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(54) **STEEL WIRE FOR SPRINGS HAVING EXCELLENT FATIGUE PROPERTIES, AND SPRING**

(57) This steel wire for springs: contains specific amounts of C, Si, Mn, Cr, Al, Ca and Ti, with the remainder comprising iron and unavoidable impurities; has oxide inclusions, which are present in a cross section parallel to the longitudinal direction of the wire spring and have minor axes of at least 1 μm, containing specific amounts of CaO, $Al_2O_3$, $SiO_2$ MgO, MnO and $TiO_2$ The steel wire for springs satisfies CaO + $Al_2O_3$ + $SiO_2$ + MgO + MnO + $TiO_2 \geq 80\%$, and the number of oxide inclusions having a minor axis of 2 μm or greater present in the cross section exceeds 0.002/mm$^2$.



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## Description

Technical Field

**[0001]** The present invention relates to a steel wire rod for a spring excellent in fatigue properties and a spring.

Background Art

**[0002]** With increase in requirement for weigh reduction and high output of automobiles and the like, improvement of fatigue properties has been required in springs such as valve springs and suspension springs. Further improvement of fatigue properties has been required also in steel wire rods for springs, such as rolled steels used as materials thereof and drawn wire rods obtained by subjecting the rolled steels to wire drawing. In particular, a request for improvement of fatigue properties is very strong in steel wire rods for valve springs.

**[0003]** In the steel wire rods for springs, which require high fatigue strength, it is necessary to reduce as possible nonmetallic inclusions becoming start points of wire breakage or fatigue breakage, or to reduce the size thereof. For example, in steels for valve springs, a technology has been proposed in which inclusions are controlled to a system containing $SiO_2$-$Al_2O_3$-CaO-MgO-MnO and the like, using so-called "Si-killed steel" which deoxidizes using Si so as not to form $Al_2O_3$ harmful to fatigue properties, thereby refining the inclusions. In addition, there have been proposed a method of controlling composition of nonmetallic inclusions to a low-melting-point region, thereby refining the inclusions, a method of extending inclusions during hot rolling, thereby fragmenting the inclusions, and the like:

**[0004]** For example, Non-Patent Document 1 describes that, in a steel for a valve spring, deformation during hot working is accelerated by controlling a composition of inclusions to a CaO-$Al_2O_3$-$SiO_2$-based or MnO-$Al_2O_3$-$SiO_2$-based amorphous stabilized composition, thereby preventing start points of fatigue breakage from being formed to improve fatigue properties.

**[0005]** The present inventors also variously propose steel wire rods for springs excellent in fatigue properties and the like. For example, Patent Document 1 proposes a technology in which the whole inclusions have a low melting point and are easily deformable, and hard $SiO_2$ is less likely to be formed, even when phase separation occurs at the time of heating before hot rolling or during hot rolling. Further, Patent Document 2 proposes a technology in which fragmentation of inclusions during hot rolling is accelerated by forming many fine grains in the inclusions to enhance refinement thereof. Furthermore, Patent Document 3 proposes a technology in which at least one of $LiO_2$, $Na_2O$ and $K_2O$ is allowed to be positively contained, in order to decrease the melting point and viscosity of composite oxide-based inclusions to be formed, thereby finally refining the inclusions.

**[0006]** In addition, Patent Document 4 describes that addition of $ZrO_2$ as an unconventional oxide component contributes to securing of an amorphous phase. Further, Patent Document 5 describes that oxide-based inclusions are finely fragmented by allowing $B_2O_3$ to be contained in a composite oxide (for example, such as a CaO-$Al_2O_3$-$SiO_2$-based composite oxide or a CaO-$Al_2O_3$-$SiO_2$-MgO-based composite oxide), thereby being able to remarkably improve wire drawability and fatigue strength.

Prior Art Documents

Patent Documents

**[0007]**


Patent Document 1: Japanese Patent No. 4134204

Patent Document 2: Japanese Patent No. 4347786

Patent Document 3: Japanese Patent No. 4423050

Patent Document 4: JP-A-2010-202905

Patent Document 5: JP-A-2009-263704


Non-Patent Document

**[0008]** Non-Patent Document 1: Tsuyoshi Mimura, 182nd and 183rd Nishiyama Memorial Technical Lecture "Inclusion Control and High Cleanliness Degree Steel Production Technology", edited by The Iron and Steel Institute of Japan, Tokyo, 2004, p. 125

## Summary of the Invention

### Problems to Be Solved by the Invention

**[0009]** However, for example, in the above Patent Document 3, Li having strong deoxidizing force is positively added as a formation origin of oxide-based inclusions. However, there is a problem that control of the $LiO_2$ concentration is difficult, because Li is easily vaporized. Further, in the above Patent Document 3, there is difficulty in production, as described as "the $Li_2O$ concentration in inclusions cannot be measured by a conventional EPMA (Electron Probe X-ray Micro Analyzer), and therefore, an analytical method according to SIMS (Secondary Ion Mass Spectrometry) has been uniquely developed". Furthermore, from experimental results of the present inventors, it has been revealed that $ZrO_2$ described in the above Patent Document 4 and $B_2O_3$ described in the above Patent Document 5 may conversely deteriorate fatigue properties.
**[0010]** The present invention has been made in view of the above circumstances, and an object thereof is to provide a steel wire rod for a spring extremely excellent in fatigue properties, and a spring.

### Means for Solving Problems

**[0011]** The steel wire rod for a spring excellent in fatigue properties in the present invention, which is capable of solving the problems includes:

C: 0.2 to 1.2% (% means mass%, hereinafter the same, unless otherwise vindicated),
Si: 1.0 to 3%,
Mn:0.1 to 2%,
Cr: 3% or less (not inclusive of 0%),
Al: 0.0002 to 0.005%,
Ca: 0.0002 to 0.002%,
Ti: 0.0003 to 0.010%, and
balance: iron and unavoidable impurities, and

an average composition of oxide-based inclusions having a minor axis of 1 μm or more which are present in a cross section parallel to a longitudinal direction of a steel satisfies, by mass%, CaO: 35% or less (inclusive of 0%), $Al_2O_3$: 40% or less (inclusive of 0%), $SiO_2$: 30 to 95%, MgO: 8% or less (inclusive of 0%), MnO: 5% or less (inclusive of 0%), $TiO_2$: 3 to 10%, and $CaO+Al_2O_3+SiO_2+MgO+MnO+TiO_2 \geq 80\%$, and
the number of oxide-based inclusions having a minor axis of 2 μm or more which are present in the cross section is more than 0.002 inclusions/$mm^2$.
**[0012]** In particular, it is preferred that the average composition of the oxide-based inclusions satisfies: CaO: 10 to 35%, $Al_2O_3$: 10 to 40%, $SiO_2$: 30 to 70%, MgO: 8% or less (inclusive of 0%), MnO: 5% or less (inclusive of 0%), $TiO_2$: 3 to 10%, and $CaO+Al_2O_3+SiO_2+MgO+MnO+TiO_2 \geq 80\%$, and the number of the oxide-based inclusions having a minor axis of 2 μm or more which are present in the cross section is more than 0.002 inclusions/$mm^2$.
**[0013]** In the steel wire rod for a spring, the average composition of the oxide-based inclusions may further satisfy, by mass%, $ZrO_2$: less than 1% (not inclusive of 0%) and $Na_2O$: less than 5% (inclusive of 0%).
**[0014]** The steel wire rod for a spring may further include Ni: 0.5% or less (not inclusive of 0%), and Cu: 0.5% or less (not inclusive of 0%).
**[0015]** The steel wire rod for a spring may further include V: 0.5% or less (not inclusive of 0%).
**[0016]** The spring excellent in fatigue properties, which is capable of solving the problems, is obtained using the steel wire rod for a spring.

### Advantageous Effects of the Invention

**[0017]** According to the present invention, chemical components of a steel wire rod for a spring, and a composition and the number of oxide-based inclusions are appropriately controlled. Therefore, a steel wire rod for a spring extremely excellent in fatigue properties can be obtained.

### Mode for Carrying Out the Invention

**[0018]** In order to provide a steel wire rod for a spring having extremely excellent fatigue properties, the present inventors have made studies also after disclosure of the above Patent Documents 1 to 3 and the like. Conventionally, for improvement of fatigue properties, it is effective to refine, oxide-based inclusions by fragmentation due to extension during hot rolling, and there has been proposed a method of controlling a composition of oxide-based inclusions obtained by Si deoxidization to a $SiO_2$-containing composition in which amorphousness is relatively stable, for example, $SiO_2$-CaO-$Al_{2O}$3-MgO-MnO or the like. In that case, as a means for realizing refinement even when the inclusions are crystallized, the technology of Patent Document 2 is proposed as a method for controlling a crystallization state (a fine grain phase is precipitated without being completely crystallized).

**[0019]** However, according to subsequent studies of the present inventors, it has been found that even when the size is so fine as to usually scarcely become a start point of failure, a void occurs at an interface between steel as a matrix and the oxide-based inclusion depending on a crystallization form, and may become the start point of failure under severer test conditions. On that basis, it has been found that amorphousness of the oxide-based inclusions can be kept more stable by allowing $TiO_2$ to be contained in the oxide-based inclusions based on $SiO_2$-CaO-$Al_2O_3$-MgO-MnO as reported in the above Patent Documents, thereby obtaining high fatigue properties. Thereby, high fatigue properties can be realized in a composition in which analysis or control of the oxide-based inclusions is easier. Here, in the oxide-based inclusions in which $TiO_2$ is allowed to be contained, based on $SiO_2$-CaO-$Al_2O_3$-MgO-MnO, an average composition thereof satisfies, by mass%, CaO+$Al_2O_3$+$SiO_2$+MgO+MnO+$TiO_2$≥80%. In addition to the effect due to the oxide-based inclusions based on $SiO_2$-CaO-$Al_2O_3$-MgO-MnO as reported in the above Patent Documents, the effect due to $TiO_2$ is exerted by containing 80% or more of these in total.

**[0020]** Then, in order to exert the above effect due to $TiO_2$ it has been found that it is useful to allow Ti to be contained within a range of from 0.0003 to 0.010% as a component in steel, thus completing the present invention.

**[0021]** In the present invention, the reason why fatigue properties are improved by allowing a predetermined amount of $TiO_2$ to be contained in the above oxide-based inclusions is not clear in detail. However, it is considered as follows.

**[0022]** That is, containing of $TiO_2$ in the above oxide-based inclusions obtained by Si deoxidization causes separation into two phases of a $TiO_2$-concentrated phase (A phase) and a $SiO_2$-concentrated phase (B phase). The reason for the separation into two phases is considered because $TiO_2$ has a property to be separated from $SiO_2$ as two liquid phases at a molten steel stage. As a result, the $SiO_2$ concentration in the $SiO_2$-concentrated phase (B phase) is increased to suppress crystallization of gehlenite, spinel (MgO-$Al_2O_3$) and the like, which is liable to occur in Si-killed steel. On the other hand, also in the $TiO_2$-concentrated phase (A phase), the liquidus temperature is decreased to suppress crystallization by containing $TiO_2$ in the oxide-based inclusions. As a result, it is presumed that it becomes possible to enhance amorphous stability of the oxide-based inclusions.

**[0023]** On the other hand, Patent Documents 1 to 5 described above do not disclose the above characterizing portion in the present invention. For example, in the above Patent Document 4, $TiO_2$ is mentioned as an impurity of the inclusions. However, it is not described at all that fatigue properties are improved by controlling the $TiO_2$ amount within a predetermined range as in the present invention. As a matter of fact, in all of Examples of the above Patent Document 4, examples of containing impurities such as FeO and $TiO_2$ in an amount of 1.0% are only disclosed, and this does not provide the effect of improving fatigue properties due to addition of $TiO_2$ (see No. 14 in the table described later). In the first place, the above Patent Document 4 is different from the present invention in the composition of the oxide-based inclusions in that $ZrO_2$ is contained in an amount of 1% or more.

**[0024]** The present invention is described in detail below.

**[0025]** As described above, in the present invention, Ti is contained within a range of 0.0003 to 0.010% as a component in steel and $TiO_2$ is contained in the above oxide-based inclusions of $SiO_2$-CaO-$Al_2O_3$-MgO-MnO within a range of 3 to 10%.

**[0026]** In this description, the steel wire rod for a spring includes both a steel after rolling (rolled steel) and a drawn wire rod obtained by subjecting the rolled steel to wire drawing. In the present invention, these are called the "steel wire rod" as a whole.

**[0027]** In this description, the oxide-based inclusions mean oxide-based inclusions in which oxide forming elements such as Ca, Al, Si, Ti, Mn, Mg, Na, Cr and Zr bond to oxygen. The above oxide-based inclusions can be observed under an electron microscope and measured by an energy dispersive X-ray spectrometry (EDX) or a wavelength-dispersive X-ray spectrometry (WDX). The details of measuring methods will be described later.

**[0028]** First, the composition of the oxide-based inclusions is described. As described above, in the present invention, for the oxide-based inclusions contained in steel, the average composition of the oxide-based inclusions having a minor axis of 1 $\mu$m or more which are present in a cross section parallel to a longitudinal direction of the steel satisfies, by mass%, CaO: 35% or less (inclusive of 0%), $Al_2O_3$: 40% or less (inclusive of 0%), $SiO_2$: 30 to 95%, MgO: 8% or less (inclusive of 0%), MnO: 5% or less (inclusive of 0%), $TiO_2$: 3 to 10%, and CaO+$Al_2O_3$+$SiO_2$+MgO+MnO+$TiO_2$≥80%, and preferably satisfies CaO: 10 to 35%, $Al_2O_3$: 10 to 40%, $SiO_2$: 30 to 70%, MgO: 8% or less (inclusive of 0%), MnO: 5% or less (inclusive of 0%), $TiO_2$ 3 to 10%, and CaO+$Al_2O_3$+$SiO_2$+MgO+MnO+$TiO_2$≥80%. The number of the oxide-based inclusions having a minor axis of 2 $\mu$m or more which are present in the above cross section is preferably more than 0.002 inclusions/$mm^2$.

**[0029]** First, the composition of the oxide-based inclusions is described. As described above, in the present invention, in the oxide-based inclusions contained in steel, the average composition of the oxide-based inclusions having a minor axis of 1 μm or more which are present in a cross section parallel to a longitudinal direction of the steel satisfies, by mass%, CaO: 35% or less (inclusive of 0%), $Al_2O_3$: 40% or less (inclusive of 0%), $SiO_2$: 30 to 95%, MgO: 8% or less (inclusive of 0%), MnO: 5% or less (inclusive of 0%), $TiO_2$: 3 to 10%, and $CaO+Al_2O_3+SiO_2+MgO+MnO+TiO_2 \geq 80\%$, and the number of the oxide-based inclusions having a minor axis of 2 μm or more which are present in the above cross section is more than 0.002 inclusions/$mm^2$.

[CaO: 35% or less]

**[0030]** CaO is a basic oxide, and when it is contained in $SiO_2$ of an acidic oxide, the liquidus temperature of the oxide is decreased to have an effect of suppressing crystallization of the oxide-based inclusions. It may therefore be contained in the inclusions. The content thereof is desirably 10% or more, and more preferably 15% or more. However, when the CaO content is too high, the oxide-based inclusions are crystallized. Therefore, the upper limit thereof is 35% or less. The upper limit of the CaO content is preferably 30% or less.

[$SiO_2$: 30 to 95%]

**[0031]** $SiO_2$ is an acidic oxide and a component which is essential for making the oxide-based inclusions amorphous. In order to effectively exert such an effect, the lower limit of the $SiO_2$ content is 30% or more. The lower limit of the $SiO_2$ content is preferably 40% or more. However, when the $SiO_2$ content is more than 95%, extensibility of the above inclusions is decreased to cause easy formation of voids, resulting in deterioration of fatigue properties. Therefore, the upper limit of the $SiO_2$ content is 95% or less, preferably 70% or less, and more preferably 50% or less.

[$Al_2O_3$: 40% or less]

**[0032]** $Al_2O_3$ is an amphoteric oxide, and when it is contained in $SiO_2$ of an acidic oxide, the liquidus temperature of the oxide is decreased to have an effect of suppressing crystallization of the oxide. It may therefore be contained in the inclusions. The content thereof is desirably 10% or more, and more preferably 20% or more. On the other hand, when the upper limit of the $Al_2O_3$ content is more than 40%, an $Al_2O_3$ crystal phase such as corundum is crystallized in molten steel and during a solidification process, or a $MgO \cdot Al_2O_3$ crystal phase such as spinel is crystallized together with MgO. Further, these crystal phases are formed in a rolling temperature range. These solid phases are hard and remain as coarse inclusions to deteriorate fatigue properties. From such a viewpoint, the upper limit of the $Al_2O_3$ content is required to be 40% or less, and is preferably 30% or less.

[MgO: 8% or less (inclusive of 0%)]

**[0033]** MgO is not an essential component in the present invention, but has an effect of controlling a $SiO_2$-based oxide to an optimum composition to decrease the melting point thereof. In order to effectively exert such an action, the lower limit of the MgO content is preferably 0.2% or more. However, when the MgO content is too large, the melting point of the $SiO_2$-based oxide is increased, or MgO-based crystals are formed. For this reason, the upper limit thereof is 8% or less. It is preferably 5% or less, and more preferably 3% or less.

[MnO: 5% or less (inclusive of 0%)]

**[0034]** Similarly to the above case of MgO, MnO is also not an essential component in the present invention. However, MnO has an effect of decreasing the melting point of the $SiO_2$-based oxide. In order to effectively exert such an action, the lower limit of the MnO content is preferably 0.1% or more, and more preferably 0.5% or more. However, in a high Si steel containing Si in an amount of 1.0% or more as in the present invention, it is not realistic to control MnO to an excessively high concentration. Therefore, the upper limit of the MnO content is 5% or less.

[$TiO_2$: 3 to 10%]

**[0035]** $TiO_2$ is an oxide component which is the characteristics feature in the present invention. As described above, containing of $TiO_2$ in $SiO_2$ of the acidic oxide causes separation into two phases of the $TiO_2$-concentrated phase (A phase) and the $SiO_2$-concentrated phase (B phase), and both phases have an action of suppressing crystallization. As a result, it can be realized that crystallization of $SiO_2$-cntaining oxide-based inclusions obtained in Si-killed steel during hot working is suppressed, and that occurrence of voids at interfaces between the steel and the oxide-based inclusions is suppressed, thereby further improving fatigue properties. Such effects are obtained by controlling the lower limit of the $TiO_2$ content to 3% or more. Therefore, the $TiO_2$ content is 3% or more. It is preferably 4% or more, and more preferably 5% or more. However, when the $TiO_2$ content is too large, a $TiO_2$-based oxide is formed alone as a crystal phase. Therefore, fatigue properties are decreased. For this reason, the upper limit of the $TiO_2$ content is 10% or less. It is preferably 8% or less, and more preferably 7% or less.

[$CaO+Al_2O_3+SiO_2+MgO+MnO+TiO_2 \geq 80\%$]

**[0036]** In the present invention, it is necessary to control the contents of the respective oxides as described above and to control the total of these contents to 80% or more, thereby keeping amorphousness of the oxide-based inclusions to improve fatigue properties. The larger total amount of the above oxides is better, and preferably 90% or more. It is most preferably 100%.

**[0037]** As described above, the oxide-based inclusions contained in the steel wire rod for a spring in the present invention are basically CaO, $Al_2O_3$, $SiO_2$, MgO, MnO and $TiO_2$, and the balance is impurities. The above impurities include, for example, impurities unavoidably contained in a production process and the like. The above impurities can be contained to such an extent that desired fatigue properties are obtained without adversely affecting a crystallization state or form of the oxide-based inclusions. However, in relation to the total amount of the above oxide-based inclusions, the total amount of the impurities is required to be controlled to at most 20%.

**[0038]** The above impurities include, for example, $ZrO_2$, $Na_2O$, $Cr_2O_3$ and the like. Of these, when the concentration of $ZrO_2$ in the oxide-inclusions is increased, crystallization of the above inclusions is accelerated to deteriorate fatigue properties. It is therefore preferably decreased as much as possible. The $ZrO_2$ content is preferably less than 1%, more preferably 0.5% or less, and most preferably not contained. Further, $Na_2O$ has a wide allowance, compared to the above $ZrO_2$ so that it may be contained in an amount of about 5%.

[Number of oxide-based inclusions having a minor axis of 2 μm or more which are present in a cross section parallel to a longitudinal direction of steel: more than 0.002 inclusions/$mm^2$]

**[0039]** In the present invention, it is necessary to control the contents of the respective oxides and the total amount thereof, and to satisfy that the number of the oxide-based inclusions having a minor axis of 2 μm or more is more than 0.002 inclusions/$mm^2$. Thereby, high fatigue properties are secured, and homogeneity is also improved. The number of the oxide-based inclusions having a minor axis of 2 μm or more is preferably 0.005 inclusions/$mm^2$ or more, more preferably 0.01 inclusions/$mm^2$ or more and still more preferably 0.05 inclusions/$mm^2$ or more. The above "oxide-based inclusions" as used herein mean oxide-based inclusions in which oxide forming elements such as Ca, Al, Si, Ti, Mn, Mg, Na, Cr and Zr bond to oxygen, and should not be limited to the above-mentioned oxides (CaO, $Al_2O_3$, $SiO_2$, MgO, MnO and $TiO_2$). Further, of the above oxide-based inclusions, the ones having "a minor axis of 2 μm or more" are particularly specified, because the oxide-based inclusions having a minor axis of less than 2 μm have relatively little adverse effects on fatigue properties.

**[0040]** Components in steel are described below.

[C: 0.2 to 1.2%]

**[0041]** C is an element necessary for securing predetermined strength, and in order to effectively exert such properties, the C content is 0.2% or more. It is preferably 0.5% or more. However, when the C content is excessive, steel becomes brittle and therefore does not become practical. Therefore, the upper limit thereof is 1.2% or less. The upper limit of the C content is preferably 0.8% or less, and more preferably 0.7% or less

[Si: 1.0 to 3%]

**[0042]** Si is an important element contributing to high strengthening of the steel wire rod for a spring and improvement of fatigue properties. Further, it is also a useful element for enhancing softening resistance and improving setting resistance. Furthermore, Si is an essential element also for controlling to a composition of desired oxide-based inclusions. In order to effectively exert such actions, the Si content is 1.0% or more. The Si content is preferably 1.4% or more, and more preferably 1.8% or more. However, when the Si content is excessive, hard pure $SiO_2$ may possibly be formed during solidification, and surface decarburization and surface flaws are increased to deteriorate fatigue properties in some cases. For this reason, the upper limit of the Si amount is 3% or less. It is preferably 2.4% or less, and more preferably 2.2% or less.

[Mn: 0.1 to 2%]

**[0043]** Mn is an element acting as a deoxidizing agent and additionally increasing hardenability, thereby contributing to the enhancement of strength. In order to effectively exert such actions, the lower limit of the Mn content is 0.1% or more. It is preferably 0.5% or more. However, when the Mn amount is excessive, toughness and ductility are deteriorated. For this reason, as the upper limit thereof, it is 2% or less. It is preferably 1% or less.

[Cr: 3% or less (not inclusive of 0%)]

**[0044]** Cr is an element for improving matrix strength of the steel wire rod for a spring by solid solution strengthening. Further, similarly to the case of Mn, Cr also effectively acts on improvement of hardenability. The Cr amount is preferably 0.5% or more, and more preferably 0.9% or more. However, when Cr is excessive, the steel wire rod for a spring tends to become brittle to increase sensitivity of the oxide-based inclusions. Therefore, fatigue properties are deteriorated. Then, the upper limit of the Cr amount is 3%. As the upper limit of the Cr amount, it is preferably 2% or less, and more preferably 1 % or less.

[Al: 0.0002 to 0.005%]

**[0045]** When the Al content is increased and particularly exceeds 0.005%, the production amount of hard oxides mainly composed of $Al_2O_3$ is increased, and the oxides remain as coarse oxides even after further reduction. Therefore, fatigue properties are decreased. Accordingly, the Al content is 0.005% or less, preferably 0.002% or less, and more preferably 0.0015% or less. However, when the Al content is less than 0.0002%, the $Al_2O_3$ content in the oxide-based inclusions is excessively decreased to form crystal phases containing a large amount of $SiO_2$ Accordingly, the lower limit of the Al content is 0.0002% or more, and preferably 0.0005% or more.

[Ca: 0.0002 to 0.002%]

**[0046]** Ca is a component contained in the steel wire rod by slag refining for controlling the composition of the oxide-based inclusions. In the present invention, it is an effective element for controlling the CaO content in the oxide-based inclusions to suppress crystallization of the oxide-based inclusions, thereby improving fatigue properties. In order to exert such an effect, the Ca content is 0.0002% or more, preferably 0.0003% or more, and more preferably 0.0005% or more. However, when the Ca content is excessive and is more than 0.002%, the ratio of CaO becomes too high, resulting in crystallization of the oxides. Accordingly, the Ca content is 0.002% or less, preferably 0.001% or less, and more preferably 0.0008% or less.

[Ti: 0.0003 to 0.010%]

**[0047]** Ti is an element which is the characteristic feature in the present invention. A predetermined amount of Ti is added to appropriately control the $TiO_2$ content in the oxide-based inclusions, thereby more enhancing amorphous stability to further improving fatigue properties. In order to obtain such an effect, the Ti content is required to be 0.0003% or more. It is preferably 0.0005% or more, and more preferably 0.0008% or more. However, when the Ti content is increased to be more than 0.010%, the $TiO_2$-based oxide is formed alone as a crystal phase. Accordingly, the Ti content is 0.010% or less. It is preferably 0.0050% or less, and more preferably 0.0030% or less.

**[0048]** The elements in steel used in the present invention are as described above, and the balance is iron and unavoidable impurities. The above unavoidable impurities include, for example, elements introduced depending on situations of raw materials, materials, production facilities and the like, such as S, P, H and N.

**[0049]** Further, in the present invention, the following selective components may be contained.

[Ni: 0.5% or less (not inclusive of 0%)]

**[0050]** Ni is an effective element for suppressing decarburization of ferrite formed in hot rolling at the time of producing the steel wire rod for a spring or in heat treatment at the time of producing the spring. Further, Ni has an action to increase toughness of the spring after hardening and tempering. As the lower limit of the Ni amount, it is preferably 0.05% or more, more preferably 0.15 % or more, and still more preferably 0.2% or more. On the other hand, when the Ni amount is excessive, the residual austenite amount is increased during hardening and tempering treatment to decrease the tensile strength. For this reason, as the upper limit of the Ni amount, it is preferably 0.5% or less, and more preferably 0.3% or less.

[Cu: 0.5% or less (not inclusive of 0%)]

**[0051]** Cu is an effective element for suppressing decarburization of ferrite formed during hot rolling at the time of producing the steel wire rod for a spring or in heat treatment at the time of producing the spring. Therefore, it may be contained in an amount of 0.05% or more. As the upper limit thereof, it is preferably 0.5% or less, and more preferably 0.3% or less.

[V: 0.5% or less (not inclusive of 0%)]

**[0052]** V bonds to carbon, nitrogen or the like to form fine carbide, nitride or the like, and an element useful for improving hydrogen brittleness resistance and fatigue properties. Further, V is an element contributing to improvement of toughness, proof stress, setting resistance and the like by refinement effect of grains. As the lower limit of V amount, it is preferably 0.05% or more, and more preferably 0.10% or more. However, when the V amount is excessive, the amount of carbide that is not soluted in austenite during heating for hardening is increased, resulting in difficulty to obtain sufficient strength and hardness. Additionally, coarsening of nitride is brought about to cause easy occurrence of fatigue breakage. Further, when the V amount is excessive, the residual austenite amount is increased to decrease the hardness of the spring. For this reason, as the upper limit of the V amount, it is preferably 0.5% or less, and more preferably 0.4% or less.

**[0053]** A method for producing the steel wire rod for a spring in the present invention is described below. In the present invention, it is important to produce it, particularly paying attention to respective steps of a smelting step and hot working so as to obtain the desired composition and number of oxide-based inclusions. However, the other steps are not particularly limited, and methods usually used for the production of steel wire rods for springs can be appropriately selected and used.

**[0054]** The preferred smelting step and hot step used in the present invention are as follows.

(Smelting step)

**[0055]** First, deoxidization by Si is performed, and C, Si, Mn, Cr, Ti, Al, Ni and V are added so as to provide the composition specified in the present invention. Thereafter, slag refining is performed using $CaO\text{-}SiO_2$-based slag according to a conventional method, thereby controlling to a composition of $CaO\text{-}Al_2O_3\text{-}SiO_2\text{-}MgO\text{-}MnO\text{-}TiO_2$. At this time, the above slag is fully suspended in molten steel, thereby being able to adjust the number of oxide-based inclusions having a minor axis of 2 μm or more to a predetermined range. In the present invention, a predetermined amount of $TiO_2$ is contained as the oxide-based inclusions. However, a controlling method thereof is also not particularly limited, and it should be sufficient to add Ti during smelting so that the Ti amount in the steel is controlled within a range of 0.0003 to 0.010%, based on a method usually used in the technical field in the present invention. A method for adding Ti is not particularly limited, and for example, an iron-based alloy containing Ti may be added to perform adjustment, or the Ti concentration in molten steel may be controlled by controlling a slag composition.

[Hot step]

**[0056]** After a cast slab obtained is heated in a heating furnace at 1100 to 1300°C, blooming is performed at 900 to 1200°C. Thereafter, hot rolling is performed at 800 to 1100°C to a desired diameter.

**[0057]** The steel rod for a spring in the present invention is thus obtained. However, after the above hot rolling, wire drawing may be further performed to obtain the steel wire rod for a spring. Wire drawing conditions are not particularly limited, and a method usually used can be employed.

**[0058]** The steel wire rod for a spring in the present invention is very useful as a material for a processed product requiring high fatigue properties. The above processed products include, for example, springs such as valve springs to be used in engines or suspensions of automobiles, clutch springs, brake springs and suspension springs; steel wires such as steel cords; and the like.

**[0059]** A production method of the above spring is not particularly limited, and the spring can be produced according to a conventional method. Specifically, the above steel wire rod for a spring is annealed as needed, and thereafter subjected to stripping treatment, lead patenting treatment, wire drawing and oil tempering treatment to produce the spring.

**[0060]** The present invention is described below in more detail with reference to examples, but the present invention should not be construed as being limited by the following examples, changes may be made without departing from the spirit described above and later, and these should be understood to be included in the technical scope of the present invention.

Examples

[Production of cast slab]

**[0061]** Using a small-sized melting furnace having a volume of 150 kg/1ch, test steels having various chemical components shown in the following Table 1 were smelted, and cast slabs of 245 mm diameter x 480. mm were prepared. In smelting, using a crucible of a MgO-based refractory during smelting, at least one of Ni and V was added as needed, as well as C, Si, Mn and Cr, and adjustment to a predetermined concentration was performed. Thereafter, Ti and Ca were added in this order, and each concentration of Ti and Ca was adjusted. In this example, a Ni-Ca alloy was used as Ca to be added to molten steel, and a Fe-Ti alloy was used as a Ti source. The chemical components of the cast slabs thus obtained are shown in Table 1.

[Table 1]

| Test Steel No. | Chemical Components (mass%) Balance: Iron and Unavoidable Impurities | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | C | Si | Mn | Cr | Al | Ca | Ti | Ni | V |
| 1 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0005 | 0.0005 | 0.0018 | 0.25 | 0.10 |
| 2 | 0.55 | 1.45 | 0.87 | 0.70 | 0.0005 | 0.0003 | 0.0015 | - | - |
| 3 | 0.63 | 1.40 | 0.60 | 0.65 | 0.0007 | 0.0005 | 0.0020 | - | 0.09 |
| 4 | 0.60 | 2.20 | 0.50 | 1.75 | 0.0010 | 0.0005 | 0.0028 | 0.20 | 0.30 |
| 5 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0003 | 0.0002 | 0.0025 | 0.25 | 0.10 |
| 6 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0010 | 0.0005 | 0.0025 | 0.25 | 0.10 |
| 7 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0008 | 0.0008 | 0.0007 | 0.25 | 0.10 |
| 8 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0008 | 0.0008 | 0.0005 | 0.25 | 0.10 |
| 9 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0020 | 0.0010 | 0.0006 | 0.25 | 0.10 |
| 10 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0008 | 0.0005 | 0.0020 | 0.25 | 0.10 |
| 11 | 0.65 | 2.00 | 0.90 | 0.90 | 0.0008 | 0.0005 | 0.0040 | 0.25 | 0.10 |
| 12 | 0.63 | 1.40 | 0.60 | 0.65 | 0.0003 | 0.0015 | 0.0020 | - | 0.09 |
| 13 | 0.60 | 2.00 | 0.90 | 0.90 | 0:0010 | 0.0010 | 0.0020 | 0.25 | 0.10 |
| 14 | 0.63 | 1.40 | 0.60 | 0.65 | 0.0005 | 0.0005 | 0.0002 | - | 0.09 |
| 15 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0003 | 0.0005 | 0.0130 | 0.25 | 0.10 |
| 16 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0005 | 0.0005 | 0.0020 | 0.25 | 0.10 |
| 17 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0005 | 0.0005 | 0.0018 | 0.25 | 0.10 |
| 18 | 0.60 | 2.00 | 0.90 | 0.90 | 0.0005 | 0.0005 | 0.0018 | 0.25 | 0.10 |

**[0062]** Each cast slab obtained was heated in a heating furnace at a temperature of 1100 to 1300°C, and then, blooming was performed at 900 to 1200°C. Thereafter, hot rolling was performed at 830 to 1100°C, thereby obtaining a hot-rolled steel having a diameter of 8.0 mm.

(Measurement of the composition and number of oxide-based inclusions)

**[0063]** For the hot-rolled steel (diameter: 8.0 mm) thus obtained, one micro sample having L (L is a length in a rolling direction) of 20 mm or more was cut out in a longitudinal direction thereof (corresponding to the rolling direction) so as to include a central axis of the hot-rolled steel, and a cross section including the above central axis was polished. This polished surface was observed using an electron probe X-ray micro analyzer (EPMA, trade name "JXA-8500F") manufactured by JEOL Datum Ltd., and for oxide-based inclusions having a minor axis of 1 μm or more, the component composition was quantitatively analyzed. The observation area of the polished surface was from 100 to 1000 $mm^2$, and the component composition in a center part of the oxide-based inclusions was quantitatively analyzed by characteristic X-ray wavelength dispersion spectrometry. Elements to be analyzed were Ca, Al, Si, Ti, Mn, Mg, Na, Cr and Zr. The average composition of the oxide-based inclusions was determined by previously determining the relationship between the X-ray intensity of each element and the element concentration, as a calibration curve by using a known substance, and quantifying the element amount contained in each sample from the X-ray intensity obtained from the above oxide-based inclusions to be analyzed and the above calibration curve, followed by conversion to the oxide. In Ti oxides, a plurality of valences can be taken, but all are calculated as $TiO_2$.

**[0064]** Further, of the oxide-based inclusions which were present in the above polished surface, the value obtained by dividing the number of oxide-based inclusions having a minor axis of 2 μm or more by the above observation area (100 to 1000 $mm^2$) was taken as the inclusion number of oxide-based inclusions (inclusions/$mm^2$).

[Fatigue strength test (breakage ratio)]

**[0065]** The above hot-rolled steel (diameter: 8.0 mm) was stripped and wire-drawn to a diameter of 7.4 mm, followed by patenting and cold wire drawing to a diameter of 4.0 mm. Then, oil tempering treatment was performed by continuously performing oil quenching and tempering in a lead bath at about 450°C, and thereafter, a wire of 4.0 mm diameter x 650 mm length was obtained. After the wire thus obtained was subjected to treatment equivalent to strain relieving annealing at 400°C, shot peening was performed, and low temperature annealing at 200°C was performed. Thus, a test piece for measuring fatigue strength was prepared.

**[0066]** The above test piece was tested using a Nakamura-type rotational bending tester with nominal stress: 970 MPa, rotational speed: 4000 to 5000 rpm, and the number of times of stoppage: $2\times10^7$ times. Of broken test pieces, the number A of test pieces broken from inclusions as start points and the number B of test pieces in which the above test was stopped because the predetermined number of times of stoppage was attained were each measured, and the breakage ratio was determined by the following equation.

$$\text{Breakage ratio (\%)} = [A/(A+B)]\times100$$

**[0067]** These results are shown in Table 2. The test No. in Table 2 shows that the test steel No. in Table 1 having the same number was used.

[Table 2]

| Test No. | Average Composition of Oxide-Based Inclusions (mass%) | | | | | | | | | Number of Oxide-Based Inclusions Having Minor Axis of 2 μm or More (inclusions/mm$^2$) | Breakage Ratio (%) |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | CaO | $Al_2O_3$ | $SiO_2$ | MgO | MnO | $TiO_2$ | $Na_2O$ | $ZrO_2$ | Total ($CaO+Al_2O_3+SiO_2+MgO+MnO+TiO_2$) | | |
| 1 | 20 | 19 | 47 | 4 | 1 | 6 | | | 97 | 0.050 | 20 |
| 2 | 22 | 19 | 40 | 6 | 3 | 7 | | | 97 | 0.050 | 23 |
| 3 | 23 | 17 | 50 | 1 | 2 | 7 | | | 100 | 0.050 | 23 |
| 4 | 18 | 22 | 46 | 4 | 1 | 6 | | | 97 | 0.050 | 20 |
| 5 | 13 | 13 | 64 | 3 | 1 | 4 | | | 98 | 0.200 | 20 |
| 6 | 25 | 23 | 35 | 5 | 1 | 5 | 3 | | 94 | 0.050 | 20 |
| 7 | 22 | 20 | 45 | 4 | 1 | 6 | | | 98 | 0.060 | 23 |
| 8 | 34 | 12 | 43 | 4 | 0 | 5 | | | 98 | 0.015 | 27 |
| 9 | 15 | 25 | 45 | 5 | 1 | 6 | | | 97 | 0.030 | 27 |
| 10 | 20 | 22 | 48 | 0 | 2 | 6 | | | 98 | 0.100 | 27 |
| 11 | 12 | 12 | 64 | 3 | 0 | 8 | | | 99 | 0.100 | 27 |
| 12 | 40 | 14 | 35 | 3 | 1 | 6 | | | 99 | 0.050 | 67 |
| 13 | 29 | 29 | 25 | 4 | 1 | 7 | | | 95 | 0.040 | 67 |
| 14 | 23 | 18 | 50 | 1 | 2 | 1 | | | 95 | 0.050 | 33 |
| 15 | 20 | 19 | 40 | 4 | 1 | 15 | | | 99 | 0.040 | 57 |
| 16 | 20 | 19 | 47 | 4 | 1 | 6 | | | 97 | 0.001 | 43 |
| 17 | 0 | 8 | 78 | 0 | 2 | 10 | | | 98 | 0.010 | 30 |
| 18 | 0 | 1 | 90 | 0 | 3 | 5 | | 0.5 | 99 | 0.010 | 30 |

**[0068]** All of Test Nos. 1 to 11, 17 and 18 in Table 2 satisfy the chemical component composition and oxide composition specified in the present invention, and it is known that they are excellent in fatigue properties.

**[0069]** On the other hand, Test Nos. 12 to 16 did not satisfy any one of the requirements in the present invention. Therefore, fatigue properties were decreased.

**[0070]** In Test No. 12, the Si amount and the Al amount were within the ranges in the present invention, but the Si amount and the Al amount were relatively low. Therefore, the CaO amount in the oxide-based inclusions was increased to cause a decrease in fatigue properties

**[0071]** In Test No: 13, the Ti amount and the Al amount were within the ranges in the present invention, but the amounts thereof were relatively larger than in the other examples. Therefore, the $SiO_2$ amount in the oxide-based inclusions was decreased to cause a decrease in fatigue properties.

**[0072]** In Test No. 14, the Ti amount was small. Therefore, the $TiO_2$ amount in the oxide-based inclusions was decreased to cause a decrease in fatigue properties.

**[0073]** In Test No. 15, the Ti amount was large. Therefore, the $TiO_2$ amount in the oxide-based inclusions was increased to cause a decrease in fatigue properties.

**[0074]** In Test No. 16, stirring during slag refining was weaker than in the other examples. Therefore, suspension became insufficient, and the number of oxide-based inclusions having a minor axis of 2 μm or more was decreased to cause a decrease in fatigue properties

**[0075]** Although the present invention has been described in detail and by reference to the specific embodiments, it is apparent to one skilled in the art that various modifications or changes can be made without departing from the spirit and scope of the present invention.

**[0076]** This application is based on Japanese Patent Application No. 2014-014633 filed on January 29, 2014, the content of which is incorporated herein by reference.

Industrial Applicability

**[0077]** The steel wire for a spring in the present invention is more excellent in fatigue properties than the conventional one, and suitable for valve springs, suspension springs and the like.

## Claims

**1.** A steel wire rod for a spring excellent in fatigue properties, comprising:

C: 0.2 to 1.2% (% means mass%, hereinafter the same, unless otherwise indicated),
Si: 1.0 to 3%,
Mn: 0.1 to 2%,
Cr: 3% or less (not inclusive of 0%),
Al: 0.0002 to 0.005%,
Ca: 0.0002 to 0.002%,
Ti: 0.0003 to 0.010%, and
balance: iron and unavoidable impurities,
wherein an average composition of oxide-based inclusions having a minor axis of 1 μm or more which are present in a cross section parallel to a longitudinal direction of a steel satisfies, by mass%, CaO: 35% or less (inclusive of 0%), $Al_2O_3$: 40% or less (inclusive of 0%), $SiO_2$: 30 to 95%, MgO: 8% or less (inclusive of 0%), MnO: 5% or less (inclusive of 0%), $TiO_2$: 3 to 10%, and $CaO+Al_2O_3+SiO_2+MgO+MnO+TiO_2 \geq 80\%$, and
the number of oxide-based inclusions having a minor axis of 2 μm or more which are present in the cross section is more than 0.002 inclusions/$mm^2$.

**2.** The steel wire rod for a spring according to claim 1, wherein the average composition of the oxide-based inclusions further satisfies, by mass%, $ZrO_2$ less than 1% (not inclusive of 0%) and $Na_2O$: less than 5% (inclusive of 0%).

**3.** The steel wire rod for a spring according to claim 1 or 2, further comprising at least one of Ni: 0.5% or less (not inclusive of 0%), Cu: 0.5% or less (not inclusive of 0%) and V: 0.5% or less (not inclusive of 0%).

**4.** A spring obtained using the steel wire rod for a spring according to any one of claims 1 to 3.

## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2015/052595

A. CLASSIFICATION OF SUBJECT MATTER
*C22C38/00*(2006.01)i, *C22C38/38*(2006.01)i, *C22C38/58*(2006.01)i, *C21D8/06* (2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00-38/60

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

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1922-1996 | Jitsuyo Shinan Toroku Koho | 1996-2015 |
| Kokai Jitsuyo Shinan Koho | 1971-2015 | Toroku Jitsuyo Shinan Koho | 1994-2015 |

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
|---|---|---|
| A | JP 63-140068 A (Nippon Steel Corp.), 11 June 1988 (11.06.1988), claims; table 1 (Family: none) | 1-4 |
| A | JP 2008-291325 A (Kobe Steel, Ltd.), 04 December 2008 (04.12.2008), claims 1 to 4 & US 2010/0086432 A1 & WO 2008/146533 A1 & EP 2163657 A1 & KR 10-2009-0130416 A & CN 101675176 A & BR PI0809215 A2 | 1-4 |
| A | JP 10-1746 A (Kobe Steel, Ltd.), 06 January 1998 (06.01.1998), claims 1 to 5 (Family: none) | 1-4 |

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

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"A" document defining the general state of the art which is not considered to be of particular relevance
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"&" document member of the same patent family

| | |
|---|---|
| Date of the actual completion of the international search<br>08 April 2015 (08.04.15) | Date of mailing of the international search report<br>21 April 2015 (21.04.15) |
| Name and mailing address of the ISA/<br>Japan Patent Office<br>3-4-3,Kasumigaseki,Chiyoda-ku,<br>Tokyo 100-8915,Japan | Authorized officer<br><br>Telephone No. |

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**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2015/052595

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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Form PCT/ISA/210 (continuation of second sheet) (July 2009)

## REFERENCES CITED IN THE DESCRIPTION

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