the value ΔNi is, the better. For example, a value ΔNi is preferably 0.90% or less, and yet preferably 0.85% or less.

[0041] Here, the term "a Ni concentration in a surface layer" means the maximum Ni content obtained by using a specimen prepared by the same method as used in the measurement of "a Cu concentration in a surface layer" stated above and measuring a Ni content in the range of 0.3 mm from the surface toward the center of the interior by the EPMA quantitative linear analysis under the same conditions as described above. Fig. 3 shows the relationship between a Ni concentration (%) and a distance from a surface.

[0042] ΔCu and ΔNi which characterize the present invention have been explained above.

[0043] In a spring steel wire rod according to the present invention, it is preferable to control the thickness and the composition of scale in an appropriate manner as stated below and by so doing pickling performance is further improved.

(Thickness of scale)

[0044] A preferable thickness of scale is 40 μm or less. As it will be explained hereunder in detail, it is preferable that the thickness of scale is basically in the range of 5 to 35 μm in consideration of the exfoliation of scale caused by the crevices (cracks) formed in the scale.

[0045] It sometimes happens that crevices of a micron level form in scale, for example, during cooling after rolling and handling of a rolled wire rod. As crevices increase, scale tends to exfoliate more easily from the surface of a base steel and hence it is estimated that pickling performance improves. In general, as the thickness of scale is reduced, the strength of the scale is lowered and crevices are likely to form. However, if the thickness of scale is reduced excessively, the ductility of the scale itself is improved, the internal stress is reduced, and hence crevices are decreased. For those reasons, it is preferable that the thickness of scale is in the above range.

(Composition of scale)

[0046] It is preferable that the composition of scale basically satisfies the ranges of, in volume percentage, 2% to 10% (yet preferably 3% to 7%) as fayalite, 2% to 20% (yet preferably 10% to 18%) as wustite, 35% to 70% (yet preferably 37% to 50%) as magnetite, and 20% to 60% (yet preferably 30% to 55%) as hematite. As stated above, in the present invention, the composition of scale is controlled so that the percentage of fayalite which is hardly exfoliative may be reduced and the percentages of wustite and magnetite which are excellent in scale detachability may be increased, and hence pickling performance is further improved.

[0047] A spring steel wire rod according to the present invention has been explained above.

[0048] A method for fabricating such a spring steel wire rod as stated above is explained hereunder.

[0049] A method for fabricating a spring steel wire rod includes (i) a heating process, (ii) a soaking process, (iii) a descaling process preceding a hot-rolling process, and (iv) a hot-rolling process. In the present invention in particular, for example, prescribed high-pressure water shower is applied in (iii) a descaling process preceding a hot-rolling process in order to rapidly remove scale including fayalite, and prescribed cooling water shower is applied in (iv) a hot-rolling process in order to prevent Cu from concentrating in fayalite formed during hot rolling, and thereby it has been possible to suppress ΔCu and ΔNi to considerably low levels. As shown in the Example to be described later, by the present invention, even though a steel containing Si abundantly and Cr, Cu, and Ni is used, the concentration of Cu and Ni in a surface layer is considerably suppressed, the thickness of scale is reduced, and hence it is possible to provide a spring having a tensile strength of about 1,600 MPa or more, excellent in surface properties.

[0050] Each process is hereunder explained in detail.

(i) Heating process

[0051] Heating conditions are not particularly limited but basically a billet is heated to a temperature in the range of 700°C to 1,000°C (750°C to 900°C) at a heating rate of 10°C/min or higher. When a heating rate is lower than 10°C/min, the concentration of Cr into a surface layer cannot be prevented effectively. A higher heating rate is desirable and a preferable heating rate is 15°C/min or higher. Further, when a heating temperature exceeds the above range, the concentration of Cu and Ni advances and the amounts of Cu and Ni in the surface layer increase. In contrast, when a heating temperature is lower than the above range, heating is insufficient and hence rough rolling fails.

(ii) Soaking process

[0052] In the process, basically it is preferable to soak a billet for 20 to 60 minutes (yet preferably 30 to 50 minutes) at 1,050°C to 1,250°C (yet preferably 1,100°C to 1,200°C). The soaking conditions are determined so as to prevent Cu and Ni from concentrating in a surface layer and suppress the progress of grain boundary oxidation. For example, the concentration of Cu and Ni tends to advance when a soaking temperature or a soaking time exceeds the above range, and in contrast the concentration of Cu into austenite crystal grain boundaries advances when a soaking temperature or a soaking time is lower than the above range.

[0053] In the present invention, a heating temperature in a heating process and a soaking temperature in a soaking process are not necessarily identical. In the Example which will be described later for example, the soaking temperature is higher than the heating temperature by about 200°C to 300°C and the reason is that the temperature at the soaking rises during the residence time after heating before soaking.

(iii) Descaling process preceding hot-rolling process

[0054] In the process, in order to rapidly remove scale containing fayalite, it is preferable to apply high-pressure water shower for about 1 to 10 seconds (yet preferably 3 to 7 seconds) with a water pressure in the range of about 80 kgf/mm² (nearly 785 MPa) to 160 kgf/mm² (nearly 1,569 MPa), and yet preferably about 100 kgf/mm² (nearly 981 MPa) to 120 kgf/mm² (nearly 1,176 MPa). Thereby it is possible to carry out the succeeding hot-rolling process soon. When a water pressure of the shower is lower than 80 kgf/mm², the thickness of scale increases and that may undesirably cause surface defects caused by bite during hot rolling to appear, and the Cu concentration in a surface layer to increase. On the other hand, when a water pressure of the shower exceeds 160 kgf/mm², the temperature of a billet before hot rolling lowers and rolling is hardly carried out.

[0055] In a descaling process preceding a hot-rolling process, the descaling means is not limited to such high-pressure water shower as stated above and, for example, mechanical descaling such as shot blasting may be adopted.

(iv) Hot-rolling process

[0056] In the process, prescribed cooling water shower is applied in order to prevent Cu from concentrating into fayalite formed during hot rolling and further control the composition of scale properly.

[0057] Specifically, cooling with the shower is applied in a finish-rolling process after the application of rough rolling. In general, the flow rate of the shower water is preferably in the range of 100 to 200 t/hr, and yet preferably 120 to 180 t/hr. When the flow rate of the shower water is less than 100 t/hr, the intended functions of removing scale (fayalite) and reducing ΔCu and ΔNi are not effectively exhibited. On the other hand, when the flow rate of the shower water exceeds 200 t/hr, a steel material is excessively cooled and a supercooled structure undesirably precipitates.

[0058] A preferable finish-rolling temperature is basically in the range of 800°C to 1,000°C (yet preferably 900°C to 950°C) mainly in order to properly control the thickness and the composition of scale.

[0059] Further, from the same viewpoint as above, it is preferable to control a cooling rate to, for example, 4°C/sec to 20°C/sec (yet preferably 6°C/sec to 15°C/sec) in the temperature range of a temperature after the completion of the finish rolling to about 700°C. When a cooling rate is lower than 4°C/sec in the above temperature range, the thickness and the like of scale increase and pickling performance deteriorates. On the other hand, when a cooling rate exceeds 20°C/sec in the above temperature range, the retention time in the temperature range decreases, the percentage of wustite formed in the temperature range is reduced, and hence pickling performance deteriorates.

[0060] In the present invention, besides such a spring steel wire rod as stated above, a spring fabricated from such a steel wire rod is also included. By the present invention, scale flaws called red scale do not appear at all and it is possible to produce a spring which is outstandingly excellent in surface properties and has further improved fatigue resistance.

[0061] A method for fabricating a spring is not particularly limited and it is possible to adopt an ordinarily used method in an appropriate manner. As typical examples, a spring can be fabricated through any one of the spring forming processes (a) to (c) below.

- (a) Pickling → surface coating treatment → drawing → quenching and tempering (oil tempering),
- (b) Lead patenting (LP) → pickling → surface coating treatment → drawing → oil tempering, and
- (c) Annealing → pickling → surface coating treatment → skin shaving (SV) → LP → pickling → surface coating treatment → drawing → oil tempering.

[0062] As shown in the Example which will be described later, by the present invention, a rolled wire rod having low ΔCu and ΔNi values can be obtained and hence a spring outstandingly excellent in surface properties can be obtained by any of the methods described in the above spring forming processes (a) to (c).

[0063] The treatment methods described in the above spring forming processes (a) to (c) are not particularly limited and it is possible to adopt an ordinarily used method in an appropriate manner. As typical examples, pickling treatment can be processes by dipping a steel material either in a 5% to 25% H_2SO_4 solution in the temperature range of 60°C to 90°C or in a 5% to 15% HCl solution in the temperature range of 20°C to 50°C.

Example

[0064] The present invention is hereunder explained in detail on the basis of examples. However, the examples below do not limit the present invention and any arbitrary modification in the range not deviating from the afore- and after-mentioned tenor of the present invention is also included in the technological scope of the present invention.

[0065] Various types of steels shown in Table 1 (steel types A to K, the balance consisted of Fe and unavoidable impurities) of 150 kg each were fabricated by melting and refining in a small vacuum melting furnace. Each of the steels was subjected to hot forging and a billet of 155 cm square was fabricated. Thereafter steel wire rods 13.5 mm in diameter were fabricated under the heating, soaking, and hot-rolling conditions described in the wire rod forming processes 1 to 6 shown below. Among the wire rod forming processes 1 to 6, the wire rod forming processes 1 and 2 satisfied all the fabrication conditions stipulated in the present invention and represents invention examples, and the wire rod forming processes 3 to 6 did not satisfy any of the fabrication conditions stipulated in the present invention and represents comparative examples.

(Wire rod forming process 1)

[0066] A billet was heated to about 900°C at a heating rate of 15°C/min; thereafter soaked for 50 minutes at about 1,150°C, and subjected to descaling by applying high-pressure water shower for about 5 seconds under a water pressure of 100 kgf/mm² (nearly 981 MPa). Successively, the billet was subjected to rough rolling, thereafter subjected to finish rolling (the finish-rolling temperature was 920°C) while being cooled with the shower of 150 t/hr and, after the completion

of the finish rolling, cooled at a cooling rate of 7°C/sec in the temperature range up to about 700°C. The coiling temperature was 875°C.

(Wire rod forming process 2)

[0067] A billet was heated to about 800°C at a heating rate of 20°C/min, thereafter soaked for 30 minutes at about 1,100°C, and subjected to descaling by applying high-pressure water shower for about 7 seconds under a water pressure of 150 kgf/mm² (nearly 1,471 MPa). Successively, the billet was subjected to rough rolling, thereafter subjected to finish rolling (the finish-rolling temperature was 950°C) while being cooled with the shower of 130 t/hr, and, after the completion of the finish rolling, cooled at a cooling rate of 6°C/sec in the temperature range up to about 700°C. The coiling temperature was 925°C.

(Wire rod forming process 3)

[0068] A billet was heated to about 1,050°C at a heating rate of 15°C/min; thereafter soaked for 60 minutes at about 1,280°C; and subjected to descaling by applying high-pressure water shower for about 10 seconds under a water pressure of 50 kgf/mm² (nearly 490 MPa). Successively, the billet was subjected to rough rolling; thereafter subjected to finish rolling (the finish-rolling temperature was 1,000°C) while being cooled with the shower of 50 t/hr; and, after the completion of the finish rolling, cooled at a cooling rate of 2°C/sec in the temperature range up to about 700°C. The coiling temperature was 980°C.

[0069] The wire rod forming process 3 represents a comparative example which did not satisfy the fabrication conditions stipulated in the present invention and all the processes of: the heating process (the heating temperature was too high); the soaking process (the soaking temperature was too high); the descaling process preceding the hot-rolling process (the water pressure was too low); and the hot-rolling process (the finish-rolling temperature was too high, the flow rate of the shower water was too low, and the cooling rate in the temperature range of the finish-rolling temperature to 700°C was too low) deviated from the conditions stipulated in the present invention.

(Wire rod forming process 4)

[0070] A billet was subjected to heating, soaking, and descaling preceding rolling in the same way as the aforementioned wire rod forming process 3. Successively, the billet was subjected to finish rolling, cooling, and coiling in the same way as the aforementioned wire rod forming process 2.

[0071] The wire rod forming process 4 and the after-mentioned wire rod forming process 6 represents comparative examples which did not satisfy the fabrication conditions stipulated in the present invention and the processes of: the heating process (the heating temperature was too high); the soaking process (the soaking temperature was too high); and the descaling process preceding the hot-rolling process (the water pressure was too low) deviated from the conditions stipulated in the present invention.

(Wire rod forming process 5)

[0072] A billet was subjected to heating, soaking, and descaling preceding rolling in the same way as the aforementioned wire rod forming process 1. Successively, the billet was subjected to finish rolling, cooling, and coiling in the same way as the aforementioned wire rod forming process 3.

[0073] The wire rod forming process 5 represents a comparative example which did not satisfy the fabrication conditions stipulated in the present invention and the hot-rolling process (the finish-rolling temperature was too high, the flow rate of the shower water was too low, and the cooling rate in the temperature range of the finish-rolling temperature to 700°C was too low) deviated from the conditions stipulated in the present invention.

(Wire rod forming process 6)

[0074] A billet was subjected to heating, soaking, and descaling preceding rolling in the same way as the aforementioned wire rod forming process 3. Successively, the billet was subjected to finish rolling, cooling, and coiling in the same way as the aforementioned wire rod forming process 2.

[0075] Each of the steel wire rods thus fabricated was evaluated by measuring the values of ΔCu and ΔNi by the aforementioned methods, and measuring the pickling performance and the scale thickness in the following manner.

(Evaluation of pickling performance)

[0076] A fabricated steel wire rod was cut into test pieces 100 mm in length each and the test pieces were subjected to the following pickling test (beaker test) with the number of samples (n) per test being three. The test here was carried out under the same conditions as pickling treatment adopted in commercial production.

[0077] Acid solution: 15% sulfuric acid solution, containing an inhibitor (cationic amine derivative) by 0.5% to prevent a base steel from dissolving and ferrous iron by 20 g/L as an iron component,

[0078] Dipping condition: for 10 minutes at 60°C.

[0079] Then a scale exfoliation ratio after pickling was measured as described below. In the present example, the term "a scale exfoliation ratio after pickling" was defined by the percentage of the ratio of scale exfoliated at pickling (B) to the ratio of the originally existing scale (A which will be described later) (B/A x 100 (%)):

$$(1) \quad A \quad (\%) = [(W_0 - W_1) / W_0] \times 100,$$

wherein

A was the ratio of originally existing scale (the ratio of scale to a steel wire rod),

W_0 represents the weight (g) of the steel wire rod before being dipped (as rolled, bearing scale), and

W_1 represents the weight (g) of the steel wire rod after dipped in the aforementioned acid solution at 60°C until the existing scale was completely exfoliated; and

$$(2) \quad B \quad (\%) = [(W_{01} - W_2) / W_{01}] \times 100,$$

wherein

B was the ratio of the scale exfoliated after pickled under the aforementioned conditions,

W_{01} represents the weight (g) of the steel wire rod before being dipped (as rolled), and

W_2 represents the weight (g) of the steel wire rod after dipped in the aforementioned acid solution under the aforementioned dipping condition.

[0080] In the above expressions (1) and (2), although both W_0 and W_{01} represents the weight of an as-rolled steel wire rod, different reference characters were used in order to clarify that those were the weights of different test pieces (as-rolled steel wire rods) fabricated under identical conditions. That is because A and B could not be measured using an identical test piece.

[0081] In the present invention, when a scale exfoliation ratio measured as stated above was 100%, the steel wire rod was judged as excellent in pickling performance (as acceptable: ○). (Thickness of scale)

[0082] The thickness (the maximum thickness) of scale on each of the fabricated steel wire rods was measured on the basis of a photograph (3,000 magnifications) taken with an Fe-SEM (a field emission type scanning electron microscope S-4500 made by Hitachi, Ltd.).

[0083] In the present invention, when the thickness of scale measured as stated above was 40 μm or less, the steel wire rod was judged as acceptable.

(Fabrication of a spring steel wire)

[0084] Next, a spring steel wire (an oil-tempered wire) 4.0 mm in diameter was fabricated from each of the aforementioned steel wire rods under the following conditions (corresponding to the aforementioned spring forming process (a)); Surface coating treatment → drawing (dry wire drawing) → oil tempering (heating temperature: 930°C, quenching oil temperature: 70°C, tempering temperature: 450°C, and cooling after tempering: water cooling).

(Surface roughness)

[0085] Next, in order to evaluate the surface properties of a spring fabricated as stated above, surface roughness (R_y , maximum roughness) was measured in accordance with JIS B0601 1994.

[0086] In the present invention, when surface roughness (R_y) measured as stated above was 18.0 μm or less, the spring was judged as "excellent in surface properties (acceptable: ○)."

[0087] Those results are shown in Tables 2 and 3.

EP 1 788 105 A1

[Table 1]

Steel type	C	Si	Mn	Cr	Cu	Ni	P	S	V	Ti	Nb	Si/Cu
A	0.35	1.71	0.14	0.06	0.05	0.16	0.018	0.019	-	-	-	34.2
B	0.40	1.82	0.19	1.04	0.19	0.54	0.008	0.020	-	-	-	9.6
C	0.41	1.80	0.18	1.09	0.21	0.51	0.010	0.012	0.160	0.070	-	8.6
D	0.48	1.96	0.76	0.20	0.21	0.32	0.008	0.006	0.150	0.073	-	9.3
E	0.48	2.10	0.18	1.20	0.50	0.70	0.003	0.006	-	0.080	-	4.2
F	0.46	1.95	0.16	1.05	0.39	0.60	0.005	0.009	0.107	0.065	-	5.0
G	0.60	1.52	0.52	1.85	0.37	0.2	0.010	0.013	0.165	-	-	4.1
H	0.46	2.42	0.18	1.06	0.58	0.71	0.013	0.006	0.325	-	0.030	4.2
I	0.61	1.56	0.54	0.06	0.40	0.22	0.018	0.005	-	-	-	3.9
J	0.59	1.51	0.52	0.06	0.61	0.68	0.019	0.007	-	-	-	2.5
K	0.64	2.54	0.88	0.65	0.64	0.26	0.019	0.007	-	0.080	-	4.0

[Table 2]

			Cu concentration			Ni concentration			Scale thickness (μm)	Scale exfoliation ratio (%)	Judgment		Judgment
No.	Steel type	Code	Surface layer	In steel	ΔCu	Surface layer	In steel	ΔN i				Ry	
			(%)	(%)	(%)	(%)	(%)	(%)				(μm)	
1	A	A-1	0.41	0.05	0.36	0.17	0.16	0.01	31	100	○	122	○
2	A	A-4	0.44	0.05	0.39	1.21	0.16	1.05	30	98	X	19.8	X
3	A	A-3	0.58	0.05	0.53	0.18	0.16	0.02	32	97	X	21.7	X
4	B	B-1	0.19	0.19	0.00	0.58	0.54	0.04	32	100	○	13.8	○
5	B	B-4	0.21	0.19	0.02	1.71	0.54	1.17	18	93	X	25.4	X
6	B	B-3	0.78	0.19	0.59	1.21	0.54	0.67	20	92	X	26.4	X
7	C	C-1	0.25	0.21	0.04	0.65	0.51	0.14	19	100	○	14.5	○
8	C	C-2	0.38	0.21	0.17	0.52	0.51	0.01	21	100	○	15.8	○
9	C	C-3	0.45	0.21	0.24	1.59	0.51	1.08	36	93	X	19.7	X
10	C	C-4	0.74	0.21	0.53	0.53	0.51	0.02	33	95	X	19.0	X
11	D	D-1	0.21	0.21	0.00	0.35	0.32	0.03	33	100	○	15.2	○
12	D	D-2	0.22	0.21	0.01	0.38	0.32	0.06	35	100	○	14.8	○
13	D	D-3	0.28	0.21	0.07	1.39	0.32	1.07	36	95	X	22.5	X
14	D	D-4	0.78	0.21	0.57	1.25	0.32	0.93	37	92	X	27.8	X

[Table 3]

No.	Steel type	Code	Cu concentration			Ni concentration			Scale thickness (μm)	Scale exfoliation ratio (%)	Judgment	Ry (μm)	Judgment
			Surface layer	In steel	ΔCu	Surface layer	In steel	ΔNi					
			(%)	(%)	(%)	(%)	(%)	(%)					
15	E	E-1	0.25	0.19	0.06	1.55	0.70	0.85	23	100	○	15.2	○
16	E	E-6	0.22	0.19	0.03	1.89	0.70	1.19	25	89	X	22.5	X
17	E	E-3	0.72	0.19	0.53	0.71	0.70	0.01	21	91	X	19.8	X
18	E	E-2	0.21	0.19	0.02	1.61	0.70	0.91	18	100	○	14.3	○
19	F	F-1	0.40	0.39	0.01	0.85	0.60	0.25	33	100	○	10.1	○
20	F	F-4	0.45	0.39	0.06	1.92	0.60	1.32	36	90	X	25.4	X
21	F	F-3	0.95	0.39	0.56	0.91	0.60	0.31	38	92	X	26.8	X
22	F	F-2	0.62	0.39	0.23	1.01	0.60	0.41	28	100	○	12.1	○
23	G	G-1	0.39	0.37	0.02	0.52	0.20	0.32	38	100	○	15.8	○
24	G	G-4	0.40	0.37	0.03	1.62	0.20	1.42	35	90	X	30.5	X
25	G	G-3	0.99	0.37	0.62	0.39	0.20	0.19	36	88	X	34.8	X
26	H	H-1	0.59	0.58	0.01	0.75	0.71	0.04	22	100	○	149	○
27	H	H-5	0.65	0.58	0.07	1.99	0.71	1.28	28	92	X	28.2	X
28	H	H-3	1.21	0.58	0.63	0.98	0.71	0.27	29	95	X	26.3	X
29	I	I-1	1.91	0.40	1.51	0.55	0.22	0.33	33	85	X	39.8	X
30	J	J-1	2.52	0.61	1.91	0.95	0.68	0.27	21	84	X	42.1	X
31	K	K-1	0.66	0.64	0.02	0.52	0.26	0.26	15	41	X	38.5	X
32	K	K-2	0.64	0.64	0.00	0.58	0.26	0.32	12	32	X	37.1	X

[0088] Among the steel types A to K shown in Table 1, the steel types A to H are the examples which satisfy the steel compositions stipulated in the present invention, the steel types I and J are the comparative examples wherein the ratios (Si/Cu) are lower than the range stipulated in the present invention, and the steel type K is the comparative example wherein the Si content exceeds the range stipulated in the present invention.

[0089] In Tables 2 and 3, for example, the code "A-1" represents the case of using the steel type A shown in Table 1 and adopting the wire rod forming process 1 as the fabrication method, and the code "A-2" represents the case of using the steel type A shown in Table 1 and adopting the wire rod forming process 2 as the fabrication method. The same is applied to other codes.

[0090] The results shown in Tables 2 and 3 lead to the following consideration.

[0091] Firstly, the cases of Nos. 1, 4, 7, 8, 11, 12, 15, 18, 19, 22, 23, and 26 are the invention examples wherein the values ΔCu and ΔNi stipulated in the present invention satisfy the ranges stipulated in the present invention and, in any of the cases, the scale exfoliation ratio is 100% and the pickling performance is outstandingly excellent. Further, as a result of examining the compositions of the scale of the wire rods by the X-ray diffraction method, it was confirmed that the composition was controlled in the desirable range in any of the cases (not shown in the tables). Furthermore, the surface properties of the oil-tempered wires fabricated from the aforementioned wire rods were good. In addition, the tensile strength of the oil-tempered wires was measured in accordance with JIS Z2241 and resultantly it was confirmed that any of the oil-tempered wires had a high strength of about 1,900 to 2,100 MPa or more (not shown in the tables).

[0092] In contrast, the cases of Nos. 2, 3, 5, 6, 9, 10, 13, 14, 16, 17, 20, 21, 24, 25, 27, and 28 are the comparative examples wherein springs are fabricated by adopting any of the wire rod forming processes 3 to 6 which deviate from the fabrication conditions stipulated in the present invention, the value ΔCu or ΔNi deviates from the range stipulated in the present invention, and hence the scale exfoliation ratio is low and intended pickling performance cannot be obtained. Further, the surface properties of the oil-tempered wires fabricated from such wire rods also deteriorate.

[0093] Further, the cases of Nos. 29 to 32 are the comparative examples wherein the compositions of the steels deviate from the requirement of the present invention, thus the value ΔCu or ΔNi deviates from the range stipulated in the present invention, and hence the scale exfoliation ratio is low and intended pickling performance cannot be obtained. Further, the surface properties of the oil-tempered wires fabricated from such wire rods also deteriorate.

[0094] Here, in the present examples, the spring steel wire rods were fabricated through the aforementioned spring forming process (a). However, the spring forming process is not limited to the spring forming process (a) and it has been experimentally confirmed that a spring steel wire rod outstandingly excellent in surface properties can be obtained even when, for example, the aforementioned spring forming process (b) or (c) is adopted.

Claims

1. A spring steel wire rod comprising:

C: 0.35% to 0.7% (by mass, the same is hereunder applied unless otherwise specified);

Si: 1.5% to 2.50%;

Mn: 0.05% to 1.0%;

Cr: 0.05% to 1.9%;

Cu: 0.05% to 0.7%;

Ni: 0.15% to 0.8%;

P: 0.02% or less (excluding 0%); and

S: 0.02% or less (excluding 0%),

wherein the ratio of Si to Cu (Si/Cu) is in the range of 4.0 or more, and

the difference between the concentration of Cu in the surface layer and the concentration of Cu in the steel is 0.50% or less and the difference between the concentration of Ni in the surface layer and the concentration of Ni in the steel is 1.00% or less.

2. The spring steel wire rod according to Claim 1, wherein said spring steel wire rod further contains at least one element selected from among the group comprising:

V: 0.07% to 0.4%;

Ti: 0.01% to 0.1%; and

Nb: 0.01% to 0.1%.

3. A spring fabricated from the spring steel wire rod according to Claim 1 or 2.

FIG. 1

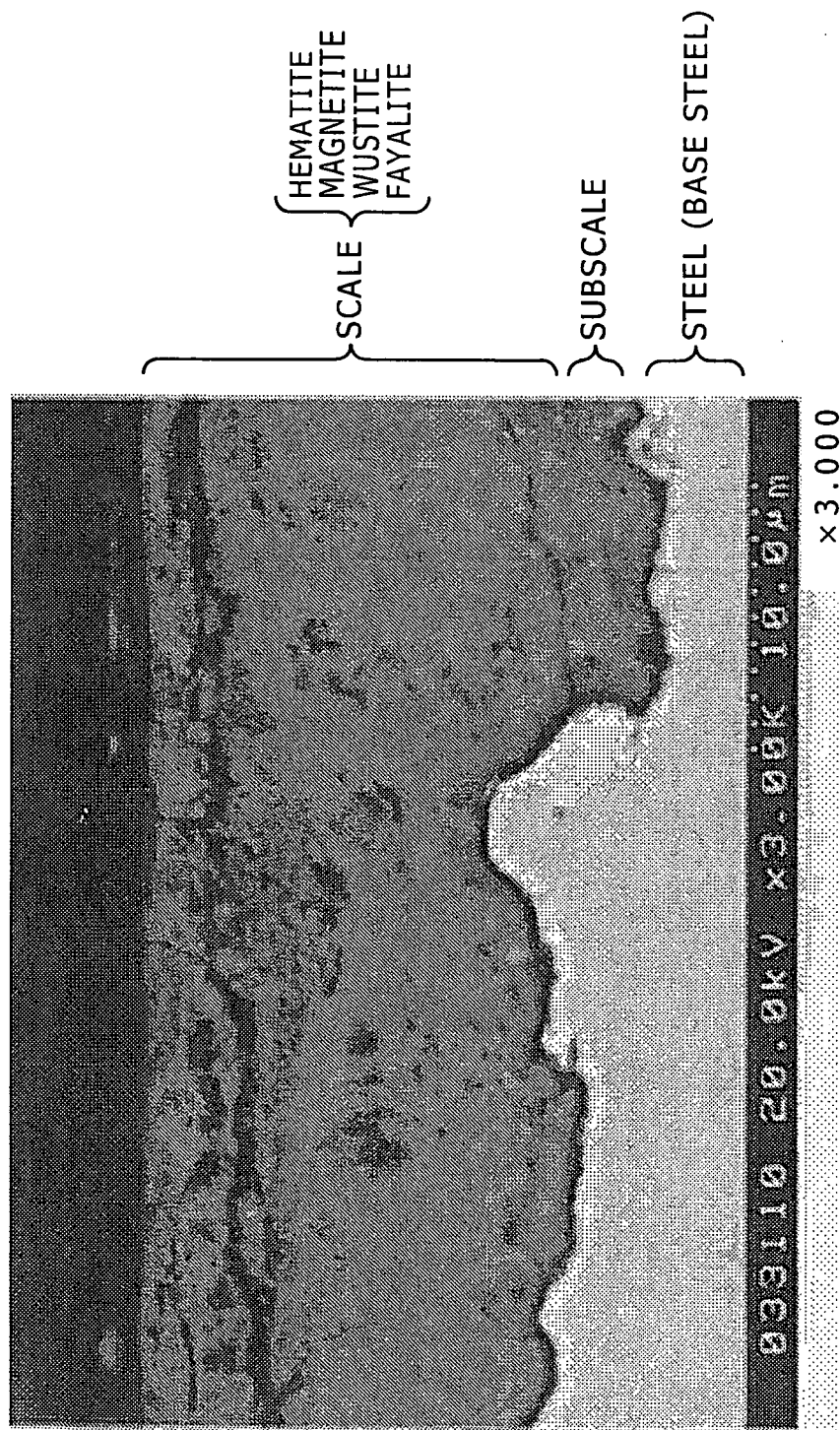


FIG. 2

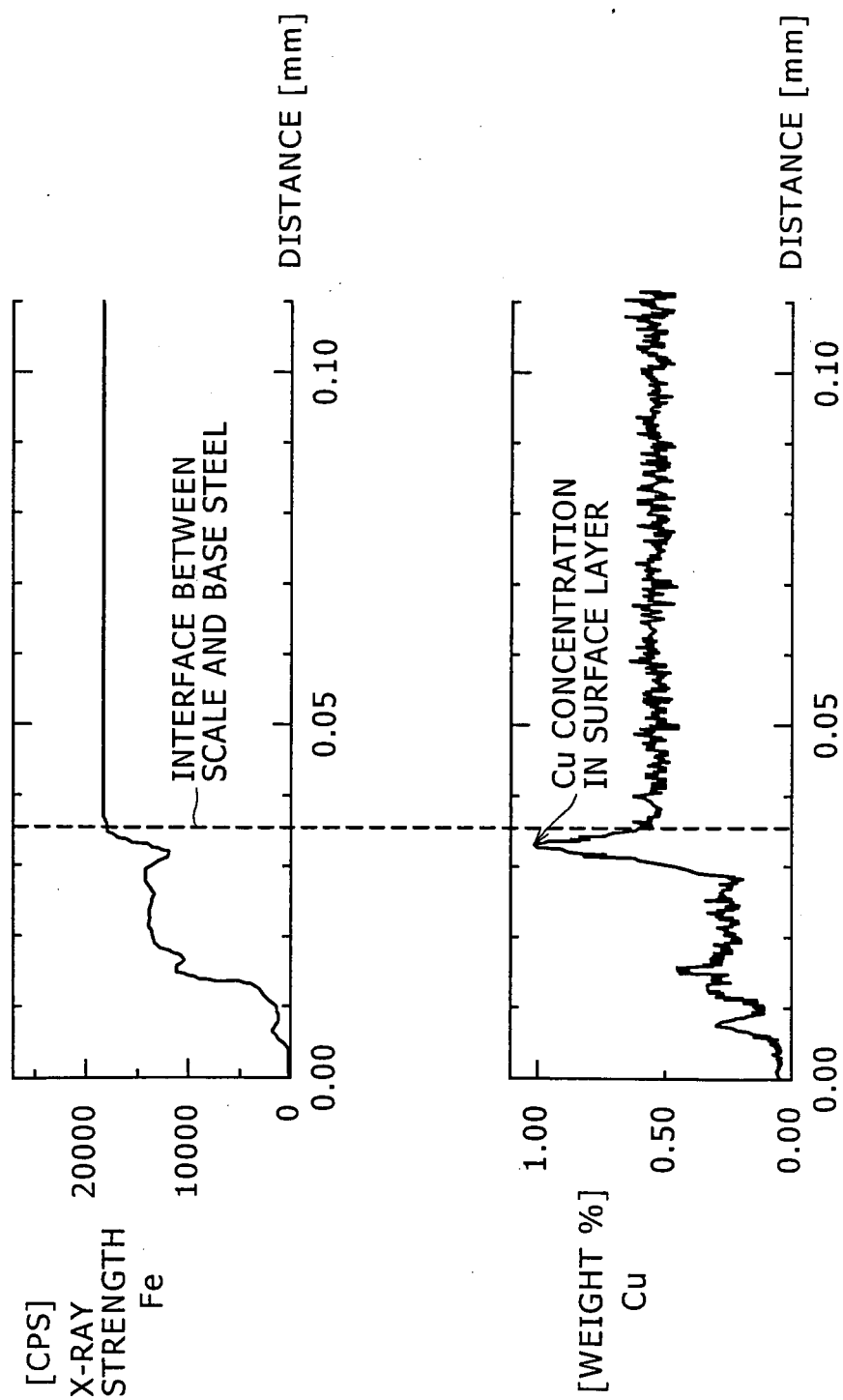
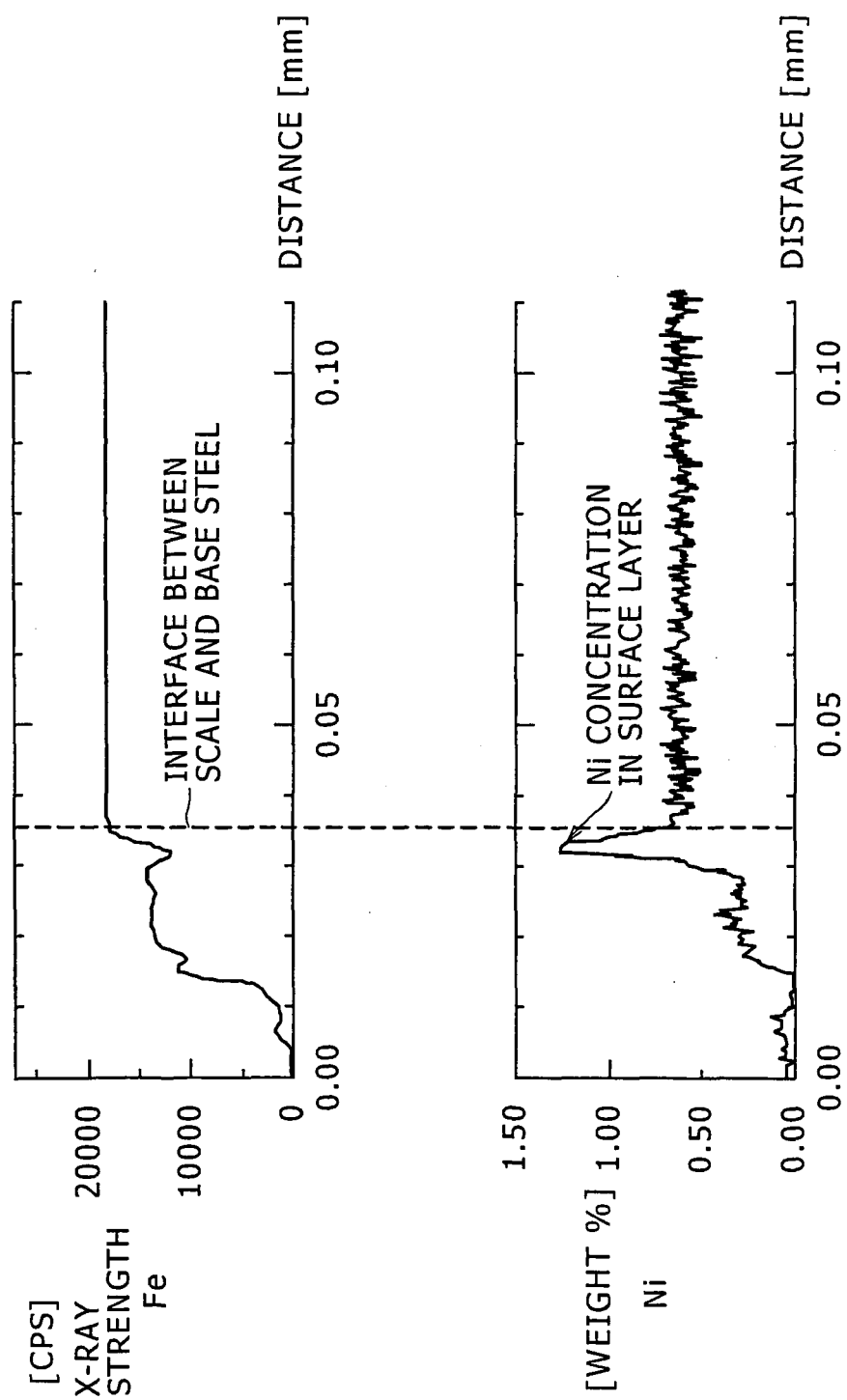


FIG. 3





DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	US 5 846 344 A (KAWAGUCHI YASUNOBU [JP] ET AL) 8 December 1998 (1998-12-08) * columns 8-10; claims 1-104; table 1 *	1-3	INV. C22C38/34
X	US 5 951 944 A (MOTOMURA HIROHARU [JP] ET AL) 14 September 1999 (1999-09-14) * claims 1-17; tables 1-4 *	1-3	
X	C. WEGST, M. WEGST: "STAHLSCHLÜSSEL" 2004, VERLAG STAHLSCHLÜSSEL WEGST GMBH, DÜSSELDORF, XP002415353 * page 180; examples 384,385 *	1-3	
X	LIKHOV V K ET AL: "Assimilation of production of wire rod for manufacture of safety critical springs" STEEL IN THE USSR, METALS SOCIETY, LONDON, GB, vol. 18, no. 2, February 1988 (1988-02), pages 81-83, XP002133957 ISSN: 0038-9218 * page 83, right-hand column; figure 2 *	1-3	TECHNICAL FIELDS SEARCHED (IPC)
A	US 6 322 641 B1 (MAKII KOICHI [JP] ET AL) 27 November 2001 (2001-11-27) * claims 1-8; tables 1-4 *	1-3	C22C
A	JP 08 295993 A (NIPPON STEEL CORP) 12 November 1996 (1996-11-12) * abstract *	1-3	
A	JP 10 008203 A (NIPPON STEEL CORP) 13 January 1998 (1998-01-13) * abstract *	1-3	
A	US 2004/129354 A1 (NAGAO MAMORU [JP] ET AL) 8 July 2004 (2004-07-08) * abstract; claims 1-13; tables 1,2 *	1-3	
		-/--	
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 18 January 2007	Examiner Catana, Cosmin
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			



DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
A	EP 0 713 924 A2 (DAIDO STEEL CO LTD [JP] DAIDO STEEL CO LTD) 29 May 1996 (1996-05-29) * tables 1,2 *	1-3	
A	JP 61 170542 A (DAIDO STEEL CO LTD) 1 August 1986 (1986-08-01) * abstract; table 1 *	1-3	
			TECHNICAL FIELDS SEARCHED (IPC)
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 18 January 2007	Examiner Catana, Cosmin
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document			

 2
 EPO FORM 1503 03.02 (P04C01)

**ANNEX TO THE EUROPEAN SEARCH REPORT
ON EUROPEAN PATENT APPLICATION NO.**

EP 06 02 1771

This annex lists the patent family members relating to the patent documents cited in the above-mentioned European search report.
The members are as contained in the European Patent Office EDP file on
The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

18-01-2007

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5846344	A	08-12-1998	NONE	
US 5951944	A	14-09-1999	NONE	
US 6322641	B1	27-11-2001	BR 0001117 A	24-07-2001
			DE 10017069 A1	18-01-2001
			FR 2792002 A1	13-10-2000
			JP 3435112 B2	11-08-2003
			JP 2000355736 A	26-12-2000
JP 8295993	A	12-11-1996	NONE	
JP 10008203	A	13-01-1998	JP 3548341 B2	28-07-2004
US 2004129354	A1	08-07-2004	AU 2003207212 A1	02-09-2003
			BR 0303066 A	09-03-2004
			CN 1498283 A	19-05-2004
			EP 1473375 A1	03-11-2004
			WO 03066923 A1	14-08-2003
			JP 2003226937 A	15-08-2003
EP 0713924	A2	29-05-1996	DE 69514081 D1	27-01-2000
			DE 69514081 T2	20-04-2000
			JP 8158013 A	18-06-1996
			US 5643532 A	01-07-1997
JP 61170542	A	01-08-1986	NONE	

REFERENCES CITED IN THE DESCRIPTION

This list of references cited by the applicant is for the reader's convenience only. It does not form part of the European patent document. Even though great care has been taken in compiling the references, errors or omissions cannot be excluded and the EPO disclaims all liability in this regard.

Patent documents cited in the description

- JP 6297026 A [0008] [0009] [0009] [0011]
- JP 2004223523 A [0009] [0011] [0011]