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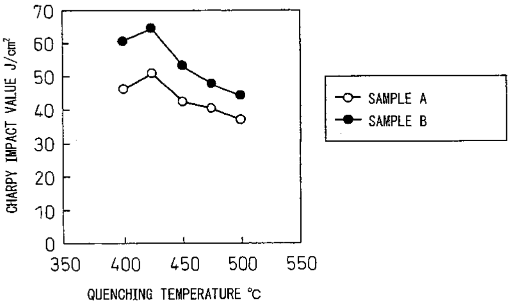
(54) STEEL FOR HIGH-STRENGTH SPRING AND HEAT-TREATED STEEL WIRE FOR HIGH-STRENGTH SPRING

(57) The present invention provides a high strength heat treated steel wire for spring having a tensile strength of 2000 MPa or more which is coiled in the cold state and can achieve both sufficient atmospheric strength and coilability and spring steel used for that steel wire, that is, a high strength heat treated steel wire for a spring **characterized by** comprising, by mass%, C: 0.5 to 0.9%, Si: 1.0 to 3.0%, Mn: 0.1 to 1.5%, Cr: 1.0 to 2.5%, V: over 0.15 to 1.0%, and Al: 0.005% or less, controlling N to 0.007% or less, further containing one or two of Nb: 0.001 to less than 0.01% and Ti: 0.001 to less 0.005%, and having a tensile strength of 2000 MPa or more, having cementite-based spheroidal carbides and alloy-based spheroidal carbides in a microscopic visual field satisfying an area percentage of carbides with a circle equivalent diameter of 0.2 μm or more of 7% or less and a density of carbides with a circle equivalent diameter of 1 grain/μm^2 or less, having a prior austenite grain size number of #10 or more, and having retained austenite of 15 mass% or less.

Fig. 1



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Description

TECHNICAL FIELD

[0001] The present invention relates to spring steel which is cold-coiled and has a high strength and high toughness and to heat treated steel wire for a spring.

BACKGROUND ART

[0002] Due to trends toward weight reduction and higher performance of automobiles, springs have been strengthened and high strength steel having a tensile strength in excess of 1500 MPa after heat treatment has been applied to springs. In recent years, steel wire having a tensile strength in excess of 1900 MPa has also been demanded. The purpose is to secure a material hardness which does not cause problems when the material is used as a spring even though the material softens to some extent by heating in strain reduction annealing, nitriding, and the like when producing the spring.

[0003] Further, by nitriding and shot-peening, it is known that the surface layer hardness increases and the durability in spring fatigue is remarkably improved, but the characteristics in the spring are not decided by surface layer hardness. Rather the strength and hardness inside the spring material have great effects. Therefore, it is important to set chemical composition which enable the internal hardness to be maintained extremely high.

[0004] As a means to this, there is an invention adding V, Nb, Mo, and other elements to form fine carbides which dissolve upon quenching and precipitate upon tempering and using these to restrict the movement of dislocations and thus improving settling resistance (for example, see Japanese Patent Publication (A) No. S57-32353).

[0005] On the other hand, the method of production of a coil spring made of steel includes hot coiling heating the steel to the austenite region for coiling, then quenching and tempering it and cold coiling a high strength steel wire comprised of steel quenched and tempered beforehand. In cold coiling, oil tempering, high frequency treatment, etc. enabling rapid heating and rapid cooling when producing the steel wire can be used, so it is possible to reduce the grain size of the prior austenite of the spring material and as a result produce a spring excellent in breakage property. Further, this method has the advantage that the heating furnace and other equipment on the spring manufacturing line can be simplified, so leads to a reduction of the equipment cost for spring makers. Cold coiling of springs is therefore being shifted to in recent years. In suspension springs as well, while a large diameter of steel wire is used compared with valve springs, cold coiling is introduced due to the above advantage.

[0006] However, if the steel wire for a cold-coiled spring increases in strength, it often breaks during cold coiling and cannot be formed into a spring shape. Up until now, both strength and workability (coilability) could not be simultaneously obtained with this, so strength and workability had to be obtained by what may be said to be the industrially disadvantageous techniques of hot coiling or quenching and tempering after hot coiling.

[0007] Further, when cold coiling a heat treated steel wire of high strength and nitriding it to secure strength, it had been considered effective to add large amounts of V, Nb, and other so-called alloy elements causing fine carbides to precipitate in the steel. However, if adding a large amount of such elements is added, it will not be able to dissolve by the heating of the quenching and will grow to coarse grains resulting in so-called undissolved carbides causing breakage at the time of cold coiling. Because of this, technology focusing on the undissolved carbide is also seen.

[0008] There is an invention aiming an improvement of performance by not only such alloy elements, but also controlling the carbides based on the cementite present in large amounts in the steel (for example, see Japanese Patent Publication (A) No. 2002-180198).

DISCLOSURE OF THE INVENTION

[0009] The present invention has as its task to provide a heat treated steel wire for a spring with a tensile strength of 2000 MPa or more which is coiled in a cold state and can achieve both sufficient strength in the atmosphere and coilability and spring steel used for that steel wire.

[0010] The inventors discovered that by controlling the N, which was not focused on until now, even if adding alloy elements, it is possible to suppress the formation of undissolved carbides and possible to secure toughness and workability and thereby developed a heat treated steel wire for a spring achieving both a high strength and coilability. That is, the gist of the present invention is as follows.

(1) High strength spring steel characterized by comprising, by mass%, C: 0.5 to 0.9%, Si: 1.0 to 3.0%, Mn: 0.1 to 1.5%, Cr: 1.0 to 2.5%, V: over 0.15 to 1.0%, and Al: 0.005% or less, controlling N to 0.007% or less, further containing one or two of Nb: 0.001 to less than 0.01% and Ti: 0.001 to less 0.005%, and having a balance of Fe and unavoidable impurities.

(2) High strength spring steel according to (1) characterized by further containing one or two of W: 0.05 to 0.5% and

Mo: 0.05 to 0.5%.

(3) High strength spring steel according to (1) or (2) characterized by further containing, by mass%, one or two or more of Ni: 0.05 to 3.0%, Cu: 0.05 to 0.5%, Co: 0.05 to 3.0%, and B: 0.0005 to 0.006%.

(4) High strength spring steel according to any one of (1) to (3) characterized by further containing, by mass%, one or two or more of Te: 0.0002 to 0.01%, Sb: 0.0002 to 0.01%, Mg: 0.0001 to 0.0005%, Zr: 0.0001 to 0.0005%, Ca: 0.0002 to 0.01%, and Hf: 0.0002 to 0.01%.

(5) A high strength heat treated steel wire for a spring characterized by having steel compositions according to any one of (1) to (4) having a tensile strength of 2000 MPa or more, having cementite-based spheroidal carbides and alloy-based spheroidal carbides in a microscopic visual field satisfying
an area percentage of carbides with a circle equivalent diameter of 0.2 μm or more of 7% or less and
a density of carbides with a circle equivalent diameter of 1 grain/μm^2 or less,
having a prior austenite grain size number of #10 or more, and
having retained austenite of 15 mass% or less.

BRIEF DESCRIPTION OF THE DRAWINGS

[0011]

FIG. 1 is a view explaining the effect of Nb addition when decreasing N (relationship of tempering temperature and Charpy impact value).

FIG. 2(a) is a view showing an example of observation of undissolved carbides by a scan type electron microscope. (b) is a view showing an example of elemental analysis by X-rays of alloy-based undissolved carbides, and (c) is a view showing an example of elemental analysis by X-rays of cementite-based undissolved carbides Y.

BEST MODE FOR CARRYING OUT THE INVENTION

[0012] The present inventors set the chemical ingredients to obtain a high strength and controlled the shape of the carbides in the steel by heat treatment so as to secure a coiling property sufficient for producing a spring in a steel wire and thereby reached the present invention.

[0013] The details will be explained hereunder. First, the reasons for limiting the chemical compositions and range of compositions of the high strength spring steel will be explained.

[0014] C is an element which greatly affects the basic strength of a steel material and is set to 0.5 to 0.9% so as to obtain a strength more sufficient that the past. If less than 0.5%, a sufficient strength cannot be obtained. In particular, even when omitting the nitriding for improving spring performance, 0.5% or more of C is required to secure a sufficient spring strength. If over 0.9%, a substantial hypereutectoid appears, and a large amount of coarse cementite precipitates, therefore the toughness is remarkably lowered. This simultaneously lowers the coiling property. Further, the relationship with the microstructure is also close. If less than 0.5%, the number of carbides is small, so the regions where carbide distribution is locally smaller than other parts (hereafter described as "carbide poor regions") easily increase and sufficient strength and toughness or coilability (ductility) are hard to obtain. Therefore, preferably it is 0.55% or more, from the viewpoint of the balance of strength-coiling, more preferably 0.6% or more.

[0015] On the other hand, when the amount of C is great, the alloy-based and cementite-base carbides tend to be hard to dissolve by the heat during the quenching. When the heating temperature in the heat treatment is high or when the heating time is short, the strength and coilability are often insufficient. Further, the undissolved carbides also affect the carbide poor regions. If the C in steel forms undissolved carbides, the de facto C in the matrix is decreased, so as previously explained, the area ratio of the carbide poor regions sometimes increase. Further, if the amount of C increases, the form of the martensite during tempering becomes the general lath martensite in medium carbon steel, while when the amount of C is great, it is known that the form changes to lenticular martensite. As a result of R&D, it was discovered that the carbide distribution of the tempered martensite structure formed by tempering the lenticular martensite is lower in carbide density compared with the case of tempering the lath martensite. Consequently, by increasing the amount of C, the increase of the lenticular martensite and undissolved carbides sometimes causes the carbide poor regions to increase. For this reason, it is preferably 0.7% or less. More preferably, by making it 0.65% or less, it is possible to relatively easily reduce the carbide poor regions.

[0016] Si is an element necessary for securing strength, hardness, and settling resistance of a spring. If the amount is small, the required strength and settling resistance are insufficient, therefore 1.0% is made the lower limit. Further, Si has the effect of spheroidizing and refining the carbide precipitates of the grain boundary. By actively adding it, there is the effect of reducing the grain boundary area percentage of grain boundary precipitates. However, when adding too large an amount, the material not only hardens, but also embrittles. Therefore, 3.0% is set as an upper limit to prevent embrittlement after quenching and tempering. Further, Si is an element contributing to tempering softening resistance.

To prepare a high strength wire rod, it is preferable to add a large amount to a certain extent. Specifically, it is preferable to add 2% or more. On the other hand, to obtain a stable coilability, it is preferable to make it 2.6%.

[0017] Mn is used for deoxidation and for fixing S in the steel as MnS, to raise quenching, and to sufficiently obtain hardness after heat treatment. 0.1% is set as the lower limit in order to secure this stability. Further, the upper limit is set at 2.0% in order to prevent embrittlement caused by Mn. Further, to simultaneously achieve strength and coilability, it is preferably 0.3 to 1%. Further, when giving priority to coiling, making it 1.0% or less is effective.

[0018] Cr is an effective element to improve quenching and softening resistance in tempering. Further, it is an effective element not only for securing tempering hardness, but also for increasing the surface layer hardness after nitridation and the depth of the hardened layer in nitridation such as seen in recent high strength valve springs. However, if the added amount is large, not only is an increase in cost incurred, but also the cementite seen after quenching and tempering coarsens. Further, it has the effect of stabilizing and coarsening the alloy-based carbides. As a result, the wire rod becomes brittle, so there is also the negative effect that the rod easily breaks during coiling. Consequently, when adding Cr, if 0.1% or more, the effect is not clear. Further, 2.5%, at which embrittlement becomes remarkable, was made the upper limit. However, in the present invention, the carbides are finely controlled by setting the N, so a large amount of Cr can be added, therefore the amount added was made one easily giving a high strength. Further, when performing nitriding, the addition of Cr enables the hardened layer obtained by the nitridation to be made deeper. Because of this, addition of 1.1% or more is preferable. Further, to make the rod suitable for nitridation for an unprecedented high strength spring, addition of 1.2% or more is preferable.

[0019] Cr blocks the dissolution of cementite by heating, so particularly if $C>0.55\%$, that is, the amount of C is great, suppression of the amount of Cr enables the formation of coarse carbides to be suppressed and enables both strength and coilability to be easily achieved. Therefore, preferably the added amount is made 2.0% or less. More preferably it is made 1.7% or less.

[0020] As V can be utilized for the hardening of the steel wire at the tempering temperature and the hardening of the surface layer during nitriding due to the secondary precipitation and hardening for precipitating and hardening the carbides during tempering. Further it is effective for suppressing coarsening of the austenite grain size due to the formation of nitrides, carbides, and carbonitrides. Addition is therefore preferable. However, until now, because the nitrides, carbides, and carbonitrides of V are formed at even the austenitizing temperature A_3 point of steel, when insufficiently dissolved, they easily remain as undissolved carbides (nitrides). The undissolved carbides not only become the cause of breakage during spring coiling, but also "wastefully consume the V". They reduce the improvement effect of the tempering softening resistance and secondary precipitation hardening by the added V and reduce the performance of the spring. Therefore, up until now, it was industrially assumed that 0.15% or less was preferable. However, in the present invention, controlling the amount of N enables the formation of V-based nitrides, carbides, and carbonitrides at the austenitizing temperature A_3 point or more to be suppressed, so it is possible to add a larger amount of V by that amount. The added amount of V was therefore made over 0.15% to 1.0%. If the added amount is 0.15% or less, there is little effect of adding V such as the improvement of hardness of the nitrided layer and increase of depth of the nitrided layer and a sufficient fatigue limit (durability) of conventional steel or more cannot be secured. Further, if the added amount is over 1.0%, coarse undissolved inclusions are formed and the toughness is reduced. In the same way as Mo, an overcooled structure is easily formed and cracks or breakage during drawing are easily caused. For those reasons, 1.0%, where industrially stable handling is easy, was made the upper limit.

[0021] Nitrides, carbides, and carbonitrides of V are formed even at the austenitizing temperature A_3 point of steel or more, so when dissolution is insufficient, they easily remain as undissolved carbides (nitrides). Therefore, if considering the current ability to control the amount of nitrogen industrially, making it industrially 0.5% or less is preferable and making it 0.4% or less is more preferable.

[0022] On the other hand, with surface hardening treatment by nitridation, the rod is heated to a maximum of a temperature of 300°C or more, so to suppress hardening of the top surface layer and softening of the inner portion hardness by nitridation, it is necessary to add over 0.15%. Preferably, addition of 0.2% or more is preferable.

[0023] Al is a deoxidation element and influences the formation of oxides. In particular, in high strength valve springs, hard oxides such as Al_2O_3 easily become the starting points of breakage, so it is necessary to avoid this. For this reason, it is important to strictly control the amount of Al. In particular, when the tensile strength as a heat treated steel wire is over 2100 MPa, strict control of the oxide-forming elements is essential to reduce fluctuations in the fatigue strength. In the present invention, Al was set to 0.005% or less. This is because if over 0.005%, Al_2O_3-based oxides are easily formed, so breakage caused by the oxides occurs and a sufficient fatigue strength and quality stability cannot be secured. Further, when requiring high strength fatigue, it is preferable made 0.003% or less.

[0024] In the present invention, the control of N is an important point. In the present invention, a strict limit value of $N \leq 0.007\%$ is set. This is because in the present invention, the role of N is newly focused on. The effects of N control and the reasons for the provisions in the present invention will be explained below. In steel, the effects of N are as follows: 1) N is present in ferrite as dissolved N which suppresses the movement of the dislocations in the ferrite and thereby causes the ferrite to harden. 2) nitrides are formed with Ti, Nb, V, Al, B, and other alloy elements and affect the performance of the steel material. The mechanism and the like will be explained later. 3) N affects precipitation behavior of cementite and other iron-based carbides and affects the performance of the steel material performance.

[0025] In spring steel, C and alloy elements such as Si and V enable strength to be secured, so the effect of hardening of dissolved N is not that great. On the other hand, if considering cold working (coiling) of a spring, suppression of movement of dislocations suppresses deformation of the worked parts and causes embrittlement of the worked parts, so reduces the coiling characteristics.

[0026] Further, among the elements defined in claim 1, V forms precipitates in the steel at a high temperature. These chemical compositions are mainly nitrides at a high temperature. Along with the cooling, the form changes to carbonitrides and carbides along with cooling. Consequently, the nitrides formed at a high temperatures easily become nuclei for the precipitation of V carbides. These easily form undissolved carbides during the heating in the patenting and quenching process. Further, these become nuclei, so they easily grow in size. Further, if seen from the viewpoint of cementite, with the high strength springs like the present, due to the required strength, the tempering temperature is made 300 to 500°C. In spring steel, due to its characteristic composition system, the Fe-based carbides formed during tempering are complexly changed in form to ε-carbides and θ-carbides (so-called cementite Fe_3C). Because of that, the ductility and other mechanical properties of the steel are affected. N also has an influence on the formation of carbides. When the amount of N is small, the ductility and toughness at 350 to 500°C are improved. In the present invention, N was limited to $N \leq 0.007\%$ in order to reduce the above harmful effects of N.

[0027] Further, as explained before, small amounts of one or two of Ti and Nb are added. Originally, if the N amount can be suppressed to 0.003% or less, good performance is obtained without adding one or both of Ti and Nb, but industrially stably making the amount 0.003% or less becomes disadvantageous in the point of manufacturing cost. Therefore, small amounts of one or two of Ti and Nb are added. If adding Ti and Nb, these elements form nitrides at a high temperature, so substantially reduce the dissolved nitrogen. Therefore, the same effect as with reducing the amount of N added can be obtained. Because of that, the upper limit of the added amount of N may be increased. However, if the amount of N exceeds 0.007%, the amount of V, Nb, or Ti nitrides becomes larger. As a result, the undissolved carbides become greater and the TiN and other hard inclusions increase, so the toughness falls and the fatigue limit characteristics and coiling characteristics fall. Therefore, the upper limit of the amount of N was limited to 0.007%.

[0028] That is, even when adding one or two of Ti and Nb, if the amount of N becomes too great or if the amount of Ti or Nb becomes too great, again Ti or Nb nitrides will be formed and conversely become harmful, so the amounts of Ti and Nb added must be kept very small. Because of this, the upper limit of the amount of N is preferably made 0.005% or less, more preferably 0.004% or less. By this precise N control, embrittlement of ferrite is suppressed and formation of V-based nitrides is suppressed whereby formation and growth of undissolved carbides are suppressed. Further, by controlling the form of the Fe-based carbides, the toughness can be improved. That is, if N exceeds 0.007%, V-based nitrides easily form large amounts of undissolved carbides, and the steel becomes embrittled depending on the form of the ferrite and carbides.

[0029] In this way, even when adding Ti or Nb, if considering the ease of heat treatment and the like, 0.005% or less is preferable. Further, it is said to be preferable that the lower limit of the amount of N be small, but N easily enters from the atmosphere in the steelmaking process and the like, so considering the manufacturing cost and the ease of the denitrification process, 0.0015% or more is preferable.

[0030] Nb forms nitrides, carbides, and carbonitrides. The nitrides are produced at a higher temperature than with V. Due to this, formation of Nb nitrides during cooling consumes the N in the steel and can suppress the formation of V-based nitrides. As a result, the formation of V-based undissolved carbides can be suppressed, so temper softening resistance, workability and coilability can be secured.

[0031] Further, other than the Nb-based carbonitrides suppressing the coarsening of the austenite grain size, they can be utilized for hardening the steel wire at the tempering temperature and hardening the surface layer during nitriding. However, if the added amount is too great, undissolved carbides with Nb-based nitride nuclei easily remain, so addition of a large amount should be avoided. Specifically, when the Nb added amount is less than 0.001%, almost no effect of addition is recognized. Further, if 0.01% or more, the large amount of addition forms coarse undissolved inclusions, lowers the toughness, and, like with Mo, easily forms an overcooled structure easily causing cracks and breakage during drawing. Therefore, the amount is made the 0.01% where industrially stable handling is easy.

[0032] FIG. 1 is a view showing the results of measurement of the impact values of materials of the chemical compositions shown in Table 1, that is, the results of measurement of the impact values of the samples A and B heat treated by the method of the examples described below. As shown in FIG. 1, it is learned that steels in which a slight amount of Nb is added to control the N give overall high impact values.

Table 1

	Steel compositions (mass %)											
	C	Si	Mn	F	S	Cr	Mo	V:	W	Nb	N	S-Al
Sample A	0.61	2.20	0.53	0.002	0.004	1.21	0.13	0.20	0.16	-	0.0049	0.002
Sample B	0.61	2.21	0.54	0.002	0.004	1.19	0.13	0.20	0.16	0.009	0.0050	0.002

[0033] In the present invention, when adding Ti, this added amount is 0.001% to less than 0.005%. Ti is a deoxidizing element and an element forming nitrides and sulfides, so has an effect on the formation of oxides, nitrides, and sulfides. Consequently, addition of a large amount facilitates formation of hard oxides and nitrides, so if adding this carelessly, it forms hard carbides and lowers the fatigue limit. Like with Al, in particular in high strength springs, it lowers the stability of fluctuation of the fatigue strength more than the fatigue limit itself of the spring. If the amount of Ti is great, the breakage rate due to inclusions becomes greater, so it is necessary to control this amount. The amount is made less than 0.005%.

[0034] On the other hand, Ti forms TiN in the molten steel at a high temperature, so acts to reduce the sol.N in the molten steel. In the present invention, limiting the N to suppress the formation of the V-based nitrides and further suppress the growth of the V-based undissolved carbides is the point of the technology. For this reason, if consuming the N at a temperature of the V-based nitride formation temperature or more, it is possible to suppress the growth of V-based nitrides and V-based carbonitrides growing using these as nuclei during cooling. That is, adding Ti substantially reduces the amount of N bonding with V, so reduces the temperature of formation of the V-based nitrides and further suppresses V-based undissolved carbides.

[0035] Consequently, large addition of Ti should be avoided from the viewpoint of the formation of Ti-based undissolved carbonitrides and oxides, but the addition of a small amount enables the temperature of formation of V-based nitrides to be reduced, so rather can reduce the undissolved carbides. The added amount is 0.001% or more. If less than 0.001%, there is no effect of N consumption, there is no effect of suppressing V-based undissolved carbides, and the effect of improvement of the workability (coilability) cannot be seen. However, the amount of addition of Ti is preferably 0.003% or less.

[0036] The steel of the present invention has the above stated chemical compositions as basic compositions and further may have added to it compositions in order to improve the properties of the steel. That is, further, one or both of W and Mo are added when strengthening the temper softening resistance. W not only improves quenching, but also acts to form carbides in the steel and raise the strength and is effective for conferring temper softening resistance. Therefore, adding as much as possible is preferable. W forms carbides at a lower temperature compared to Ti, Nb, and the like, so it does not easily form undissolved carbides. Further, it can confer temper softening resistance by precipitation hardening. That is, in nitriding and strain relief annealing as well, the inner hardness will not be greatly decreased. If the added amount is 0.05% or less, the effect is not seen, while if 0.5% or more, coarse carbides are formed and conversely the ductility and other mechanical properties are liable to be impaired, so the added amount of W was set to 0.05 to 0.5%. Further, if considering the ease of heat treatment, 0.1 to 0.4% is preferable. In particular, to avoid an overcooled structure right after rolling and other negative effects and obtain the maximum extent of temper softening resistance, adding 0.15% or more is further preferable.

[0037] Mo improves hardenability and precipitates as carbides at a temperature of about the tempering and nitriding temperature, so can confer temper softening resistance. Therefore, even after high temperature tempering, strain relief annealing or nitriding in the process, or other heat treatment, the steel does not soften and can exhibit a high strength. This suppresses the decrease of the spring internal hardness after nitriding and facilitates hot setting and strain relief annealing, so improves the fatigue characteristics of the final spring. That is, it is possible to make the tempering temperature higher when controlling the strength. Making the tempering temperature higher is advantageous in decreasing the grain boundary area percentage of the grain boundary carbides. That is, annealing at a high temperature the grain boundary carbides precipitating in a film is effective for causing spheriodization and reducing the grain boundary area ratio. Further, the Mo forms Mo-based carbides separate from cementite in the steel. In particular, compared with V etc., it has a lower precipitation temperature, so has the effect of suppressing the coarsening of the carbides. If the added amount is 0.05% or less, no effect is recognized. However, if the added amount is great, an overcooled structure easily is formed in the softening heat treatment before rolling or drawing and easily causes cracks and breakage at the time of drawing. That is, when drawing, it is preferable to first patent the steel material to convert it to a ferrite-pearlite structure.

[0038] However, Mo is an element which confers large hardenability, so when the added amount becomes large, the time until the end of the pearlite transformation becomes longer, an overcooled structure is easily formed in the cooling after rolling or in the patenting process and becomes a cause of breakage when drawing, or, when not breaking but having internal cracks, the characteristics of the final product are greatly degraded. If Mo exceeds 0.5%, the hardenability becomes great and industrially making a ferrite-pearlite structure becomes difficult, so this was made the upper limit. To suppress the formation of a martensite structure causing a drop in the production ability in the rolling, drawing, or other production process and facilitate industrially stable rolling and drawing, 0.4% or less is preferable and 0.2% or so is more preferable.

[0039] Further, if comparing W and Mo with V, Nb, and Ti similarly having an effect of strengthening the temper softening resistance, V, Nb, and Ti form nitrides as explained above and facilitate the growth of carbides with these as nuclei, while W and Mo do not form nitrides much at all, so are free of the effects of the amount of N and can strengthen the softening resistance if added. In other words, strengthening of the softening resistance is possible even with V, Nb, and T, but the amounts added end up being self restricted for addition for strengthening the softening resistance while avoiding undissolved carbides. Therefore, when no formation of undissolved carbides and a high softening resistance are necessary, addition of W or Mo not forming nitrides, causing precipitation of carbides at a relatively low temperature, and functioning as precipitation strengthening elements would be extremely effective. Further, one or more of Ni, Cu, Co, and B may be added to secure strength by strengthening the matrix when the optimal balance of the softening resistance and workability by control of the carbides cannot be obtained in achieving both strength and workability.

[0040] Ni improves the hardenability and enables stable increase of strength by heat treatment. Further, it improves the ductility of the matrix and improves the coilability. However, quenching and tempering increase the retained austenite, so the settling and uniformity of the material are inferior after forming the spring. If the added amount is 0.05% or less, an effect in increasing the strength and improving the ductility cannot be recognized. On the other hand, addition of a large amount of Ni is not preferable. At 3.0% or more, the negative effect of the greater retained austenite becoming greater becomes remarkable and the effect of improving the hardenability and ductility become saturated, which is disadvantageous from the point of cost and the like.

[0041] In regards to Cu, adding Cu can prevent decarburization. A decarburized layer decreases fatigue life after processing the spring, so effort is made to reduce it as much as possible. Further, when the decarburized layer becomes deep, the surface layer is removed by the process called peeling. Further, in the same way as Ni, there is an effect of improving the corrosion resistance. By suppressing a decarburized layer, the improvement of the fatigue life and peeling of the spring can be omitted. The effect of suppression of decarburization and effect of improvement of the corrosion resistance by Cu can be exhibited at 0.05% or more. As explained later, even if adding Ni, even over 0.5%, embrittlement easily causes rolling marks. Therefore, the lower limit was made 0.05% and the upper limit was made 0.5%. The addition of Cu does not harm the mechanical properties much at all, but when adding Cu 0.3%, the hot rollability is degraded, so cracks sometimes are formed at the billet surface at the time of rolling. Because of that, it is preferable to change the amount of Ni added to prevent cracking during rolling in accordance with the amount of Cu added, that is, [Cu%]<[Ni%]. In the range of Cu of 0.3% or less, no rolling marks will be caused, so there is no need to define the amount of Ni added for the purpose of preventing rolling marks.

[0042] Co decreases hardenability in some cases, but can improve the high temperature strength. Further, it inhibits the formation of carbides, so acts to suppress the formation of coarse carbides at issue in the present invention. Consequently, it can suppress the coarsening of the cementite and other carbides. Therefore, addition is preferable. When added, if 0.05% or less, the effect is small. However, if a large amount is added, the hardness of the ferrite phase increases and the ductility is lowered, so the upper limit was made 3.0%. Industrially, stable performance is obtainable at 0.5% or less.

[0043] B is an element improving the hardenability and effective for cleaning the austenite grain boundaries. The P, S, and other elements segregating at the grain boundaries and lowering the toughness are rendered harmless and the breakage characteristics are improved by addition of B. At this time, if B bonds with N and forms BN, this effect is lost. The added amount was therefore made 0.0005% where the effect becomes clear as the lower limit and 0.0060% where the effect is saturated as the upper limit. However, if even a small amount of BN is formed, embrittlement is caused, so full consideration so as not to form BN is necessary. Consequently, preferably the amount is 0.003 or less. More preferably, it is effective to use the Ti, Nb, and other nitride-forming elements to fix the free N and make B 0.0010 to 0.0020%.

[0044] These Ni, Cu, Co, and B are mainly effective for strengthening the ferrite phase of the matrix. These are elements effective when securing strength by strengthening the matrix when an optimal balance of softening resistance and workability cannot be obtained by control of carbides in order to achieve both strength and workability.

[0045] Further, one or two or more of Te, Sb, Mg, Zr, Ca, and Hf are added as elements to control the form of the oxides and sulfides when further higher performance and stabler performance are sought.

[0046] Te has the effect of making the MnS spheroidal. If less than 0.0002%, that effect is not clear, while if over 0.01%, the negative effects of decreasing the toughness of the matrix, causing hot breakage, and decreasing the fatigue durability become remarkable, so 0.01% is set as the upper limit.

[0047] Sb has the effect of spheroidizing MnS. If less than 0.0002%, that effect is not clear, while if over 0.01%, the negative effects of decreasing the toughness of the matrix, causing hot breakage, and decreasing the fatigue limit become remarkable, so 0.01% is set as the upper limit.

[0048] Mg forms oxides in molten steel higher than the MnS formation temperature and is already present in the molten steel at the time of MnS formation. Therefore, it can be used as nuclei for precipitation of MnS and thereby can control the distribution of MnS. Further, in numerical distribution, Mg-based oxides disperse in the molten steel finer than the Si- and Al-based oxides often seen in conventional steels, so the MnS with Mg-based oxides as nuclei finely disperse in the steel. Therefore, even with the same S content, the MnS distribution differs depending upon the presence of Mg. By adding this, the MnS grain size becomes further finer. This effect can be sufficiently obtained even in small amounts. If adding Mg, the MnS becomes finer. However, if over 0.0005%, hard oxides easily form. Further, MgS and other sulfides also start to be formed and a drop in fatigue strength and a drop in coilability are incurred. Therefore, the amount of Mg added is made 0.0001 to 0.0005%. If used for a high strength spring, 0.0003% or less is preferable. These elements are used in very small amounts, but by using large amounts of Mg-based refractories, about 0.0001% can be added. Further, by carefully selecting the auxiliary materials and using auxiliary materials having a low Mg content, the amount of Mg added can be controlled.

[0049] Zr is an oxide- and sulfide-forming element. In spring steel, it finely disperses the oxides, so like with Mg forms the nuclei for precipitation of MnS. Due to this, the fatigue limit is improved and the ductility is increased, so the coilability is improved. If less than 0.0001%, this effect is not seen, while even if added in an amount over 0.0005%, formation of hard oxides is promoted, so even if the sulfides are finely dispersed, trouble due to the oxides easily occurs. Further, by the addition of a large amount, in addition to oxides, ZrN, ZrS, and other nitrides and sulfides are formed and cause manufacturing trouble and decrease the fatigue durability characteristics of the spring, so the amount was made 0.0005% or less. Further, when used for a high strength spring, this added amount is preferably made 0.0003% or less. These elements are very small in amounts, but can be controlled by carefully selecting the auxiliary materials and precisely controlling the refractories and the like.

[0050] For example, by liberally using Zr refractories at locations like the ladle, tundish, and nozzle contacting the molten steel for long periods of time, it is possible to add about 1 ppm to about 200 tons of molten steel. Further, auxiliary materials should be added considering this and so as not to exceed the prescribed ranges. As the method of analysis of Zr within the steel, it is possible to sample 2 g from a part of the measured steel material not influenced by the surface scale, treat the sample by a method similar to JIS G 1237-1997 Appendix 3, then measure it by ICP. At that time, the calibration curve in ICP is set to be suited for a very small amount of Zr.

[0051] Ca is an oxide- and sulfide-forming element. In spring steel, it makes MnS spheroidal and thereby can suppress the length of the MnS acting as the starting point of fatigue and other breakage and render it harmless. This effect is not clear if less than 0.0002%, while even if added in an amount over 0.01%, not only does the yield become poor, but also oxides and CaS and other sulfides are formed and manufacturing trouble and a decrease in fatigue limit characteristics are caused, so the amount was made 0.01% or less. The added amount is preferably 0.001% or less.

[0052] Hf is an oxide-forming element and becomes the nuclei for precipitation of MnS. Due to this, by fine dispersal, Zr is an oxide- and sulfide-forming element. In spring steel, the oxides finely disperse, so like Mg, these become nuclei for precipitation. Due to this, the fatigue limit is improved and the ductility is increased, so the coilability is improved. The effect is not clear if less than 0.0002%, while even if added in an amount of over 0.01%, not only does the yield become poor, but also oxides and ZrN, ZrS, and other nitrides and sulfides are formed and manufacturing trouble and a decrease in fatigue limit characteristics are caused, so the amount was made 0.01% of less. The added amount is preferably 0.003% or less.

[0053] Below, the preferable range of content of other compositions will be explained.

[0054] For P and S, while not prescribed in the claims, restriction is necessary. P makes the steel harden, but further causes segregation and makes the material become brittle. In particular, the P segregated at the austenite grain boundaries causes a drop in impact value and delayed breakage due to penetration of hydrogen and the like. Therefore, less is better. Accordingly, the amount is preferably made P: 0.015% or less where this embrittlement tendency becomes remarkable. Further, in the case of a high strength where the tensile strength of the heat treated steel wire exceeds 2150 MPa, the amount is preferably made less than 0.01%.

[0055] S, like P, causes embrittlement of the steel when present in the steel. Its influence is made much smaller by Mn, but MnS also takes the form of inclusions, so the breakage characteristics decline. In particular, in high strength steel, breakage sometimes occurs due to a very fine amount of MnS, so the S is preferably reduced as much as possible. Making the amount 0.015% or less where these negative effects become remarkable is preferable. Further, in the case of a high strength where the tensile strength of the heat treated steel wire exceeds 2150 MPa, the amount is preferably made less than 0.01%.

[0056] t-O is made 0.0002 to 0.01%. Steel contains oxides formed through the deoxidation process and dissolved O. However, when the total amount of oxygen (t-O) is great, it means that there is a large amount of oxide-based inclusions. If the size of the oxide-based inclusions is small, they will not affect spring performance, but if there is a large amount of large oxides present, they will have a great effect on spring performance. If the amount of oxygen is over 0.01%, the spring performance is remarkably reduced, so the upper limit is preferably made 0.01%. The smaller the amount of oxygen the better, but even if less than 0.0002%, the effect is saturated, so this is preferably made the lower limit. If considering ease in the actual deoxidation process and the like, adjustment to 0.0005 to 0.005% is preferable.

[0057] In the present invention, the tensile strength is preferably made 2000 MPa or more. If the tensile strength is high, the fatigue characteristics of the spring tend to be improved. Further, even when applying nitridation or other surface hardening treatment, if the basic strength of the steel wire is high, high fatigue characteristics and settling characteristics can be obtained. On the other hand, if the strength is high, the coilability declines and spring production becomes difficult. Because of this, it is important to not only improve the strength, but also to impart ductility enabling coiling.

[0058] From the viewpoints of fatigue, settling, and the like, strength of the steel wire becomes necessary. TS≥2000 MPa is made the lower limit. Further, when applied to a high strength spring, further higher strength is preferable. The amount is preferably 2200 MPa or more and further, for application to a high strength spring, increase of the strength to 2250 or 2300 MPa or more in a range not impairing the coilability is preferable.

[0059] For undissolved carbides, to obtain high strength, C and Mn, Ti, V, Nb, and other so-called alloy elements are added, but if adding large amounts of elements forming nitrides, carbides, and carbonitrides among these, undissolved carbides easily remain. The undissolved carbides are generally spheroidal and include ones mainly made of alloy elements and ones mainly made of cementite.

[0060] FIG. 2 shows a typical example of observation. In FIG. 2, (a) shows an example of observation of undissolved carbides by a scan type electron microscope, (b) shows an example of elemental analysis by X-rays of alloy-based undissolved carbides X, and (c) shows an example of elemental analysis by X-rays of cementite-based undissolved carbides Y. According to this, two types of structures are recognized in the steel: needle-shaped structures and spheroidal structures of the matrix. Generally, it is known that by using quenching to form needle-shaped structures of martensite and using tempering to form carbides in the steel, strength and toughness can be simultaneously achieved. However, in the present invention, as shown by X and Y in (a) of FIG. 2, not just needle-shaped structures, but also large amounts of spheroidal structures remain in some cases. These spheroidal structures are undissolved carbides. Their distribution greatly affects the performance of the steel wire for a spring. Therefore, the "undissolved carbides" referred to here include not only so-called alloy-based spheroidal carbides (X) where the above alloys form nitrides, carbides, and carbonitrides, but also cementite-based spheroidal carbides (Y) mainly comprising Fe carbides (cementite).

[0061] FIG. 2(b) and (c) show examples of analysis by EDX attached to an SEM. Conventional inventions focus on only the V, Nb, and other alloy element-based carbides. One example is FIG. 2(b). This is characterized in that the Fe peak is relatively small and the alloy peak (in this example V) is large in the carbides. The alloy-based carbides (X) strictly speaking are mostly composite carbides with nitrides (so-called carbonitrides), so here these alloy-based carbides and nitrides and their composite alloy-based spheroidal precipitates will be collectively referred to as "alloy-based spheroidal carbides".

[0062] In the present invention, it was discovered that the form of precipitation of not only the conventional alloy element-based spheroidal carbides, but also, as shown in FIG. 2 (c), the Fe_3C of a circle equivalent diameter of 3 μm or more and so-called cementite-based carbides comprising this in which slight amounts of alloy elements are dissolved is important. When simultaneously achieving high strength and workability of more than those of conventional steel wire as in the present invention, if there are many cementite-based spheroidal carbides of 3 μm or less size, the workability is greatly impaired. From here on, carbides of such spheroidal shapes mainly comprising Fe and C as shown in FIG. 2 (c) will be referred to as "cementite-based spheroidal carbides.

[0063] Note that similar results of analysis to these results are obtained even by the replica method using a transmission electron microscope. These spheroidal carbides are believed to be carbides which do not sufficiently dissolve in the quenching and tempering by oil tempering and high frequency treatment and become spheroidal and grow or shrink in the quenching and tempering process. The carbides of these dimensions not only do not contribute at all to the strength and toughness due to quenching and tempering, but conversely degrade them. That is, they fix the C in the steel and consume the C added to become the source of strength and further coarsen the same so become a source of stress concentration as well, so the mechanical properties of the steel wire are reduced.

[0064] Therefore, the following restrictions are added to the alloy-based spheroidal carbides and cementite-based spheroidal carbides at the observed plane. The following restrictions are important for eliminating the negative effects due to these.

[0065] The area percentage of the carbides with a circle equivalent diameter of 0.2 μm or more is 7% or less.

[0066] The density of carbides with a circle equivalent diameter of 0.2 μm or more is 1 carbide/μm^2 or less

[0067] When cold coiling the steel after quenching and tempering, the undissolved spheroidal carbides affect the coiling characteristics, that is, the bending characteristics up to breaking. Up to now, to obtain a high strength, the general practice was to add large amounts of not only C, but also Cr, V, and other alloy elements, but there were the negative effects that the strength became too high, the deformation ability became insufficient, and the coiling characteristics were degraded. It is believed that the cause was the coarse carbides precipitating in the steel.

[0068] These alloy-based and cementite-based carbides in the steel can be observed by etching a mirror polished sample by picral, electrolytic etching, or the like, but for detailed observation and evaluation of the dimensions and the like, a scan type electron microscope must be used for observation at a high magnification of 3000X or more. The alloy-based spheroidal carbides and the cementite-based spheroidal carbides covered here have circle equivalent diameters of 0.2 μm or more. Usually, carbides are essential for securing the strength of the steel and temper softening resistance, but if the effective particle size is 0.1 μm or less or conversely over 1 μm, rather there is no contribution to the strength or increased fineness of the austenite particle size and the deformation characteristics are just degraded. However, in the prior art, the importance is not recognized that much. The prior art only focuses on V, Nb, and other alloy-based carbides. Carbides of a circle equivalent diameter of 3 μm or less, in particular cementite-based spheroidal carbides, have been considered harmless.

[0069] These alloy-based and cementite-based carbides are observed by electrolytically etching a mirror polished sample and using a scan type electron microscope to observe it at 10000X observing in 10 fields or more. If the area percentage of the spheroidal carbides exceeds 7%, the workability is extremely inferior, so this was set as the upper limit.

[0070] Further, in the case of alloy-based and cementite-based spheroidal carbides with a circle equivalent diameter of 0.2 μm or more, not only the dimensions, but also the numbers become major factors. Consequently, the two were considered to define the scope of the present invention. That is, if the number of spheroidal carbides having a circle equivalent diameter of 0.2 μm or more is extremely large and the density in the observed plane exceeds 1 carbide/μm^2, deterioration of the coiling characteristics becomes remarkable, so this is made the upper limit. On the other hand, if the dimensions of the carbides exceed 3 μm, the effect of the dimensions becomes even larger, so it is preferable not to exceed this.

[0071] The reason for making the prior austenite grain size number #10 or larger is that in steel wire having basically a tempered martensite structure, the prior austenite grain size has a great effect on the basic properties of the steel wire along with the carbides. That is, a smaller prior austenite grain size means superior fatigue characteristics and coilability. However, no matter how small the austenite grain size, if the carbides are contained in over the prescribed amount, the effect is small. Generally, to reduce the austenite grain size, it is effective to lower the heating temperature during quenching, but this conversely increases the undissolved spheroidal carbides. Therefore, it is important to finish the steel wire to one balanced in the amount of carbides and prior austenite grain size. Here, when the carbides satisfy the above definitions, if the prior austenite grain size number is less than #10, sufficient fatigue characteristics and coilability cannot be obtained, so the prior austenite grain size number was made #10 or larger.

[0072] Further, for application to a high strength spring, finer grains are preferable. By making the number #11 or further #12 or higher, it becomes possible to simultaneously achieve high strength and coilability.

[0073] The reason for making the retained austenite 15 mass% or less is that retained austenite often remains at the segregated parts or prior austenite grain boundaries or near regions surrounded by subgrains. The retained austenite becomes martensite by work-induced transformation. If transformation is induced during spring formation, locally high hardness parts are formed in the material and, rather, the coiling characteristics as a spring are reduced. Further, recent springs are strengthened at their surfaces by shot-peening, setting, and other plastic deformation, but if the production process includes a plurality of steps of applying such plastic deformation, the work-induced martensite formed at an early stage will lower the fracture strain and lower the workability and the breakage characteristics of the spring during use. Further, when strike marks and other industrially unavoidable deformation are introduced, the wire will easily break during coiling. Further, by gradually breaking down in nitriding, strain relief annealing, and other heat treatment, the mechanical properties are changed, the strength reduced, the coilability reduced, and other negative effects are caused. Therefore, the retained austenite is reduced as much as possible and formation of work-induced martensite is suppressed so as to improve the workability. Specifically, if the amount of retained austenite exceeds 15% (mass%), the sensitivity to strike marks etc. becomes higher and the wire easily breaks during coiling or other handling, so 15% or less was restricted to.

[0074] The amount of retained austenite changes depending on the amount of C, Mn, and other alloy elements added and the heat treatment conditions. Therefore, improvement of not only the design of the compositions, but the heat treatment conditions is important.

[0075] If the martensite formation temperature (starting temperature Ms point, finishing temperature Mf point) becomes a low temperature, martensite will not be formed unless the temperature is made considerably low during quenching. Retained austenite will easily remain. With industrial quenching, water or oil is used, but the suppression of retained austenite requires advanced control of the heat treatment. Specifically, control becomes necessary to maintain the cooling refrigerant at a low temperature, maintain a low temperature as much as possible after cooling, secure a long transformation time to martensite, and the like. Industrially, the material is processed by a continuous line, so the temperature of the cooling refrigerant easily rises to near 100°C, but it is preferably maintained at 60°C or less. A low temperature of 40°C or less is more preferable. Further, to sufficiently promote martensite transformation, the material must be held in the cooling medium for at least 1 second. Securing a holding time after cooling is also important.

[0076] Further, in addition to the restrictions on the carbides etc., a structure in which the distribution of the carbides becomes smaller than that of other parts should be avoided. Specifically, in lenticular martensite and its tempered structures, the distribution of carbides is smaller than other parts and the microstructure becomes nonuniform, so there is a detrimental effect on the fatigue strength and workability.

EXAMPLES

Evaluation Items:

[0077] To evaluate the applicability of the present invention to a spring, the tensile strength, hardness after annealing, impact value, and reduction in area as measured by a tensile test are shown as evaluation items. The tensile strength is directly linked with the fatigue limit of the spring. The higher the strength, the higher the fatigue limit shown.

[0078] Further, the reduction in area measured simultaneously with the measurement of the tensile strength shows the plastic deformation behavior of the material and is an evaluation indicator of workability into a spring (coiling characteristic). The larger the reduction in area, the easier workability shown, but in general the higher the strength, the smaller the reduction in area. From the examples of conventional steel, if the reduction in area exceeds 30% evaluated by this wire diameter, it is learned that problems will not easily occur in industrial scale mass production even with other wire diameters. The prepared test piece is obtained by quenching and tempering a material of ϕ13 mm to exceed 2200 MPa, then preparing a No. 9 test piece of JIS Z 2201. This is tested based on JIS Z 2241. The tensile strength was calculated from this breaking load.

[0079] Further, in recent years, springs are often being made higher in strength by hardening by nitridation of the surface layers. The nitridation is performed by heating the spring at 400 to 500°C in a nitriding atmospheric gas and holding it there for several minutes to 1 hour so as to harden the surface layer. At this time, the inside where the nitrogen does not penetrate is heated, so is annealed and softened. It is important to suppress this softening, so the hardness after annealing simulating nitriding was used as an item for evaluation of the softening resistance.

[0080] Further, in order to evaluate the workability and fatigue resistance of the material, the Charpy impact value was made an evaluation item. Generally, it is believed that a material which has an excellent impact value is also good in breakage resistance including fatigue characteristics. Further, a brittle material is also inferior in workability, so a material with a high toughness is considered to be excellent in workability as well. In this example, the Charpy impact value of a material heat treated in the same way as one measured for tensile strength after quenching and tempering was measured. The Charpy impact value is influenced by the austenite grain size, so the austenite grain size of the same material was also measured. Note that the Charpy impact test piece is comprised of a so-called half size (5x10 mm cross-section) material obtained from a ϕ13 mm heat treated material and formed with a U-notch.

[0081] Further, when the spring is one with a finer ϕ4 mm, the heat treatment is ended in a relatively short time. Because of this, it is known that undissolved carbides easily remain and the workability is decreased. Consequently, in the invention examples as well, the material was patented and drawn to ϕ4 mm and the drawn wire was heated treated to measure the distribution of carbides and austenite grain size. Generally, if the heating temperature is low and the time is short, the austenite grain size becomes small, but the undissolved carbides tend to increase. A balance of the two should be used for overall evaluation. The results appear in the tensile strength and the elongation, so these two were evaluated. With a fine diameter material of ϕ5 mm or less, since the cross-sectional area is small, in the plastic deformation behavior, a clearer difference appears in the elongation rather than the reduction in area.

[0082] Details of the heat treatment conditions and the like of the evaluated material will be described below.

[0083] A tensile test was conducted based on the JIS by preparing a test piece with a parallel portion of ϕ6 mm and measuring the tensile strength and elongation. The amount of retained austenite was determined by mirror polishing after quenching and tempering and measurement by X-rays. Further, the hardness after annealing was determined by mirror polishing after heat treatment and measurement of the Vickers hardness at the depth of 1/2 from the surface of the radius at three points. The average value was used as the hardness after annealing.

[0084] Regarding the method for producing the material (wire rod), Invention Example 16 of the present invention produced the material by a 2t vacuum melting furnace, then rolled this into a billet. At that time, in the invention examples, the high temperature of 1200°C or more was held for a certain time. Next, in each case, the billet was rolled to ϕ13 mm.

[0085] In the other examples, the material was melted in a 16 kg vacuum melting furnace, then forged by forging to ϕ13 mm x 600 mm, then heat treated. At this time as well, in the same way, the material was held at a 1200°C or more high temperature for a certain time, then heat treated to become a predetermined high strength.

[0086] Regarding the heat treatment method, for the preparation of the evaluated test piece, unless there is a particular description otherwise, the material was held at 1200°C x 15 min → air-cooled, then heated at 950°C for 10 minutes, then charged into a lead bath heated to 650°C, further heated at 950°C x 10 min, charged into a 60°C oil bath for quenching, then, in the invention examples, adjusted in tempering temperature so that the tensile strength exceeded 2200 MPa. The tensile strength, drawability, and Charpy impact value with this heat treatment were measured.

[0087] This tempering temperature differs depending on the chemical compositions, but in regards to the present invention, the materials are heat treated in accordance with the chemical compositions so that the tensile strength becomes 2200 MPa or more. On the other hand, in regards to the comparative examples, the materials are heat treated just to match the tensile strength. Further, the materials were annealed at 400°C x 20 min simulating nitriding and measured for hardness so as to evaluate the softening resistance.

[0088] Further, for the ϕ4 mm wire rods for evaluation of carbides, unless there is a particular description otherwise, the rods were held at 1200°C x 15 min → air-cooled, then cut to ϕ10 mm, heated at 950°C for 10 minutes, then charged to a lead bath heated to 650°C. Further, this was drawn to reduce it in diameter to ϕ4 mm, heated at 950°C x 5 min, then charged into a 60°C oil bath for quenching, then adjusted in tempering temperature to give a tensile strength exceeding 2200 MPa. Further, the stress able to give a number of load cycles exceeding 10^7 in a Nakamura type rotary bending test was deemed the fatigue strength.

Table 2

Chemical compositions (mass%)											
	No.	C	Si	Mn	P	S	N	Cr	V:	Al	Ti	Nb
Inv. Ex.	1	0.58	2.22	0.66	0.008	0.004	0.0011	1.17	0.22	0.003		0.007
	2	0.65	1.93	0.44	0.007	0.007	0.0022	1.41	0.25	0.002		0.008
	3	0.71	2.23	0.81	0.003	0.003	0.0017	1.17	0.23	0.003		0.006
	4	0.76	1.89	0.51	0.008	0.005	0.0021	1.23	0.26	0.003		0.005
	5	0.81	1.94	0.54	0.008	0.008	0.0012	1.18	0.25	0.002		0.004
	6	0.66	1.89	0.63	0.005	0.009	0.0017	1.10	0.18	0.001		0.007
	7	0.68	2.10	0.77	0.004	0.003	0.0032	1.40	0.28	0.001	0.003	0.005
	8	0.66	2.02	0.42	0.008	0.006	0.0049	1.40	0.24	0.002	0.004	
	9	0.67	2.00	0.83	0.001	0.004	0.0021	1.18	0.29	0.002	0.004	
	10	0.66	2.05	0.86	0.004	0.009	0.0038	1.38	0.24	<0.001	0.003	
	11	0.69	1.80	0.67	0.005	0.002	0.0037	1.48	0.26	0.002	0.004	
	12	0.61	2.04	0.76	0.008	0.006	0.0046	1.31	0.28	0.003	0.004	
	13	0.69	2.17	0.43	0.007	0.008	0.0056	1.12	0.24	0.002	0.002	
	14	0.65	1.91	0.48	0.009	0.008	0.0025	1.16	0.26	0.002	0.003	
	15	0.61	1.86	0.68	0.002	0.005	0.0041	1.16	0.30	0.002	0.004	
	16	0.62	2.05	0.56	0.006	0.005	0.0047	1.43	0.21	0.002		0.008
	17	0.69	2.11	0.65	0.007	0.008	0.0019	1.50	0.27	0.004		0.009
	18	0.66	2.23	0.79	0.007	0.006	0.0055	1.37	0.25	0.001		0.004
	19	0.62	2.22	0.71	0.008	0.003	0.0055	1.44	0.24	0.003		0.006
	20	0.63	1.95	0.43	0.002	0.003	0.0040	1.20	0.22	0.002		0.005
	21	0.69	2.08	0.65	0.006	0.004	0.0026	1.35	0.20	0.003		0.003
	22	0.66	1.94	0.82	0.007	0.004	0.0024	1.45	0.27	0.002		0.009
	23	0.68	2.08	0.89	0.006	0.008	0.0053	1.26	0.29	0.001		0.005
	24	0.63	1.86	0.42	0.009	0.005	0.0048	1.17	0.20	0.003	0.001	0.005
	25	0.69	2.00	0.87	0.005	0.005	0.0020	1.26	0.25	0.002	0.003	0.004

Table 3

		Chemical compositions (mass%)											
	No.	Mo	W	Ni	Cu	Co	B	Ca	Zr	Hf	Te	Sb	Mg
Inv. Ex.	1	0.10	0.18						0.0003				0.0003
	2	0.25	0.16						0.0003				0.0005
	3	0.17	0.16						0.0002				0.0003
	4	0.18	0.15						0.0002				0.0004
	5	0.20	0.21						0.0003				0.0003
	6	0.20	0.18						0.0002				0.0002
	7	0.22	0.17						0.0002				0.0004
	8								0.0003				0.0003
	9								0.0001				0.0003
	10	0.15	0.16										
	11	0.15	0.16										
	12	0.25	0.15										
	13	0.21	0.17										0.0004
	14	0.15	0.21						0.0003				
	15	0.16	0.17						0.0003				0.0003
	16												
	17								0.0001				
	18		0.16						0.0003				
	19	0.11							0.0003				
	20	0.15	0.20										
	21	0.19	0.17						0.0002				
	22	0.08	0.14										0.0003
	23	0.13	0.20						0.0002				0.0003
	24								0.0002				0.0005
	25								0.0003				0.0004

Table 4

		Chemical compositions (mass%)										
	No	C	Si	Mn	P	S	N	Cr	V:	Al	Ti	Nb
Inv. ex.	26	0.67	2.07	0.48	0.008	0.001	0.0041	1.49	0.24	0.001	0.001	0.004
	27	0.70	2.26	0.81	0.008	0.008	0.0058	1.24	0.24	0.001	0.001	0.002
	28	0.68	1.86	0.85	0.005	0.005	0.0049	1.10	0.23	0.002	0.004	0.006
	29	0.67	2.24	0.48	0.008	0.002	0.0029	1.20	0.30	0.002	0.004	0.002
	30	0.66	1.85	0.78	0.005	0.008	0.0026	1.47	0.29	0.002	0.002	0.002
	31	0.62	2.11	0.54	0.007	0.005	0.0034	1.42	0.23	0.002	0.002	0.009
	32	0.61	1.80	0.25	0.007	0.005	0.0028	1.24	0.28	0.002	0.001	0.007
	33	0.65	2.01	0.26	0.002	0.003	0.0038	1.10	0.20	0.002	0.004	0.001
	34	0.68	2.11	0.28	0.003	0.005	0.00	1.10	1.24	0.003	0.004	0.001
	35	0.63	1.82	0.15	0.008	0.008	0.0043	1.28	0.24	0.002	0.004	0.009
	36	0.70	2.15	0.26	0.002	0.008	0.0054	1.39	0.20	0.001	0.004	0.004
	37	0.68	2.20	0.12	0.004	0.003	0.0029	1.17	0.25	0.001	0.004	0.005
	40	0.64	1.92	0.42	0.002	0.004	0.0025	1.26	0.28	0.003	0.004	0.002
	41	0.62	2.04	0.77	0.002	0.009	0.0036	1.24	0.29	0.001	0.002	0.009
	42	0.67	2.10	0.70	0.003	0.007	0.0036	1.11	0.21	0.002	0.004	0.003
	43	0.64	2.00	0.79	0.008	0.003	0.0028	1.31	0.20	0.001	0.004	0.009
	44	0.67	2.13	0.86	0.004	0.004	0.0053	1.36	0.22	0.003	0.004	0.004
	45	0.62	2.07	0.47	0.004	0.009	0.0041	1.32	0.22	0.003	0.002	0.006
	46	0.69	2.28	0.60	0.006	0.005	0.0047	1.43	0.28	0.003	0.002	0.008
	47	0.68	2.26	0.68	0.005	0.009	0.0040	1.24	0.23	0.002	0.003	0.004
	48	0.82	2.22	0.74	0.008	0.005	0.0019	1.16	0.18	0.003		0.002
	49	0.77	2.19	0.80	0.003	0.005	0.0015	1.12	0.22	0.002		0.007
	50	0.68	2.06	0.71	0.004	0.008	0.0025	1.33	0.17	0.002		0.006
	51	0.61	2.50	0.75	0.006	0.003	0.0015	1.05	0.42	0.003		0.008

Table 5

		Chemical compositions (mass%)											
	No.	Mo	W	Ni	Cu	Co	B	Ca	Zr	Hf	Te	Sb	Mg
Inv. Ex.	26		0.14						0.0003				0.0003
	27	0.24							0.0002				0.0003
	28	0.24	0.19										
	29	0.17	0.22						0.0002				
	30	0.16	0.21										0.0003
	31	0.19	0.18						0.0001				0.0004
	32	0.23	0.20						0.0003				0.0003
	33	0.18	0.16						0.0001				0.0002
	34	0.14	0.20						0.0001				0.0003
	35	0.12	0.21										0.0002
	36	0.15	0.19						0.0003				
	37	0.21	0.18						0.0002				0.0005
	40	0.23	0.14	0.2					0.0001				0.0004
	41	0.15	0.14		0.07				0.0002				0.0004
	42	0.12	0.17			0.15			0.0002				0.0004
	43	0.10	0.16				0.0006		0.0002				0.0005
	44	0.16	0.22					0.0005	0.0002				0.0005
	45	0.21	0.18						0.0001	0.0005			0.0005
	46	0.11	0.16						0.0001		0.002		0.0003
	47	0.09	0.19						0.0003			0.001	0.0002
	48		0.21						0.0001				0.0004
	49	0.16							0.0003				0.0004
	50								0.0002				0.0004
	51								0.0002				0.0004

Table 6

		Chemical compositions (mass%)										
	No	C	Si	Mn	P	S	N	Cr	V:	Al	Ti	Nb
Comp. ex.	52	0.65	2.05	0.67	0.007	0.001	0.0056	1.25	0.28	0.003		
	53	0.82	1.81	0.85	0.007	0.006	0.0066	1.09	0.52	0.002		
	54	0.65	1.30	0.79	0.002	0.007	0.0080	1.31	0.24	0.002	0.003	
	55	0.65	1.79	1.18	0.003	0.011	0.0100	1.35	0.26	0.001		0.007
	56	0.62	1.76	0.97	0.008	0.008	0.0040	1.21	0.55	0.001	0.044	
	57	0.63	2.44	0.76	0.004	0.005	0.0041	1.11	0.20	0.002	0.011	
	58	0.65	2.12	1.10	0.007	0.003	0.0049	1.18	0.29	0.001	0.018	0.07
	59	0.66	1.88	1.20	0.009	0.008	0.0027	1.38	0.27	0.001	0.021	
	60	0.65	1.90	1.01	0.010	0.011	0.0087	1.42	0.29	0.002		0.033
	61	0.68	2.13	0.41	0.006	0.001	0.0036	1.45	0.25	0.001		0.046
	62	0.69	1.93	1.09	0.006	0.009	0.0049	1.28	0.25	0.004		0.022
	63	0.70	1.86	0.45	0.005	0.012	0.0040	1.32	0.28	0.012	0.003	
	64	0.64	2.34	1.12	0.001	0.009	0.0022	1.30	0.25	0.007		0.007
	65	0.68	2.01	0.56	0.008	0.007	0.0050	1.29	0.06	0.001		0.003
	66	0.68	1.86	0.60	0.008	0.006	0.0050	1.49	0.10	0.001		0.006
	67	0.67	2.49	1.16	0.007	0.009	0.0021	0.76	0.21	0.003		0.008
	68	0.66	2.38	0.50	0.006	0.004	0.0053	0.65	0.21	0.002		0.007
	69	0.67	1.74	0.58	0.009	0.003	0.0052	1.31	0.28	0.001		0.009
	70	0.68	1.49	1.18	0.005	0.007	0.0059	1.11	0.24	0.003		0.004
	71	0.69	2.66	0.87	0.005	0.009	0.0057	1.12	0.27	0.002		0.003
	72	0.62	1.47	0.99	0.010	0.004	0.0037	1.27	0.27	0.002		0.006
	73	0.65	1.79	0.85	0.003	0.002	0.0054	1.40	0.21	0.003		0.007
	74	0.48	1.38	1.06	0.011	0.008	0.0034	1.13	0.29	0.001		0.007
	75	0.64	0.52	1.07	0.011	0.005	0.0024	1.43	0.23	0.003		0.006
	76	0.45	1.23	0.88	0.007	0.012	0.0051	1.18	0.29	0.002		0.005
	77	0.64	0.96	1.14	0.004	0.002	0.0055	1.18	0.23	0.002		0.007

Table 7

		With drawing						Without drawing					
		Density		Tensile strength MPa	Tensile elong ation %	γ #	Rotary bending MPa	Retained γ %	Tensile strength MPa	Hardness after annealing HV	Tensile reduc tion in area %	Impact value J/cm^2	γ #
	No.	Area ratio %	Number no./μm^2										
Inv. ex.	1	0.37	0.12	2312	7.3	12	915	6.2	2253	580	38.2	53	10
	2	0.32	0.30	2347	8.9	12	917	9.3	2254	601	34.3	57	11
	3	0.20	0.05	2325	6.8	11	923	7.7	2262	576	41.7	56	10
	4	0.20	0.38	2325	7.0	12	906	7.6	2290	612	42.5	54	11
	5	0.06	0.46	2310	7.3	11	907	8.2	2308	613	39.6	53	10
	6	0.28	0.35	2296	8.9	12	895	7.6	2251	598	45.0	55	10
	7	0.40	0.27	2324	6.1	13	902	10.3	2255	599	37.8	53	11
	8	0.02	0.03	2328	6.5	12	897	10.2	2259	601	46.9	51	10
	9	0.20	0.15	2288	8.9	12	902	10.2	2259	605	46.9	53	10
	10	0.25	0.35	2301	8.4	13	902	8.8	2269	582	35.5	61	11
	11	0.38	0.08	2331	6.3	12	919	11.4	2248	602	45.0	51	10
	12	0.28	0.15	2302	8.2	13	917	7.2	2265	584	39.9	47	11
	13	0.30	0.24	2328	7.0	12	896	7.2	2284	587	46.7	64	10
	14	0.28	0.20	2327	8.7	13	923	10.0	2262	598	36.7	52	11
	15	0.04	0.30	2299	10.2	11	894	7.6	2276	585	42.5	54	10
	16	0.23	0.15	2328	6.8	13	898	8.5	2261	600	45.0	59	10
	17	0.52	0.05	2322	10.2	12	892	10.9	2280	584	34.0	61	11
	18	0.48	0.25	2307	7.3	12	914	10.6	2273	586	33.1	49	10
	19	0.28	0.08	2290	7.2	13	925	7.2	2260	586	44.1	53	10
	20	0.12	0.14	2301	6.4	13	899	8.0	2285	583	43.7	48	12
	21	0.06	0.22	2320	6.1	12	909	9.4	2265	586	47.2	49	11
	22	0.23	0.25	2340	7.1	13	919	8.7	2254	604	45.6	53	11
	23	0.31	0.19	2319	6.7	13	901	10.3	2258	585	35.0	49	10
	24	0.31	0.23	2306	6.5	12	914	8.7	2262	591	38.7	52	11
	25	0.41	0.40	2315	8.7	13	897	9.4	2263	588	35.5	58	11

Table 8

		With drawing						Without drawing					
		Density		Tensile strength MPa	Tensile elongation %	γ #	Rotary bending MPa	Retained γ %	Tensile strength MPa	Hardness after annealing HV	Tensile reduc tion in area %	Impact value J/cm^2	γ #
	No.	Area ratio %	Number no./ μm^2										
Inv. ex.	26	0.21	0.36	2302	7.4	12	928	6.7	2241	592	34.6	51	10
	27	0.32	0.14	2299	7.1	13	919	8.2	2272	579	46.2	51	11
	28	0.43	0.04	2321	8.0	11	904	8.2	2255	587	39.9	68	10
	29	0.29	0.27	2306	6.4	11	910	9.9	2281	593	36.4	56	10
	30	0.03	0.22	2330	6.9	12	909	10.1	2279	605	35.3	54	11
	31	0.05	0.38	2303	6.9	12	922	7.5	2289	608	36.5	63	10
	32	0.21	0.20	2315	8.0	12	927	7.5	2251	588	33.5	52	10
	33	0.40	0.15	2338	6.9	11	902	9.3	2254	591	39.4	56	10
	34	0.11	0.04	2335	7.7	13	904	11.6	2248	599	35.4	50	11
	35	0.45	0.11	2328	9.1	13	909	10.8	2282	593	39.2	48	11
	36	0.41	0.27	2320	7.4	12	913	10.7	2273	591	33.0	66	11
	37	0.30	0.12	2318	8.0	11	914	11.8	2251	592	43.9	57	10
	40	0.52	0.39	2346	8.1	11	914	7.7	2271	601	38.5	51	10
	41	0.28	0.16	2312	8.1	11	922	8.1	2273	579	44.7	53	10
	42	0.10	0.10	2321	7.4	12	908	7.2	2257	588	41.9	47	10
	43	0.44	0.02	2326	8.7	13	922	11.6	2284	587	37.5	62	11
	44	0.22	0.05	2325	10.0	13	891	11.0	2255	601	44.0	56	11
	45	0.18	0.11	2307	6.4	13	897	9.2	2290	597	46.3	57	11
	46	0.01	0.21	2335	6.9	13	910	11.5	2271	590	37.8	48	11
	47	0.36	0.07	2319	9.3	11	908	8.6	2253	596	38.3	51	10
	48	0.01	0.36	2315	9.8	11	895	11.5	2279	603	32.5	55	10
	49	0.44	0.11	2330	8.3	12	905	10.8	2251	594	40.0	59	10
	50	0.46	0.07	2277	7.7	12	923	9.6	2249	586	35.6	50	10
	51	1.12	0.61	2310	7.7	12	880	11.1	2242	590	40.6	55	10

Table 9

		With drawing						Without drawing					
		Density		Tensile strength MPa	Tensile elongation %	γ#	Rotary bending MPa	Retained γ %	Tensile strength MPa	Hardness after annealing HV	Tensile reduction in area %	Impact value J/cm^2	γ#
	No.	Area ratio %	Number no./μm^2										
Inv. ex.	52	9.2	0.41	2311	1.9	11	895	10.2	2242	583	19.3	49	10
	53	7.0	0.70	2308	2.1	12	904	8.6	2236	588	16.1	51	11
	54	8.7	0.37	2306	2.0	12	924	8.8	2230	590	16.3	52	12
	55	7.5	0.61	2275	2.0	12	903	10.1	2243	585	22.2	50	10
	56	7.8	0.44	2292	2.0	13	889	9.1	2241	578	19.5	53	11
	57	4.8	1.56	2270	8.4	11	890	9.9	2228	590	23.5	20	10
	58	7.7	0.71	2280	3.3	13	892	10.7	2224	579	20.0	52	11
	59	7.7	0.27	2275	3.8	13	899	11.3	2238	575	17.1	53	11
	60	2.4	1.11	2308	3.5	13	912	7.8	2250	598	20.2	20	11
	61	8.7	2.23	2271	3.9	11	871	8.3	2235	590	14.9	20	10
	62	7.2	0.62	2285	3.3	11	889	11.8	2260	577	15.6	20	10
	63	0.25	0.39	2298	2.0	13	780	8.0	2232	580	14.5	48	11
	64	0.21	0.44	2296	2.1	12	790	7.2	2263	590	21.9	53	11
	65	0.08	0.49	2293	2.7	9	911	6.9	2263	550	18.3	19	8
	66	0.11	0.40	2316	2.1	11	895	11.5	2260	533	13.3	19	10
	67	0.40	0.41	2303	4.1	11	887	7.2	2215	518	14.0	23	10
	68	0.43	0.30	2303	2.6	12	900	7.6	2239	522	19.0	23	10
	69	1.20	0.02	2306	8.1	13	883	15.5	2231	575	25.9	21	10
	70	0.16	0.18	2306	9.8	13	898	16.1	2243	593	25.2	20	11
	71	0.06	0.34	2294	7.0	11	907	16.0	2226	592	27.3	20	10
	72	0.13	0.39	2275	1.9	8	783	6.3	2231	580	18.3	21	7
	73	0.17	0.40	2295	2.7	8	798	10.7	2252	594	22.2	19	7
	74	0.12	0.42	2197	10.9	13	748	8.9	2228	542	41.7	51	11
	75	0.24	0.24	2260	6.2	12	775	8.3	2213	536	35.5	53	10
	76	0.07	0.07	2177	6.7	12	762	10.4	2222	528	39.6	54	10
	77	0.16	0.37	2164	10.6	12	737	11.3	2248	552	37.8	57	10

[0089] Tables 2 to 9 show the chemical compositions of the present invention and the comparative steels when treated at ϕ4 mm, the cementite-based carbide poor region area ratio, the area percentage of the alloy-based/cementite-based spheroidal carbides, the density of cementite-based spheroidal carbides of a circle equivalent diameter of 0.2 to 3 μm, the density of cementite-based spheroidal carbides of a circle equivalent diameter of over 3 μm, the maximum oxide diameter, the prior austenite grain size number, the amount of retained austenite (mass%), and the resultant obtained tensile strength, hardness after annealing, impact value, and reduction in area as measured in the tensile test. That is, Tables 2 and 3 show the chemical compositions of Invention Example Nos. 1 to 25, while Tables 4 and 5 show the chemical compositions of Invention Example Nos. 26 to 51. Table 6 shows the chemical compositions of Comparative Example Nos. 52 to 77. Further, Table 7 shows the characteristics of Invention Example Nos. 1 to 25 and Table 8 shows them for Invention Example Nos. 26 to 51 respectively with drawing and without drawing. Further, Table 9 shows the characteristics of Comparative Example Nos. 52 to 77 with drawing and without drawing.

[0090] Below, the comparative examples will be explained.

[0091] In the invention examples, even the heat treated materials without drawing exhibited good performance in terms of the impact value and softening resistance after annealing, tensile characteristics, and the like and even the heat treated materials after drawing were within the limits of tensile characteristics, carbide distribution, and the like, so good performance was obtained, but the following examples were outside the limits, so did not exhibit sufficient performance.

[0092] Examples 52 and 53 are cases where neither Ti nor Nb is included. A large amount of V and Cr is added, so undissolved carbides with nitrides as nuclei are formed, so the reduction in area in the tensile test or elongation after drawing is low and the workability is lowered.

[0093] In Examples 54 and 55, while Ti and Nb are added, the N is excessive and undissolved carbides with nitrides as nuclei are formed, so the reduction in area in the tensile test or elongation after drawing is low and the workability is lowered.

[0094] In Examples 56 to 59, Ti is added to fix N as TiN, but the amount of Ti added is excessive and there are negative effects by TiN. Because of this, the distribution of inclusions becomes greater and as a result the reduction in area in the tensile test or elongation after drawing is low and the workability is lowered.

[0095] In particular, Example 57 is the case where the heating temperature during quenching is reduced and thereby a large number of undissolved carbides are formed.

[0096] Examples 60 to 62 are examples in which Nb is added, but the added amount is excessive, so a large number of undissolved carbides are observed, the reduction in area in the tensile test or elongation after drawing is low, and the workability is lowered. In Examples 63 and 64, the Al is excessive, so the oxides become larger and the fatigue characteristics decline.

[0097] Examples 65 and 66 are cases where the added amount of V is excessive. In each case, the hardness after annealing simulating nitridation is low, the prior austenite grain size tends to become coarse, and the fatigue characteristics decline. Further, in actual nitriding, compared to the invention examples in which V is added in the defined amounts, the surface layer hardness is lower, the nitriding depth is shallower even with the same nitriding time, and other differences occur in performance after nitriding.

[0098] In Examples 67 and 68, the added amount of Cr is too little, the hardness after annealing simulating nitriding is low, the surface hardened layer at the time of nitriding becomes thin, and the fatigue characteristics decline.

[0099] Examples 69 to 71 are cases where the cooling temperature at the time of quenching is high and the cooling time is short. The amount of retained austenite becomes great. Because of this, the hardness after annealing is insufficient, and, in terms of practical application, the areas around the slight handling marks become brittle due to stress induced transformation, so the workability declines.

[0100] Examples 72 and 73 are examples when the heating temperature during quenching is made too high. The prior austenite grain size becomes larger, the impact value becomes lower, and the fatigue characteristics decline.

[0101] Examples 74 to 77 are cases when C or Si are smaller than defined. The tensile strength after annealing decreases, so the fatigue strength cannot be secured

INDUSTRIAL APPLICABILITY

[0102] The present invention steels, because the area percentage and density of the cementite-based and alloy-based spheroidal carbides in the steel wire for cold-coiling springs, the austenite grain size, and the amount of retained austenite are made small, are increased in strength to 2000 MPa or more, are given coilability, and enable production of springs high in strength and excellent in breakage characteristics.

Claims

1. High strength spring steel **characterized by** comprising, by mass%,
   C: 0.5 to 0.9%,
   Si: 1.0 to 3.0%,
   Mn: 0.1 to 1.5%,
   Cr: 1.0 to 2.5%,
   V: over 0.15 to 1.0%, and
   Al: 0.005% or less,
   controlling N to 0.007% or less,
   further containing one or two of Nb: 0.001 to less than 0.01% and Ti: 0.001 to less 0.005%, and
   having a balance of Fe and unavoidable impurities.

2. High strength spring steel according to claim 1 **characterized by** further containing one or two of
   W: 0.05 to 0.5% and
   Mo: 0.05 to 0.5%.

3. High strength spring steel according to claim 1 or claim 2 **characterized by** further containing, by mass%, one or two or more of
   Ni: 0.05 to 3.0%,
   Cu: 0.05 to 0.5%,
   Co: 0.05 to 3.0%, and
   B: 0.0005 to 0.006%.

4. High strength spring steel according to any one of claims 1 to 3 **characterized by** further containing, by mass%, one or two or more of
   Te: 0.0002 to 0.01%,
   Sb: 0.0002 to 0.01%,
   Mg: 0.0001 to 0.0005%,
   Zr: 0.0001 to 0.0005%,
   Ca: 0.0002 to 0.01%, and
   Hf: 0.0002 to 0.01%.

5. A high strength heat treated steel wire for a spring **characterized by** having steel compositions according to any one of claims 1 to 4
   having a tensile strength of 2000 MPa or more,
   having cementite-based spheroidal carbides and alloy-based spheroidal carbides in a microscopic visual field satisfying
   an area percentage of carbides with a circle equivalent diameter of 0.2 μm or more of 7% or less and
   a density of carbides with a circle equivalent diameter of 1 grain/μm^2 or less,
   having a prior austenite grain size number of #10 or more, and
   having retained austenite of 15 mass% or less.

Fig. 1

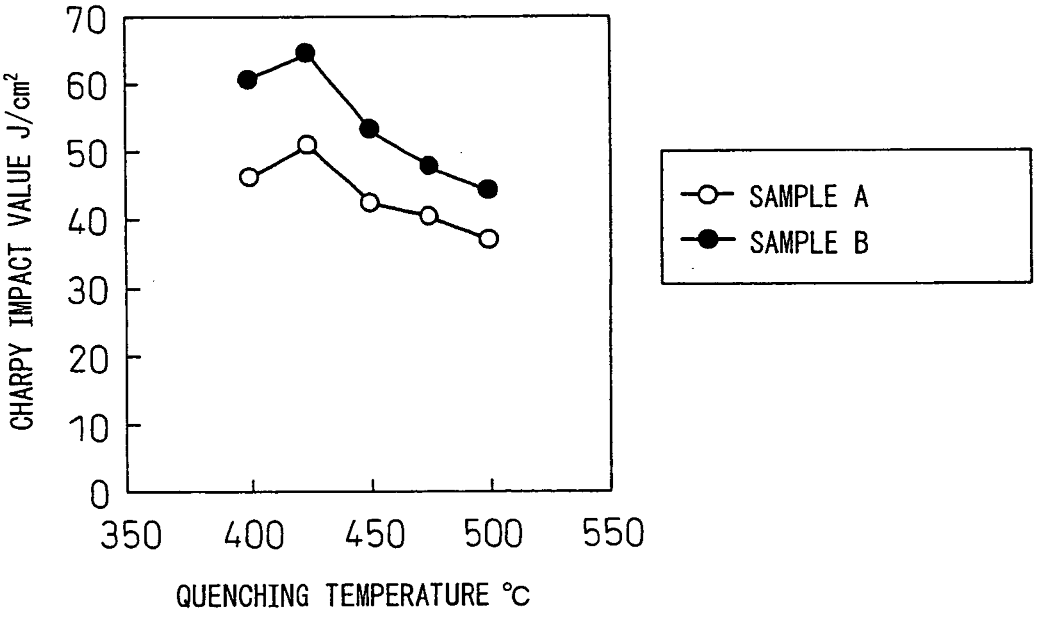
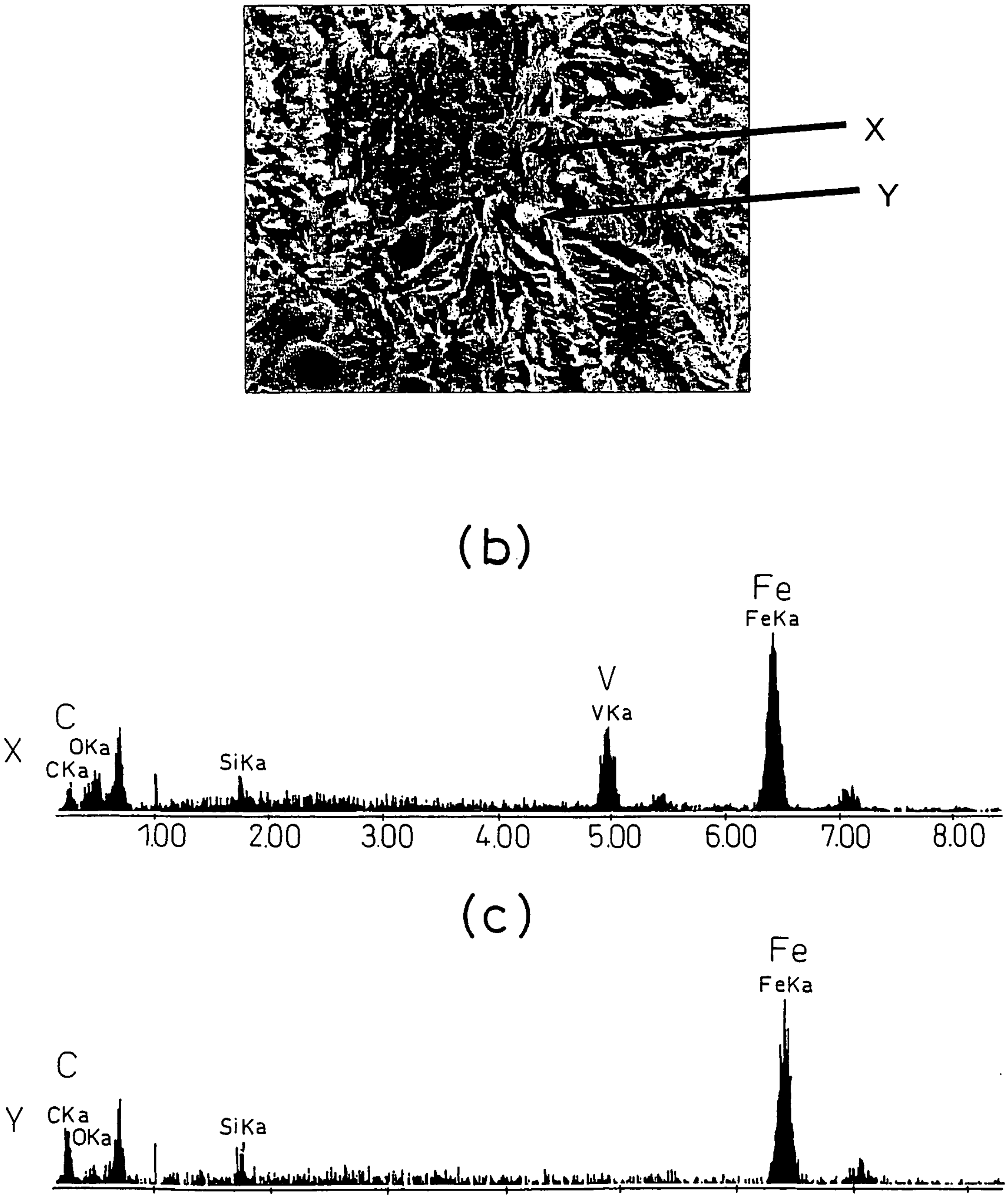

CHARPY IMPACT VALUE J/cm²
70
60
50
40
30
20
10
0
350
400
450
500
550
QUENCHING TEMPERATURE °C
SAMPLE A
SAMPLE B

Fig. 2

(a)


X
Y
(b)
Fe
FeKa
V
VKa
C
X
OKa
CKa
SiKa
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00
(c)
Fe
FeKa
C
Y
CKa
OKa
SiKa
1.00
2.00
3.00
4.00
5.00
6.00
7.00
8.00

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/322784

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

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	1996-2007
Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2006/059784 A1 (Nippon Steel Corp.), 08 June, 2006 (08.06.06), Claims; page 11, lines 9 to 13; page 21, line 12 to page 26, line 9; page 31, line 15 to page 32, line 5; page 34, lines 5 to 11; tables 1, 4, 8, 11 & JP 2004-346995 A & JP 2004-346996 A	1-5
E,X	JP 2006-342400 A (Nippon Steel Corp.), 21 December, 2006 (21.12.06), Full text (Family: none)	1-5

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

*	Special categories of cited documents:	"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
"A"	document defining the general state of the art which is not considered to be of particular relevance	"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
"E"	earlier application or patent but published on or after the international filing date	"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
"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)	"&"	document member of the same patent family
"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		

Date of the actual completion of the international search 15 January, 2007 (15.01.07)	Date of mailing of the international search report 23 January, 2007 (23.01.07)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP S5732353 A **[0004]**
- JP 2002180198 A **[0008]**