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(11) **EP 1 731 625 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
13.12.2006 Bulletin 2006/50

(21) Application number: **05709768.5**

(22) Date of filing: **04.02.2005**

(51) Int Cl.:
C22C 38/00 ^(2006.01) **C21D 8/06** ^(2006.01)
C21D 9/52 ^(2006.01) **C22C 38/34** ^(2006.01)
C22C 38/52 ^(2006.01) **F16F 1/02** ^(2006.01)

(86) International application number:
PCT/JP2005/001703

(87) International publication number:
WO 2005/075695 (18.08.2005 Gazette 2005/33)

(84) Designated Contracting States:
DE FR GB IT SE

(30) Priority: **04.02.2004 JP 2004027891**

(71) Applicant: **Sumitomo (Sei) Steel Wire Corp.**
Itama-shi, Hyogo 664-0016 (JP)

(72) Inventors:
• **FUJINO, Yoshiro**
Itami Works of Sumitomo El.Ind.Ltd
Hyogo 6640016 (JP)
• **KAWABE, Nozomu**
Itami Works of Sumitomo El.Ind.Ltd.
Hyogo 6640016 (JP)

• **MURAI, Teruyuki**
Sumitomo (SEI) Steel Wire Corp.
Hyogo 6640016 (JP)
• **YAMAO, Norihito**
Sumitomo (SEI) Steel Wire Corp.
Hyogo 6640016 (JP)
• **SHIWAKU, Takayuki**
Sumitomo (SEI) Steel Wire Corp.
Hyogo 6640016 (JP)

(74) Representative: **Cross, Rupert Edward Blount**
Boult Wade Tennant
Verulam Gardens
70 Gray's Inn Road
London WC1X 8BT (GB)

(54) **STEEL WIRE FOR SPRING**

(57) The present invention provides a spring steel wire which has a tempered martensitic structure brought about by quenching-tempering. The present spring steel wire has a 40 % or higher reduction of area and a 1,000 MPa or higher shear yield stress after subjected to heat treatment for at least 2 hours at a temperature ranging from 420°C to 480°C. The present steel wire preferably

constitutes, based on mass %, C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%, Co: 0.02 - 1.00%, and remnants consisting of Fe and impurities, or constitutes, based on mass %, C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.50%, Cr: 0.70-1.50%, and remnants consisting of Fe and impurities.

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Description**Field of the Invention**

[0001] The present invention relates to a spring steel wire having a tempered martensitic structure brought about by quenching-tempering, to a method of manufacturing the spring steel wire in a well-suited efficient manner, and to a spring manufactured from the steel wire. More particularly, the present invention relates to a high toughness spring steel wire having a high strength with excellent fatigue properties that is advantageously applicable to engine valve springs or those springs used for transmission interior parts, etc. of automobiles.

Background Art

[0002] In recent years, as momentum toward low fuel consumption increases in automobiles, the industry has made continued efforts to achieve a further reduction in size and weight of automobile parts, including parts of their engines and transmissions. In connection with this, springs including engine valve springs, springs for transmission parts, etc. have come to be exposed to increasingly severer stress environments year after year, and thus spring materials used therefor are also required to be provided with much more improved fatigue properties accordingly. Heretofore, to manufacture those engine valve springs or springs for transmission parts as described above, it has been known to use silicon-based oil tempered steel wires such as, for example, those described in the patent documents 1-3 listed below.

[0003] [Patent document 1] Japanese Patent Publication No. 2842579

[Patent document 2] Japanese Provisional Patent Publication No. 2002-194496

[Patent document 3] Japanese Patent Publication No. 3045795

DISCLOSURE OF THE INVENTION**Problem to be solved, by the invention**

[0004] However, springs such as engine valve springs or springs for transmission parts have been increasingly required to have better mechanical or physical properties in recent years, so that further improvement has come to be demanded in spring steel wires and springs worked from the steel wire. Especially, it is desired that such spring steel wires and springs manufactured therefrom be provided with fatigue properties and toughness in better balance than ever.

[0005] On the other hand, as improvement in fatigue strength (fatigue limit) is requested recently, springs worked from steel wires are typically subjected to heat treatment (nitriding treatment) at elevated temperatures (specifically, around 420-480°C).

[0006] The patent document 1 discloses a technique that aims at improving the toughness of a steel wire by providing it with a C (carbon) content ranging from 0.3% to 0.5% by weight. However, since a steel wire with a carbon content as low as less than 0.50% by weight will have a reduced thermal resistance, if a spring worked from such a low carbon content steel wire is subjected to nitriding treatment at elevated temperatures as described above, the resultant spring will have a reduced fatigue strength, so that it may undergo internal breakage when put into practical use.

[0007] The patent document 2 discloses a technique that aims at improving the fatigue strength of a steel wire by achieving a fine structure having an average grain size of 1.0-7.0 micrometers as austenite after quenching. However, if the quenching temperature is lowered to make the austenite grain size smaller, there will remain undissolved carbide, which may lower the toughness of the resultant steel wire. Further, with such reduction in toughness, the steel wire will become more susceptible to breakage while being worked into spring and consequently the mass productivity of the spring therefrom will be adversely affected thereby.

[0008] The patent document 3 discloses a technique that aims at improving a steel wire in its workability into spring by decarbonizing its surface purposely during the oil tempering so as to reduce the surface hardness, but this prior art technique is inadequate for the mass production of such a steel wire or spring because it is practically difficult to obtain a uniform decarburized layer in the surface of the steel wire. Moreover, the oxygen concentration must be well controlled when heating the steel wire (during the oil tempering), thus adding to the cost accordingly.

[0009] Further, in any of the technologies disclosed in the above-cited prior art documents, the proof stress of the material (spring) to a stress exerted inside in its torsional direction, i.e., the shear yield stress of the spring is not examined subsequent to the nitriding treatment to which the spring is subjected after worked from the steel wire.

[0010] Accordingly, a principal object of the present invention is to provide a high strength spring steel wire which is excellent not only in fatigue strength but also in toughness. Also, it is another object of the present invention to provide a spring manufactured from the above-described steel wire and a suitable method to manufacture the spring steel wire.

Means for solving problem

[0011] With the aforementioned objects in view, the present invention provides a spring steel wire, in which its reduction of area after quenching-tempering and its shear yield stress after subjected to heat treatment comparable to nitriding treatment following the above quenching-tempering are limited to specific ranges, respectively.

[0012] That is, the present invention provides a spring steel wire which has a tempered martensitic structure brought about by quenching-tempering. The present spring steel wire is characterized by a 40% or higher reduction of area and by a 1,000 MPa or higher shear yield stress after subjected to heat treatment for at least 2 hours at a temperature ranging from 420°C to 480°C.

[0013] According to the present invention, the spring steel wire preferably comprises any one of the following chemical formulations 1 through 6:

1. Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%, Co: 0.02-1.00%, and remnants consisting of Fe and impurities

2. Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, and remnants consisting of Fe and impurities

3. Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, at least one element of Ni: 0.1-1.0% and Co: 0.02-1.00%, and remnants consisting of Fe and impurities

4. Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%, Co: 0.02-1.00%, at least one element selected from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W: 0.05-0.15%, Nb: 0.05-0.15% and Ti: 0.01-0.20%, and remnants consisting of Fe and impurities

5. Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, at least one element selected from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W: 0.05-0.15%, Nb: 0.05-0.15% and Ti: 0.01-0.20%, and remnant consisting of Fe and impurities

6. Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, at least one element of Ni: 0.1-1.0% and Co: 0.02-1.00%, at least one element selected from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W: 0.05-0.15%, Nb: 0.05-0.15% and Ti: 0.01-0.20%, and remnant consisting of Fe and impurities

[0014] The present invention also provides a method of manufacturing the above-described spring steel wire in a well suited manner therefor, as will be described herein below. More specifically, the method of manufacturing the spring steel wire according to the present invention comprises patenting a steel having any one of the chemical formulations (A) through (C) given below, drawing the patented steel into a steel wire, and subjecting the resultant steel wire to quenching-tempering. The above-mentioned patenting process comprises an austenization step in which the steel is heated at 900-1,050°C for 60 to 180 seconds, and an isothermal transformation step in which the thus austenized steel is heated at 600-750°C for 20 to 100 seconds.

(A) Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%, Co: 0.02-1.00%, and remnants consisting of Fe and impurities

(B) Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, and remnants consisting of Fe and impurities

(C) Based on mass %; C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, at least one element of Ni: 0.1-1.0% and Co: 0.02-1.00%, and remnants consisting of Fe and impurities

In addition to those compositions in any one of the chemical formulations (A) through (C) given above, the steel may contain, based on mass %, at least one element selected from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W: 0.05-0.15%, Nb: 0.05-0.15%, and Ti: 0.01-0.20%.

Hereinafter, the present invention will be described in detail.

(Improving the Fatigue Properties)

[0015] The improvement of a spring in its fatigue properties may preferably be addressed in terms of the suppression of its fatigue breakage. When a spring is operated repeatedly, a repetitive stress is exerted on the spring not only in the tensile and compression directions but also in the shear direction simultaneously. Thus, with the repetitive stress applied externally, the spring undergoes a repetitive slip deformation (plastic deformation) locally or intensively and creates projections and depressions in the surface region to induce cracks leading to breakage, namely resulting in fatigue breakage. Therefore, for suppressing the fatigue breakage of the spring, it will be effective to suppress such a local or

concentrated plastic deformation. Heretofore, in order to suppress such a plastic deformation, the steel wire is typically subjected to heat treatment such as nitriding treatment after worked into spring to increase its surface hardness and thereby to increase its fatigue limit. However, nowadays, when springs have come to be used under conditions where a large stress is applied thereto, mere an increase in fatigue limit of the springs may sometimes be insufficient to allow their practical use, because such springs tend to undergo permanent set in fatigue. This may be accounted by the fact that even if a high hardness nitrided layer at the spring surface formed by the above-mentioned heat treatment such as nitriding treatment or like does not undergo permanent set in fatigue, such a large stress can reduce the strength of the inner part of the spring so as to put springs into permanent set in fatigue. Therefore, for springs, it is desired that springs are improved not only in their fatigue limit but in their torsional proof stress, i.e., shear yield stress itself, in addition to having a high strength. Under these circumstances, the inventors have studied above-described subject from various aspects to find out that an adequate torsional proof stress provided inside the material (i.e., spring) after the above-mentioned heat treatment such as nitriding treatment or like is substantially effective for meeting these requirements. More specifically, it turned out that the fatigue properties of a spring can be improved, if the spring has a 1,000 MPa or higher shear yield stress after the above-mentioned heat treatment such as nitriding treatment or like. Based on these findings, the present invention provides a spring steel wire having a shear yield stress limited to a specific range of 1,000 MPa or higher after subjected to particular heat treatment following the quenching-tempering.

(High Toughness)

[0016] However high the strength of a steel wire may be, it will undergo in-process breakage when the steel wire is worked into a spring if toughness of the steel wire is insufficient. Consequently the mass productivity of the spring will be hampered. Further, as the toughness of a steel wire used as material for a spring decreases, the fatigue properties of the spring will also decrease. Under these circumstances, the inventors have studied this problem from various aspects to find out that providing the steel wire with a 40% or higher reduction of area after quenching-tempering is effective for the prevention of in-process breakage of the steel wire when worked into spring and thus leads to excellent mass productivity of the spring. Based on these findings, the present invention provides a spring steel wire having a reduction of area limited to a specific range of 40% or higher. With a reduction of area lower than 40%, the steel wire tends to undergo in-process breakage when worked into spring and its mass productivity could be substantially compromised thereby. In this regard, the reduction of area may decrease a little when subjecting the steel wire to such particular heat treatment comparable to nitriding treatment that is accomplished at a temperature ranging from 420°C to 480°C for at least 2 hours following the quenching-tempering as described previously. However, if the steel wire has a 40% or higher reduction of area after quenching-tempering as described above, it can maintain a 35% or higher reduction of area even after the above-described heat treatment, and a spring manufactured from this steel wire can have a high fatigue properties.

[0017] Thus, according to the present invention, the reduction of area of a spring steel wire and its shear yield stress after subjected to heat treatment comparable to nitriding treatment following the above quenching-tempering are limited to specific ranges, respectively, to provide the spring steel wire and the spring manufactured from the steel wire with a high fatigue strength and high toughness in adequate balance.

[0018] In order to provide such a spring steel wire and a spring that are excellent both in fatigue properties and in toughness as described above, the present invention specifically limits the present steel wire to predetermined optimal chemical compositions and optimal manufacturing conditions, especially patenting conditions.

<Chemical compositions>

[0019] First, while the fatigue limit of a spring can be improved by increasing the surface hardness of the spring by subjecting it to the heat treatment such as nitriding treatment or like after it is worked from a steel wire, an internal hardness of the spring decreases by the heat treatment to sometimes cause the spring to undergo internal breakage in use. Thus, according to the present invention, the steel wire to be worked into a spring contains carbon (C) and silicon (Si) in a quantity (in mass %) falling in a predetermined range in order to improve the thermal resistance of a matrix of the steel wire. Besides, the steel wire contains a predetermined quantity of chromium (Cr) in order to produce carbide in the structure of the steel wire when it is tempered and to thereby increase the softening resistance of the steel wire. In addition to this predetermined Cr content, the steel wire may contain also a predetermined quantity of molybdenum (Mo), vanadium (V), niobium (Nb), Tungsten (W), or titanium (Ti) to effectively increase the softening resistance. Then the inventors have found out that, for improving the shear yield stresses of the steel wire and the spring manufactured therefrom of the present invention, it is effective to provide the steel wire with a 0.02-1.00 mass % cobalt (Co) content or a rather excess manganese (Mn) content (over 0.7 to 1.5 mass %).

Thus, the steel wire of the present invention has Mn and Co contents limited to specific ranges, respectively. The ranges of these contents and the grounds for such limitation will be described in detail herein later.

<Manufacturing Conditions>

[0020] The spring steel wire of the present invention is obtained by subjecting a steel having the above-described chemical compositions to the following processes in sequence: steel ingot making → hot forging → hot rolling → patenting → wire drawing → quenching-tempering

(Patenting Conditions)

[0021] According to the present invention, a steel rod is subjected, before wire drawing, to patenting under particular conditions to fully austenitize the structure of the steel to thereby dissolve the undissolved carbide and to obtain a homogeneous pearlitic structure through an appropriate isothermal transformation following the austenitization. Insufficient austenitization may cause the reduction of toughness and shear yield stress of the resultant steel wire. Then, for fully austenitizing the steel, it is preferred to heat the steel rod at a temperature of 900-1,050°C for 60 to 180 seconds. If the heating temperature is lower than 900°C, or if the heating temperature falls in the range of 900-1,050°C but the heating time is shorter than 60 seconds, sufficient austenitization will not be achieved and undissolved carbide will remain. However, if the heating temperature is higher than 1,050°C, or if the heating temperature falls in the range of 900-1,050°C but the heating time is longer than 180 seconds, austenite grains will become coarse, thus tending to produce martensite during the succeeding transformation, so that the drawability of the steel rod will not be secured during the wire drawing process.

[0022] For the isothermal transformation of the steel following the austenitization, it is preferred to heat the steel rod at 600-750°C for 20 to 100 seconds. If the heating temperature is higher than 750°C, or if the heating temperature falls in the 600-750°C range but the heating time is longer than 100 seconds, cementite spheroidizes in the structure of the steel, which may degrade the drawability of the steel rod. On the other hand, if the heating temperature is lower than 600°C, or if the heating temperature falls in the 600-750°C range but the heating time is shorter than 20 seconds, the transformation to pearlite will not be completed and martensite will be produced to thereby degrade the drawability.

(Quenching and Tempering)

[0023] If the steel wire obtained by drawing the steel rod which is subjected to patenting as above is then subjected to quenching at too low a temperature, undissolved carbide will remain in the structure of the steel wire, which acts to reduce the toughness of the steel wire. On the contrary, if the quenching temperature is too high, the austenite grains will grow to larger sizes and consequently the fatigue limits of the steel wire and the spring manufactured therefrom will be reduced. Thus, it is preferred that the quenching temperature be higher than 850°C but lower than 1,050°C.

<Structure>

[0024] According to the present invention, the spring steel wire has a tempered martensitic structure. Moreover, if the austenite grains (prior austenite grains) of the steel wire are rendered fine as observed after subjected to the quenching-tempering, such a steel wire and the spring manufactured from the steel wire will become hard to undergo a slip deformation locally or intensively even when a repetitive stress is applied thereto. That is to say, since the shear yield stress of the steel wire or spring can be improved by rendering fine the austenite grains (prior austenite grains), this consequently contributes to improved fatigue properties of the steel wire or spring.

[0025] Specifically, it is preferred that the average grain size of the austenite grains (prior austenite grains) fall in the range of 3.0-7.0 micrometers. The average grain size can be changed by varying the temperature for patenting the steel rod. More specifically, if the austenitization during patenting is effected at a lower temperature, the grain size will tend to become smaller, while if this austenitizing temperature is increased, the grain size tends to increase. With an average grain size smaller than 3.0 micrometers, undissolved carbide will remain due to the lower austenitizing temperature and tend to reduce the toughness of the steel wire. Meanwhile, if the average grain size is larger than 7.0 micrometers, it is difficult to improve the fatigue limit of the steel wire or the spring manufactured therefrom. Now it is to be noted that the average grain size herein is given in measurements taken on steel wires after drawing and then subjected to quenching-tempering.

[0026] Hereinafter, the description will be made on the grounds on which the elements are selected and their contents are limited to specific ranges according to the present invention. In the description to follow, numerical values accompanying the individual elements are all given in mass %.

C: 0.50-0.75

[0027] Carbon (C) is an important element which determines the strength of steel, and since a carbon content lower

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than 0.50 mass % of the total steel will not allow a resulting steel wire to have a sufficient strength, while a carbon content exceeding 0.75 mass % will result in reduced toughness, it is preferred that the carbon content ranges from 0.50 mass % to 0.75 mass %.

5 Si: 1.80-2.70

10 **[0028]** Silicon (Si) is used as a deoxidizer when melting and smelting a raw steel. Moreover, Si is solid-dissolved in steel's ferrite to improve the thermal resistance of the steel and has the effect of preventing the hardness reduction inside the steel wire (spring) due to heat treatment such as strain relief annealing or nitriding treatment to which the spring is subjected after worked from the steel wire. It is preferred that the steel have a Si content ranging from 1.80 mass % to 2.70 mass %, because the 1.80 mass % or higher Si content is required to maintain an adequate thermal resistance but the toughness will decrease if the Si content exceeds 2.70 mass %.

15 Mn: 0.1-1.5

20 **[0029]** Like Si, manganese (Mn) is used as a deoxidizer when melting and smelting a raw steel. Therefore, it is preferred that the Mn content required for such a deoxidizer has a lower limit of 0.1 mass %. Moreover, Mn has the effect of improving the hardenability of the steel wire to thereby increase its strength and improve the shear yield stress of the steel wire and the spring manufactured therefrom. However, since an Mn content higher than 1.5 mass % of the total steel tends to produce martensite in the steel during the patenting process and thus wire breakage may be caused thereby in the drawing process, the Mn content preferably has an upper limit of 1.5 mass %. Particularly, in cases where the steel contains cobalt (Co) to be described herein below, the Mn content may fall in a rather lower range of 0.1-0.7 mass %, while it is preferred for a formulation without Co content that the Mn content fall in a rather higher range of over 0.7 to 1.5 mass %. A formulation having a rather higher Mn content may contain also Co.

25 Cr: 0.70-1.50

30 **[0030]** Since chromium (Cr) acts to improve the hardenability and thus the softening resistance of the steel, it is effective for preventing the spring worked from the steel wire from softening when subjected to heat treatment such as tempering and nitriding treatment. Since a Cr content lower than 0.70 mass % of the total steel will not work to provide a sufficient effect of preventing the softening, preferably the Cr content is 0.70 mass % or higher, while a Cr content exceeding 1.50 mass % will tend to produce martensite during the patenting process to thus cause wire breakage in the drawing process and further to reduce the toughness of the patented (oil-tempered) steel. Therefore, the Cr content preferably falls in the range of 0.70 to 1.50 mass %.

35 Co: 0.02-1.00

40 **[0031]** A small quantity of cobalt (Co) added to a steel acts to improve the shear yield stress of the resultant steel wire and the spring worked from the steel wire. Also, Co is effective for improving the thermal resistance of the steel wire and for the softening prevention of the spring worked from the steel wire and subjected to the tempering and nitriding treatment. Further, Co does not act to reduce the toughness of the steel wire, so long as its content is low. A Co content lower than 0.02 mass % is hard to contribute to any improved shear yield stress for the steel wire or the spring as described above or to any improved thermal resistance for the steel wire. Also, even if the Co content exceeds 1.00 mass %, no significant improvement in effect can be observed over cases with a 1.00 mass % or lower Co content but it just adds to the manufacturing cost of the steel wire or spring. Accordingly, it is preferred that the Co content fall in the range of 0.02 mass % to 1.00 mass %. In addition, where the steel contains Co, Mn content of the steel may fall in a rather low range of 0.1-0.7 mass %, as described above.

50 Ni: 0.1-1.0

55 **[0032]** Nickel (Ni) contained in the steel has the effect of improving the corrosion resistance and toughness of the resultant steel wire. An Ni content lower than 0.1 mass % is hard to contribute to any improved properties of the steel wire as mentioned above, and even if the Ni content exceeds 1.0 mass %, no further improvement in the toughness of the resultant steel wire cannot be achieved, but it just adds to its manufacturing cost. Thus, the Ni content preferably ranges from 0.1 mass % to 1.0 mass %.

Mo, V: 0.05-0.50

W, Nb: 0.05-0.15

[0033] These elements act to produce carbide in the structure of a steel wire when it is tempered and have the effect of tending to increase the softening resistance of the steel wire. If the content of each of molybdenum (Mo), vanadium (V), tungsten (W) or niobium (Nb) is lower than 0.05 mass % of the total steel, the above-described effect will be hard to achieve. Meanwhile, if the Mo content exceeds 0.50 mass %, if the V content exceeds 0.50 mass %, if the W content exceeds 0.15 mass %, or if the Nb content exceeds 0.15 mass %, the resultant steel wire tends to have reduced toughness in either case.

Ti: 0.01-0.20

[0034] Titanium (Ti) acts to produce carbide when the steel wire is tempered and has the effect of tending to increase a softening resistance of the steel wire. A Ti content lower than 0.01 mass % will not yield the above-mentioned effect, while a Ti content higher than 0.20 mass % will produce a high-melting point non-metallic inclusion TiO in the structure of the steel wire, tending to reduce the toughness of the steel wire. Thus, the Ti content preferably ranges from 0.01 mass % to 0.20 mass %.

[0035] The spring steel wire of the present invention may have any cross-sectional shape as cut by a plane perpendicular to the longitudinal direction (drawing direction) of the steel wire, including a typical circular shape and other special or peculiar cross-sectional shapes such as an ellipse, a trapezoid, a square, a rectangle, and so on.

[0036] The spring of the present invention may be provided by subjecting the above-described spring steel wire to any known spring forming process such as coiling. Especially, it is to be noted here that by subjecting the spring worked from the present spring steel wire to heat treatment such as nitriding treatment or like, the resultant spring can have an improved surface hardness and thus an excellent fatigue limit.

BEST MODE FOR CARRYING OUT THE INVENTION

[0037] Preferred embodiments of the present invention are demonstrated hereinafter. A steel of each formulation containing chemical elements given in Table 1 with remnants consisting of Fe and impurities were melted in a vacuum melting furnace to prepare an ingot and then the resultant ingot was worked through hot forging and hot rolling into a wire rod of 6.5 mmφ. Then, the wire rod was subjected to patenting (austenitizing → isothermal transformation), shaving, annealing, and drawing processes in sequence to obtain a steel wire of 3.0 mmφ. The patenting conditions are shown in Table 2. In this typical embodiment, the respective 6.5 mmφ wire rods were patented under several varied patenting conditions, including austenitizing conditions under which the wire rods were heated at varied temperatures for varied retention times, and conditions for isothermal transformation under which the wire rods were heated also at varied temperatures for varied retention times-subsequently to the austenization, as shown in Table 2.

[0038]

[Table 1]

Formulation samples	Chemical composition (mass %)						
	C	Si	Mn	Cr	Co	Ni	Others
A	0.45	2.2	0.5	0.9	0.3	-	-
B	0.78	2.0	0.6	0.8	-	-	-
C	0.68	1.6	0.5	1.0	-	-	-
D	0.63	2.8	0.6	0.9	-	-	-
E	0.61	2.2	1.7	1.0	-	0.3	-
F	0.60	2.2	0.6	0.5	-	-	-
G	0.64	2.3	0.5	1.7	-	-	-
H	0.62	2.1	0.5	1.1	-	-	-
I	0.64	2.2	0.6	1.2	-	-	V: 0.6
J	0.63	2.1	0.5	1.1	-	-	Ti: 0.3

(continued)

Formulation samples	Chemical composition (mass %)						
	C	Si	Mn	Cr	Co	Ni	Others
K	0.55	2.4	0.5	1.3	0.2	-	-
L	0.72	2.3	0.55	1.2	0.5	-	-
M	0.63	1.9	1.2	1.4	-	0.3	-
N	0.62	2.5	0.2	0.9	0.3	-	-
O	0.64	2.3	0.8	1.1	0.4	-	-
P	0.65	2.2	0.9	0.9	0.3	0.5	-
Q	0.65	2.0	0.4	1.0	0.3	-	V: 0.15
R	0.60	2.3	1.0	0.8	-	-	Mo: 0.20
S	0.63	2.1	0.9	1.1	0.4	0.3	Ti: 0.10

[0039]

[Table 2]

Patenting conditions				
Conditions	Austenization		Isothermal transformation	
	Heating temperature (°C)	Retention time (sec)	Heating temperature (°C)	Retention time (sec)
I	920	120	630	80
II	980	60	700	30
III	880	120	650	50
IV	950	190	650	50
V	950	50	650	50
VI	1,070	60	650	50
VII	920	120	580	50
VIII	920	120	650	15
IX	920	120	650	120
X	920	120	780	50

[0040] The resultant steel wires (3.0mmφ) were then subjected to quenching-tempering. For the quenching, the conditions shown in Table 3 were used, while the tempering was carried out using a heating temperature of 450-530°C for all wires. The reduction of area (RA) and the average grain sizes (average γ grain size) of austenite grains (prior austenite grains) were measured on the respective quench-tempered wires. The results are shown in Table 3. Further, the wire quenching temperature was varied to change the average grain size of austenite grains (prior austenite grains). The average grain size of austenite grains was determined based on the intercept method subject to JIS G 0522.

[0041] Further, the shear yield stress and the fatigue properties (fatigue limit) were measured on those steel wires which were subjected, after the quenching-tempering, to heat treatment (420°C for 2 hours or 480°C for 2 hours) comparable to nitriding treatment. The results are shown also in Table 3. The shear yield stress of the steel wires which were heat-treated as above was determined from torque- θ curves obtained through twisting tests on samples of 100d in length (d: sample diameter). The fatigue limit was evaluated based on a Nakamura-type rotating bending fatigue test.

[0042]

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[Table 3]

No.	Samples	Conditions	Quenching temperature (°C)	Average γ grain size (μm)	RA (%)	Shear yield stress 420°C×2hr	Shear yield stress 480°C×2hr	Fatigue limit (MPa)
1	A	I	920	4.5	45	985	892	715
2	B	II	930	4.8	35	955	864	705
3	C	I	920	4.3	48	938	821	730
4	D	I	950	5.4	37	941	823	735
5	E	II	-	-	-	-	-	-
6	F	II	940	5.0	42	923	815	720
7	G	II	-	-	-	-	-	-
8	H	I	930	4.4	45	921	810	705
9	H	I	850	2.8	31	928	815	715
10	H	I	1,050	8.9	50	925	810	710
11	I	II	920	3.8	29	925	835	695
12	J	I	910	3.5	41	930	830	705
13	K	I	930	4.3	46	1,098	1,021	850
14	L	II	910	3.2	43	1,130	1,043	865
15	M	II	940	5.2	48	1,178	1,098	875
16	N	I	1,020	6.5	44	1,084	1,015	855
17	O	I	980	6.2	45	1,195	1,078	875
18	P	II	950	5.2	48	1,168	1,054	880
19	Q	II	930	3.5	45	1,121	1,038	865
20	R	I	920	3.4	47	1,154	1,069	870
21	S	I	940	4.4	46	1,211	1,113	895

[0043] As shown in Table 3, it is understood that the steel wires of samples No. 13 through 21 having a 40% or higher reduction of area (RA) and a 1,000 MPa or higher shear yield stress after the heat treatment comparable to nitriding treatment all have a high fatigue limit. Moreover, since the steel wires of these samples have a high shear yield stress, it is considered that these steel wires will be excellent in their permanent set properties. Thus, it is understood that the spring steel wire of the present invention is provided with high toughness while having excellent fatigue properties.

[0044] On the other hand, the samples No. 1-4, 6, and 8 having a low shear yield stress after the heat treatment comparable to nitriding treatment turned out to have a low fatigue limit. Especially, the samples No.2 and 4 had also an inferior toughness with a low reduction of area. Further, the steel wires of the samples No. 5 and 7 underwent martensite generation in their wire rod structures during patenting and then frequent wire breakage in the succeeding shaving step, and thus the experiment was forced to stop continuing. For the sample No. 11, since it had a higher V content of the total steel in addition to its low shear yield stress after the heat treatment, it had a lowered reduction of area of the steel wire to thus reduce its fatigue limit. For the sample No. 12, since it had a higher Ti content in addition to its low shear yield stress after the heat treatment, it underwent a reduction in fatigue limit owing to breakage caused by Ti-based inclusions.

[0045] For the sample No. 9, since it had a smaller average grain size of the austenite grains (prior austenite grains) in addition to its low shear yield stress after the heat treatment, it showed also a low reduction of area. On the other hand, the sample No. 10 showed a reduction in fatigue limit, because it had a large average grain size of the austenite grains (prior austenite grains) in addition to its low shear yield stress after the heat treatment.

[0046] In the same manner as the above-described embodiment, a steel having the chemical compositions of the sample K of Table 1 was worked to prepare a wire rod of 6.5mm ϕ , and the resultant wire rod was then worked into a steel wire of 3.0mm ϕ likewise as above. In this case, the patenting conditions employed were varied as shown in Table

2. The wire thus obtained was subjected to quenching-tempering (quenching temperature: 940°C, tempering temperature: 450-530°C), and the reduction of area (RA) of the resultant wire and its average grain size of the austenite grains (prior austenite grains) were measured. The results are shown in Table 4. Further, the shear yield stress and the fatigue properties (fatigue limit) were measured on those steel wires which were subjected, after the quenching-tempering, to heat treatment (420°C for 2 hours or 480°C for 2 hours) comparable to nitriding treatment. The results are shown together with the temperature conditions in Table 4. Measurement of the physical properties was carried out like the preceding examples.

[0047]

[Table 4]

No.	Samples	Conditions	Quenching temperature (°C)	Average γ grain size (μm)	RA (%)	Shear yield stress 420°C×2hr	Shear yield stress 480°C×2hr	Fatigue limit (MPa)
22	K	I	940	4.5	45	1,098	1,021	865
23	K	II	940	4.5	46	1,083	1,015	860
24	K	III	940	4.4	37	930	824	730
25	K	IV	-	-	-	-	-	-
26	K	V	940	4.3	36	934	829	728
27	K	VI	-	-	-	-	-	-
28	K	VII	-	-	-	-	-	-
29	K	VIII	-	-	-	-	-	-
30	K	IX	940	4.6	35	932	823	731
31	K	X	940	4.7	36	925	815	734

[0048] As shown in Table 4, it is understood that the samples No. 22 and 23 which were patented under particular conditions (austenitization: 900-1,050°C for 60 to 180 seconds, isothermal transformation: 600-750°C for 20 to 100 seconds) both had a high fatigue limit.

[0049] However, since the samples No. 25, and 27-29 underwent martensite generation in their wire rod structures during patenting and then frequent wire breakage in the drawing step, the experiment was forced to stop continuing. In the samples No. 24 and 26, since there remained undissolved carbide, the wires each had a lowered reduction of area and a reduced fatigue limit. Moreover, the samples No. 24 and 26 each had also a low shear yield stress. The samples No. 30 and 31 underwent cementite spheroidization in their wire rod structures so that there remained undissolved carbide, which resulted in reduced reduction of area and lower shear yield stress of each steel wire.

Industrial Applicability

[0050] Since the spring steel wire of the present invention is excellent both in fatigue properties and in toughness, it is best suited as a material for springs that are used for parts requiring an adequate fatigue strength.

Claims

1. A spring steel wire having a tempered martensitic structure brought about by quenching-tempering, the spring steel wire comprising:

- a 40 % or higher reduction of area; and
- a 1,000 Mpa or higher shear yield stress after subjected to heat treatment for at least 2 hours at a temperature ranging from 420°C to 480°C.

2. The spring steel wire according to claim 1 consisting of, based on mass %, C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%, Co: 0.02-1.0%, and remnants consisting of Fe and impurities.

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3. The spring steel wire according to claim 1 consisting of, based on mass %, C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, and remnants consisting of Fe and impurities.

5 4. The spring steel wire according to claim 1 consisting of, based on mass %;
C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%;
at least one element of Ni: 0.1-1.0% and Co: 0.02-1.00%; and
remnants consisting of Fe and impurities.

10 5. The spring steel wire according to claim 1 consisting of, based on mass %;
C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%, Co: 0.02-1.00%;
at least one element selected from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W:
0.05-0.15%, Nb: 0.05-0.15% and Ti: 0.01-0.20%; and
remnants consisting of Fe and impurities.

15 6. The spring steel wire according to claim 1 consisting of, based on mass %;
C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%;
at least one element selected from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W:
0.05-0.15%,
Nb: 0.05-0.15% and Ti: 0.01-0.20%; and
20 remnants consisting of Fe and impurities.

25 7. The spring steel wire according to claim 1 consisting of, based on mass %, C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over
0.7-1.5%, Cr: 0.70-1.50%, at least one element of Ni: 0.1-1.0% and Co: 0.02-1.00%, at least one element selected
from the group of 5 elements consisting of V: 0.05-0.50%, Mo: 0.05-0.50%, W: 0.05-0.15%, Nb: 0.05-0.15% and
Ti: 0.01-0.20%, and remnants consisting of Fe and impurities.

8. The spring steel wire according to any one of the claims 1 through 7 comprising austenite grains (prior austenite
grains) which have an average grain size in the range of 3.0-7.0 μm .

30 9. A spring manufactured from the spring steel wire according to any one of the claims 1 through 7.

10. A spring manufactured from the spring steel wire according to claim 8.

35 11. A method of manufacturing a spring steel wire, comprising the steps of:

patenting a steel consisting of chemical compositions given below;
drawing the thus patented steel into a steel wire; and
subjecting the resultant steel wire to quenching-tempering;
wherein said patenting process comprises:

40 an austenization step in which the steel is heated at 900-1,050°C for 60 to 180 seconds; and
an isothermal transformation step in which the thus austenized steel is heated at 600-750°C for 20 to 100
seconds;

45 Chemical compositions (based on mass %):
C: 0.50-0.75%, Si: 1.80-2.70%, Mn: 0.1-0.7%, Cr: 0.70-1.50%,
Co: 0.02-1.00%, and remnants consisting of Fe and impurities.

50 12. A method of manufacturing a spring steel wire, comprising the steps of:

patenting a steel consisting of chemical compositions given below;
drawing the thus patented steel into a steel wire; and
subjecting the resultant steel wire to quenching-tempering;
wherein said patenting process comprises:

55 an austenization step in which the steel is heated at 900-1,050°C for 60 to 180 seconds; and
an isothermal transformation step in which the thus austenized steel is heated at 600-750°C for 20 to 100
seconds;

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Chemical compositions (based on mass %):

C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, and remnants consisting of Fe and impurities.

13. A method of manufacturing a spring steel wire, comprising the steps of:

5 patenting a steel consisting of chemical compositions given below;
drawing the thus patented steel into a steel wire; and
subjecting the resultant steel wire to quenching-tempering;
wherein said patenting process comprises:
10 an austenization step in which the steel is heated at 900-1,050°C for 60 to 180 seconds; and
an isothermal transformation step in which the thus austenized steel is heated at 600-750°C for 20 to 100
seconds;

15 Chemical compositions (based on mass %):
C: 0.50-0.75%, Si: 1.80-2.70%, Mn: over 0.7-1.5%, Cr: 0.70-1.50%, at least one element of Ni: 0.1-1.0% and
Co: 0.02-1.00%, and remnants consisting of Fe and impurities.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/001703

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl.⁷ C22C38/00, C21D8/06, 9/52, C22C38/34, 38/52, F16F1/02 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) Int.Cl.⁷ C22C38/00, C21D8/06, 9/52, C22C38/34, 38/52, F16F1/02 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched <table border="0"> <tr> <td>Jitsuyo Shinan Koho</td> <td>1922-1996</td> <td>Jitsuyo Shinan Toroku Koho</td> <td>1996-2005</td> </tr> <tr> <td>Kokai Jitsuyo Shinan Koho</td> <td>1971-2005</td> <td>Toroku Jitsuyo Shinan Koho</td> <td>1994-2005</td> </tr> </table> Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) WPI			Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2005	Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005												
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C. DOCUMENTS CONSIDERED TO BE RELEVANT <table border="1"> <thead> <tr> <th>Category*</th> <th>Citation of document, with indication, where appropriate, of the relevant passages</th> <th>Relevant to claim No.</th> </tr> </thead> <tbody> <tr> <td>A</td> <td>JP 2004-2994 A (Kobe Steel, Ltd.), 08 January, 2004 (08.01.04), Full text & EP 1491647 A1 & WO 03/83151 A1</td> <td>1-13</td> </tr> <tr> <td>A</td> <td>JP 2000-17388 A (Sumitomo Electric Industries, Ltd.), 18 January, 2000 (18.01.00), Full text (Family: none)</td> <td>1-13</td> </tr> <tr> <td>A</td> <td>JP 2003-306747 A (Sumitomo Denko Steel Wire Kabushiki Kaisha), 31 October, 2003 (31.10.03), Full text (Family: none)</td> <td>1-13</td> </tr> </tbody> </table> ☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex. <table border="0"> <tr> <td> * Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed </td> <td> "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family </td> </tr> </table> <table border="1"> <tr> <td>Date of the actual completion of the international search 25 April, 2005 (25.04.05)</td> <td>Date of mailing of the international search report 17 May, 2005 (17.05.05)</td> </tr> <tr> <td>Name and mailing address of the ISA/ Japanese Patent Office</td> <td>Authorized officer</td> </tr> <tr> <td>Facsimile No.</td> <td>Telephone No.</td> </tr> </table>			Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.	A	JP 2004-2994 A (Kobe Steel, Ltd.), 08 January, 2004 (08.01.04), Full text & EP 1491647 A1 & WO 03/83151 A1	1-13	A	JP 2000-17388 A (Sumitomo Electric Industries, Ltd.), 18 January, 2000 (18.01.00), Full text (Family: none)	1-13	A	JP 2003-306747 A (Sumitomo Denko Steel Wire Kabushiki Kaisha), 31 October, 2003 (31.10.03), Full text (Family: none)	1-13	* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family	Date of the actual completion of the international search 25 April, 2005 (25.04.05)	Date of mailing of the international search report 17 May, 2005 (17.05.05)	Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer	Facsimile No.	Telephone No.
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/001703

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2783145 B2 (Kobe Steel, Ltd.), 06 August, 1998 (06.08.98), Full text (Family: none)	1-13
A	JP 11-246943 A (Chuo Hatsujo Kabushiki Kaisha), 14 September, 1999 (14.09.99), Full text & US 6224686 B1 & DE 19908407 A1	1-13

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Patent documents cited in the description

- JP 2842579 B [0003]
- JP 2002194496 A [0003]
- JP 3045795 B [0003]