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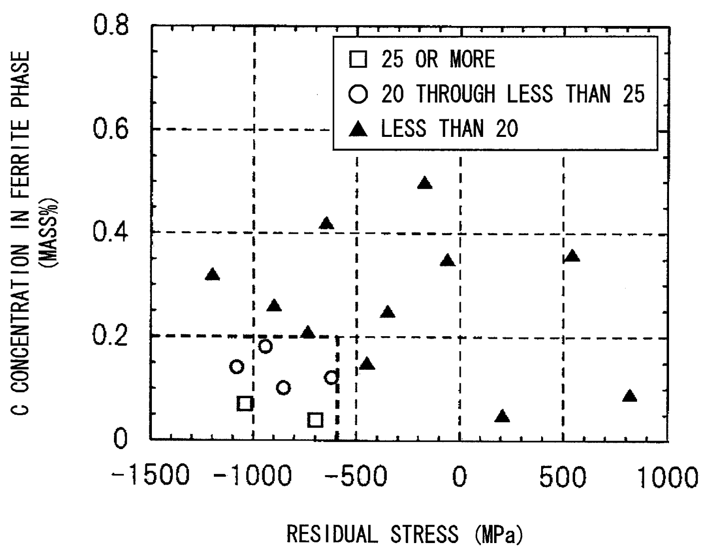
(54) HIGH-STRENGTH ULTRA-FINE STEEL WIRE AND MANUFACTURING METHOD THEREFOR

(57) The present invention provides a steel wire, including chemical components of: C: 0.7-1.2 mass%; Si: 0.05-2.0 mass%; and Mn: 0.2-2.0 mass%, with a balance including Fe and inevitable impurities, in which the steel wire has a pearlite structure, the average C concentration at a center portion of a ferrite phase in an outermost layer of the steel wire is 0.2 mass% or lower, and a residual compressive stress in the longitudinal direction of the steel wire in the outermost layer is 600 MPa or more.

FIG. 1



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Description

[Technical Field]

[0001] The present invention relates to a high-strength steel wire used for a steel cord for a vehicle tire, a saw wire and the like, and a method of manufacturing the same. More specifically, the present invention relates to an ultrathin steel wire that is strengthened through a wire-drawing working at a cold temperature using a die and that has a wire diameter of 0.04-0.4 mm and the strength of 4500 MPa grade or more.
This application claims priority on Japanese Patent Application No. 2009-148051 filed on June 22, 2009, the content of which is incorporated herein by reference.

[Background Art]

[0002] With the increasing demand for reducing the weight of a tire, there exist increasing needs for further improving a tensile strength of a steel wire for a steel cord in a vehicle tire. Similarly, there exist increasing needs for further improving the tensile strength of a steel wire for a wire saw for precisely cutting a sapphire crystal, SiC crystal and the like. In response to the needs described above, various intensive studies have been made. As a result, it has been found that it is necessary to secure a sufficient ductility, in addition to making the steel wire have higher tensile strength. There are several indices for indicating the degree of ductility, such as the number of twistings until breakage of a steel wire under a twisting test, and the presence or absence of the occurrence of cracks (delamination) appearing in a longitudinal direction of a steel wire during the twisting test. The increase in strength of the steel wire leads to a decrease in ductility, and it is important to suppress a decrease in ductility. Further, high-strength steel wire deteriorates its properties through aging at room temperature (20-40°C, several days to several years), and hence, it is also important not to substantially decrease favorable ductility through aging.
[0003] In general, a high-strength steel wire is manufactured such that a wire material having a pearlite structure is subjected to a wire-drawing working using a die. With this working, a distance between pearlite lamellas becomes small, and a large amount of dislocation is introduced into a ferrite phase, whereby the tensile strength increases. Recently, it has been found that the cementite in the pearlite structure is decomposed into fine pieces when strain on the wire excessively increases. However, because of the extremely fine structure, the relationship between mechanical properties and the location and the state in which the carbon exists has not yet been uncovered, and in particular, many unclear points concerning the cause of the deterioration of ductility still exist. In the actual high-strength steel wire, it is believed that the surface region and the central region in the steel wire do not always exhibit the same structure and the same amount of local strain, and this affects the properties of the steel wire.
[0004] In order to highly strengthen the ultrathin steel wire, it is necessary to increase the strength of an elemental wire after final patenting treatment, or increase a final strain of the wire-drawing working. However, in the past, even if the the ultrathin steel wire was highly strengthened by increasing the strength of the element wire after final patenting treatment or the strain of the wire-drawing working, the ductility thereof largely decreased when the strength exceeded 4500 MPa, which made it difficult to put it to practical use.
[0005] In view of the facts described above, as conventional findings concerning a method of highly strengthening the steel wire whose ductility is not so decreased, for example, Patent Document 1, Patent Document 2, and Patent Document 3 propose a high-carbon steel wire material for an ultrathin wire having high strength and high ductility, in which chemical components of C, Si, Mn, Cr and the like are defined. However, as can be understood from Examples disclosed in these Patent Documents, the maximum tensile strength of the steel wire is 3500-3600 MPa, and there exists a limitation on highly strengthening the steel wire.
[0006] Additionally, Patent Document 4 proposes a highly-strengthened steel and high-toughness steel wire material in which chemical components, structures of non-metallic inclusions, and an area percentage of pro-eutectoid cementite are controlled. Further, Patent Document 5 discloses a method of manufacturing the high-strength steel and high-toughness ultrathin wire steel in which chemical components of steel and area reduction rate at the final die are controlled. However, according to these techniques, it was impossible to realize the high-ductility ultrathin steel wire having a tensile strength of 4500 MPa or greater.
[0007] Another finding shows that properties of the steel cord are affected by the carbon concentration of the ferrite phase in the pearlite structure, and a guideline for improving a balance between strength and ductility by defining the concentration thereof is disclosed. For example, Patent Document 6 intends to obtain favorable properties by defining the carbon concentration in the steel wire. Patent Document 7 discloses a method of realizing a favorable carbon condition and obtaining favorable properties by further modifying heat treatment. Patent Document 8 intends to obtain favorable properties by defining the carbon concentration and the distance between lamellas in the steel wire. However, these Patent Documents do not refer to a carbon condition in an outermost layer (region from a surface to a depth of 2 μm) of the steel wire. This is because the previous techniques were not able to perform measurement (and control).

[0008] Patent Document 9 defines variations in the carbon concentration. Patent Document 10 defines a degree of difference in the distance between lamella, which affects the variations of the carbon concentration. However, these Patent Documents only refer to the entire variations, and do not define the carbon concentration at a specific location. On the other hand, Patent Document 11 describes a steel wire and a method of manufacturing the steel wire for obtaining favorable properties by defining C concentration ratio in the ferrite phase at a surface layer portion of the steel wire and the ferrite phase at a center portion of the steel wire. However, Patent Document 11 only defines a relative value at the center portion and the surface layer portion, and does not define the absolute value to be used as a clear index. Further, the measurement is performed for the inside of the steel wire below 10 μm or more from the surface of the steel wire, and the C concentration in a region (outermost layer) from the surface to a depth of 2μm is not controlled.

[0009] On the other hand, as for a residual stress in the outermost layer of the steel wire, Patent Document 12 and Patent Document 13 define a range of the residual stress in terms of fatigue and longitudinal crack resistance. However, although Patent Document 12 and Patent Document 13 describe that the residual compressive stress is favorable, an absolute value thereof is small, and the range for keeping an extremely excellent ductility and strength in balance is not defined. Further, there has not existed any example that discloses the relationship with the carbon condition in the outermost layer.

[0010] Ductility of the ferrite phase plays a main role in the ductility of the high-strength ultrathin steel wire, and thus, the ductility of the high-strength ultrathin steel wire can be secured by maintaining the ductility of the ferrite phase. In general, however, as the strain of the wire-drawing working increases, the cementite is decomposed, C atoms are diffused in the ferrite phase, and the carbon concentration in the ferrite phase increases. Non-Patent Document 1 describes that, in a cold-rolled steel sheet, as the carbon concentration in the ferrite phase increases, a dynamic strain aging in which dislocation in the ferrite phase fixes with carbon occurs during tensile test, which causes a large decrease in the ductility.

[Related Art Documents]

[Patent Documents]

[0011]

Patent Document 1: Japanese Unexamined Patent Application, First Publication No. S60-204865

Patent Document 2: Japanese Unexamined Patent Application, First Publication No. S63-24046

Patent Document 3: Japanese Examined Patent Application, Second Publication No. H3-23674

Patent Document 4: Japanese Unexamined Patent Application, First Publication No. H6-145895

Patent Document 5: Japanese Unexamined Patent Application, First Publication No. H7-113119

Patent Document 6: Japanese Unexamined Patent Application, First Publication No. H11-199980

Patent Document 7: Japanese Unexamined Patent Application, First Publication No. 2008-208450

Patent Document 8: Japanese Unexamined Patent Application, First Publication No. 2006-249561

Patent Document 9: Japanese Unexamined Patent Application, First Publication No. 2001-220649

Patent Document 10: Japanese Unexamined Patent Application, First Publication No. 2007-262496

Patent Document 11: Japanese Unexamined Patent Application, First Publication No. 2003-334606

Patent Document 12: Japanese Unexamined Patent Application, First Publication No. H11-199979

Patent Document 13: Japanese Unexamined Patent Application, First Publication No. 2001-279381

[Non-Patent Document]

[0012]

Non-Patent Document 1: Journal of Japan Institute of Metal, Vol. 45, No. 9, (1981) 942-947

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0013] According to the related techniques, tensile strength of a steel wire can be highly increased by making the amount of wire-drawing working extremely large at the time of drawing working of the steel wire. However, a decrease in ductility cannot be avoided. In view of the circumstances described above, the present invention provides a high-strength steel wire, in particular, a high-strength ultrathin steel wire having both high strength of 4500 MPa or more and excellent ductility.

[Means for Solving the Problems]

[0014] The present invention employs the following measures for solving the problems described above.

(1) A first aspect of the present invention provides a steel wire, which includes chemical components of: C: 0.7-1.2 mass%; Si: 0.05-2.0 mass%; and, Mn: 0.2-2.0 mass%, with a balance including Fe and inevitable impurities, in which the steel wire has a pearlite structure, the average C concentration at a center portion of a ferrite phase in an outermost layer of the steel wire is 0.2 mass% or lower, and a residual compressive stress in the longitudinal direction of the steel wire in the outermost layer is 600 MPa or more.
(2) The steel wire described in (1) above may further include one or more chemical components of: Cr: 0.05-1.0 mass%; Ni: 0.05-1.0 mass%; V: 0.01-0.5 mass%; Nb: 0.001-0.1 mass%; Mo: 0.01-0.1 mass%; and, B: 0.0001-0.01 mass%.
(3) The steel wire described in (1) or (2) above may be a high-strength ultrathin steel wire having a tensile strength of 4500 MPa or more.
(4) The high-strength ultrathin steel wire described in (3) above may be a steel cord.
(5) The high-strength ultrathin steel wire described (3) above may be a saw wire.
(6) A second aspect of the present invention provides a method of manufacturing a steel wire having a tensile strength of 4500 MPa or more, the steel wire including chemical components of C: 0.7-1.2 mass%; Si: 0.05-2.0 mass%; and, Mn: 0.2-2.0 mass%, with a balance including Fe and inevitable impurities, the method including: applying a patenting treatment to the steel wire to generate a pearlite structure, drawing the steel wire so as to control the average C concentration at a center portion of a ferrite phase in the pearlite structure in an outermost layer of the steel wire to be 0.2 mass% or lower, and, applying a residual compressive stress of 600 MPa or more to the steel wire.

[Effects of the Invention]

[0015] According to a steel wire of the present invention, a carbon concentration at a center of a ferrite phase in the outermost surface layer of the steel wire having a pearlite structure is controlled, and the residual compressive stress is added, whereby the steel wire can exhibit the high strength and ductility. Further, it is possible to provide a high-strength steel wire having the sufficient ductility and tensile strength, whereby it is possible to reduce weight of a manufactured product.

[Brief Description of the Drawings]

[0016]

FIG. 1 is a diagram showing results obtained by examining a relationship between average C concentration at a center portion of a ferrite phase in a surface of an ultrathin steel wire having 4500 MPa or more, residual stress at the surface, and ductility;
FIG. 2A is a diagram showing a process of cutting out a block in a method of obtaining a needle specimen from a region located 1 μm inside from the surface of the ultrathin steel wire;
FIG. 2B is a diagram showing a process of fixing the cut out block on a needle mount;
FIG. 2C is a diagram showing the cut out block subjected to machining using a focused ion beam (FIB) device;
FIG. 2D is a diagram showing the cut out block as viewed from above;
FIG. 2E is a diagram showing a needle specimen obtained by applying FIB machining to the cut out block, as viewed from above;

FIG. 2F is a diagram showing the needle specimen as viewed from the side; and,
FIG. 3 is a diagram showing C distribution measured by a three-dimensional atom probe technique (3DAP) and C concentration at a center portion of the ferrite phase.

[Embodiments of the Invention]

[0017] The present inventors made various analyses on primary factors of ductility of the high-strength steel wire, and found that, in the pearlite structure of heavily drawn wire, the concentration of carbon (hereinafter, referred to as C) in the ferrite phase in the outermost layer of the steel wire and the residual stress in the outermost layer of the steel wire in the longitudinal direction of the steel wire strongly affect the ductility of the steel wire. It is considered that this is because, at the time of bending and twisting, the strong stress is applied to the outermost layer of the steel wire as compared with the inner side thereof, and the outermost layer of the steel wire becomes a starting point of breakage. Although there has been a method of analyzing the residual stress in the outermost layer, there does not exist a method of accurately measuring the C concentration in the ferrite phase in the outermost layer of the steel wire within 2 μm from the surface of the steel wire. This time, by developing this method and investigating the relationship with properties, the present inventors found that the balance between the strength and ductility of the ultrathin steel wire can be largely improved by controlling such that the C concentration in the ferrite phase in the outermost layer of the steel wire is a specified value or lower, and at the same time, the residual stress in the longitudinal direction of the steel wire is a compressive stress, and the compressive stress is a specified value or more.

[0018] The outermost layer of the steel wire is subjected to heavier working, and receives more considerable temperature changes due to the friction heat and the like, as compared with the inner portion of the steel wire, and hence, it has a structure and state obviously different from the inner portion of the steel wire. Then, cementite is further decomposed, and the ferrite phase in the outermost layer exhibits the higher C concentration than that in the inner portion. Accordingly, the inventors discovered that the steel wire exhibiting an excellent balance between the strength and the ductility can be largely achieved by controlling the structure and the like of the outermost layer because the properties are affected primarily by the outermost layer of the steel wire.

[0019] In general, the high-strength steel wire is obtained such that a wire material having the pearlite structure is strengthened by applying the high wire-drawing working using a die and the like. When the high-strength steel wire described above is manufactured, high wire-drawing strain is generated at the time of the high wire-drawing working, which leads to occurrence of a phenomenon in which the cementite in the pearlite structure is finely decomposed, and C is dissolved into the ferrite phase.

[0020] The present inventors combined the three-dimensional atom probe technique (hereinafter, referred to as 3DAP) capable of measuring a local C concentration in the fine region, with a needle-specimen creating technique from the outermost layer of the steel wire which has become available for the first time in the present specification, and investigated in detail the relationship between the C concentration and the strength/ductility of the steel wire in the ferrite phase at every location in the steel wire. As a result, the present inventors found that the ductility significantly decreases especially when the C concentration in the ferrite phase in the surface layer portion of the steel wire is high, or the residual stress in the same outermost layer is tensile stress or weak compressive stress in the longitudinal direction of the steel wire (see FIG. 1).

[0021] In other words, it is found that, in order to secure the sufficient ductility, it is necessary to satisfy a condition that both the carbon state and the residual stress in the outermost layer of the steel wire fall within respective appropriate ranges at the same time. The findings described above were not made until a method of investigating the local C concentration in the outermost layer of the steel wire was newly developed, and it became possible to investigate the carbon state in the outermost layer of the steel wire.

[0022] On the basis of the findings above, the present inventors reached the conclusion that, in order to realize the strengthened steel wire having the sufficient ductility, it is necessary for an average C concentration in the center portion of the ferrite phase in the outermost layer of the steel wire to be a specified value or lower, and further, for the residual stress in the longitudinal direction of the steel wire on the surface to be a sufficient degree of compressive stress.

[0023] Further, the present inventors prepared specimens having a tensile strength of 4500MPa or more through various manufacturing methods, and investigated a relationship between the tensile strength and ductility, the average C concentration at the center portion of the ferrite phase in the pearlite structure in the surface, and the residual stress on the surface. The average C concentration at the center portion of the ferrite phase in the outermost layer of the steel wire was measured using the 3DAP, and the residual stress was investigated using the X-ray diffraction method. The measurement of the tensile strength was made using the tensile strength tester, and the twisting test, which is one of ductility evaluations, was made using the twisting tester. As an index for ductility, the number of twistings until breakage of the steel wire was measured.

[0024] FIG. 1 shows results obtained by investigating the relationship between the average C concentration at the center portion of the ferrite phase located at a position 1 μm below the surface of the steel wire, the residual stress in the longitudinal direction of the steel wire in the outermost layer of the steel wire, and, the ductility represented by the number of twistings until breakage of the steel wire under the twisting test. Here, the white circles (favorable ductility) represent specimens with the twisting number of 20 or more, and the white squares (extremely favorable ductility) represent specimens with the twisting number of 25 or more. Further, the black triangles (poor ductility) represent specimens with the twisting number of less than 20. The steel wire having the tensile strength of 4500 MPa or more and the favorable ductility was observed only when the average C concentration at the center portion of the ferrite phase in the outermost layer of the steel wire is 0.2 mass% or lower, and at the same time, the residual stress is a large compressive stress of -600MPa or lower. Further, the steel wire having the extremely favorable ductility was observed when the average C concentration at the center portion of the ferrite phase is 0.1 mass% or lower, and at the same time, the residual stress is a strong compressive stress of -600MPa or lower.

[0025] On the basis of the results described above, in order to achieve both the high strength and the sufficient ductility, it is desirable that the average C concentration at the center portion of the ferrite phase in the outermost layer of the steel wire be 0.2 mass% or lower, more preferably, 0.1 mass% or lower, and at the same time, the residual stress in the longitudinal direction of the steel wire be -600 MPa, more preferably, -700 MPA or lower. The less the average C concentration is, the more favorable it is, and, in theory, the central portion of the ferrite phase in the pearlite structure of the final patenting material exhibits the lowest carbon concentration. Thus, the lowest value of the average C concentration at the central portion of the ferrite phase in the outermost layer may be set at 0.0001 mass%. The maximum value of the residual compressive stress corresponds to the yield stress in theory, and may be set substantially at -3000 MPa. It is not practical to apply the compressive stress larger than the value above, because it leads to significant increase in cost.

Here, the outermost layer of the steel wire means a region from a surface to a depth of 2 μm excluding a plated layer or other foreign-substance layers on the surface. Further, the central portion of the ferrite phase in the pearlite structure in the outermost layer of the steel wire means a region (region of half of the ferrite phase width) from the central plane of the ferrite phase to a portion located at one-fourth of the width of the ferrite phase toward both sides thereof.

[0026] According to one embodiment of the present invention based on the findings described above, there is provided a steel wire including C: 0.7-1.2 mass%, Si: 0.05-2.0 mass%, Mn: 0.2-2.0 mass% with a balance including Fe and inevitable impurities. This steel wire having the pearlite structure to which the wire-drawing working is applied is **characterized in that** the average C concentration at the center portion of the ferrite phase in the outermost layer is 0.2 mass% or lower, and the residual compressive stress in the longitudinal direction of the steel wire in the outermost layer of the steel wire is 600 MPa or more. Hereinbelow, the bases on the limitations described above will be described in detail. Note that, in the following description, the term "%" means "mass%" unless otherwise specified.

[0027] C: C is effective in increasing the tensile strength of the wire after the patenting treatment and the hardening rate of the wire at the time of the wire-drawing working. This makes it possible to increase the tensile strength with the smaller strain at the time of the wire-drawing working. When the amount of C content is 0.7% or lower, it is difficult to achieve the high-strength steel wire that is the object of the present invention. On the other hand, when the amount of C content exceeds 1.2%, pro-eutectoid cementite segregates in the austenite grain boundary at the time of the patenting treatment, and the wire-drawing workability deteriorates, which causes the breakage during the wire-drawing working. Therefore, the amount of C content is specified to be in the range of 0.7-1.2%.

[0028] Si: Si is an element effective in strengthening the ferrite phase in the pearlite, and in deoxidizing the steel. The effects described above cannot be expected when the amount of Si content is less than 0.05% . On the other hand, when the amount of Si exceeds 2%, hard SiO_2-based inclusions likely occur, which are harmful to the wire-drawing workability. Therefore, the amount of Si content is specified to be in the range of 0.05-2.0%.

[0029] Mn: Mn is an element not only necessary for deoxidation and desulfurization, but also effective in improving hardenability of the steel and increasing the tensile strength after the patenting treatment. However, the effect described above cannot be obtained when the amount of Mn content is less than 0.2%. On the other hand, when the amount of Mn content exceeds 2.0%, the effect described above saturates, and the treatment time for completing the pearlite transformation during the patenting treatment becomes longer, which reduces productivity. Therefore, the amount of Mn content is specified to be in the range of 0.2-2.0%.

[0030] The steel wire according to the embodiment of the present invention may further include one or more elements of Cr, Ni, V, Nb, Mo, and B for the following reasons.

[0031] Cr: Cr makes distances between the cementite phases in the pearlite finer, increases the tensile strength after the patenting treatment, and improves the hardening rate of the wire at the time of the wire-drawing working. However, the operation described above has only a smaller effect when the amount of Cr content is less than 0.05%. On the other hand, when the amount of Cr content exceeds 1.0%, the time for completing the pearlite transformation at the time of the patenting treatment becomes longer, which deteriorates productivity. For this reason, it is preferable that the amount of Cr content be specified to be in the range of 0.05-1.0%.

[0032] Ni: Ni has an effect that makes the pearlite generated through transformation at the time of the patenting treatment favorable for the wire-drawing workability. However, the effect cannot be obtained when the amount of Ni content is less than 0.05%, and the effect commensurate with the added amount cannot be obtained when the amount of Ni content exceeds 1.0%. For this reason, it is preferable that the amount of Ni content be specified to be in the range of 0.05-1.0%.

[0033] V: V has an effect that makes the distance between the cementite phases in the pearlite finer and increases the tensile strength at the time of the patenting treatment. This effect is not sufficient when the amount of V content is less than 0.01 %, and the effect saturates when the amount of V content exceeds 0.5%. For this reason, it is preferable that the amount of V content be specified to be in the range of 0.01-0.5%.

[0034] Nb: Similar to V, Nb has an effect that makes the distance between the cementite phases in the pearlite fmer and increases the tensile strength at the time of patenting treatment. This effect is not sufficient when the amount ofNb content is less than 0.001 %, and the effect saturates when the amount of Nb content exceeds 0.1 %. For this reason, it is preferable that the amount of Nb content be specified to be in the range of 0.001-0.1%.

[0035] Mo: Similar to V, Mo has an effect that makes the distance between the cementite phases finer, and increases the tensile strength at the time of the patenting treatment. This effect is not sufficient when the amount of Mo content is less than 0.01 %, and the effect saturates when the amount of Mo content exceeds 0.1 %. For this reason, it is preferable that the amount of Mo content be specified to be in the range of 0.01-0.1 %.

[0036] B: B has a function and effect of being bound to N to become BN, and prevents deterioration through aging due to N, and it is necessary that the steel contain 0.0001 % or more of B in order to sufficiently utilize this effect. On the other hand, when B is added to the steel such that the amount of B content exceeds 0.01 %, the effect saturates, and adding B exceeding this value is not preferable as it causes the increase in manufacturing cost. For this reason, in the present invention, when B is added in the steel, it is preferable that the amount of B content be specified to be in the range of 0.0001-0.01%.

[0037] Although other elements are not particularly defined, preferable ranges of elements contained as inevitable impurities are P: 0.015% or lower, S: 0.015% or lower, and N: 0.007% or lower. When the amount of A1 content exceeds 0.005%, the Al_2O_3-based inclusions, which are the hardest among the inclusions in the steel, are likely generated, which cause the breakage of the wire at the time of wire-drawing working or wire-stranding working. For this reason, 0.005% or lower is a preferable range of Al.

[0038] Additionally, although inevitable impurities other than the elements described above may be contained through manufacturing processes, it is preferable to reduce the intrusion of those inevitable impurities as much as possible.

[0039] In order to obtain the pearlite structure of the heavily drawn ultrathin-steel wire having 0.2 mass% of the average C concentration at the center portion of the ferrite phase in the outermost layer of the steel wire and the sufficient amount of residual compressive stress, it is the most effective to select one process from among each of A group, B group, and C group described below and adopt the selected processes in the manufacturing processes after the final patenting treatment. However, a sufficient effect cannot be obtained when three processes selected unbalancedly from only one group are adopted and the selection is not made from all of the three groups. Further, the properties may be deteriorated when two types of processes are adopted from the same group. Yet further, when selection is made from all of the groups and further one more process is selected from any of the groups, the effect commensurate with this selection cannot be obtained. This is because, although the processes in the same group basically have a similar effect, it is probable that those processes cancel effects with each other when the different processes are adopted. Therefore, as described above, it is preferable that one process be adopted from among each of the three groups.

(Processes in A group)

[0040] A1: In a final step, a skin pass process is inserted one time, preferably plural times.

[0041] The skin-pass wire drawing, which is one of the important processes, is a method for drawing the wire under an area reduction rate especially smaller than that of the ordinary wire drawing (10% or more). It is preferable for the area reduction rate to be in the range of 1% to 6%, and more preferably, in the range of 2% to 5%. It is difficult to apply the working to the entire surface of the steel wire when the area reduction rate is less than 1%. When the area reduction rate exceeds 7%, the amount of working is too great, which makes it impossible to obtain the preferable residual compressive stress in the surface and carbon concentration in the ferrite phase. The skin-pass wire drawing may be made independently using a single-die type or made using a double-dies type simultaneously with the ordinary wire drawing. The compressive residual stress can be applied to the surface of the steel wire, and at the same time, the lamella structure on the surface can be made further uniform by performing the skin pass process with the area reduction rate of 1%-6% one time, preferably, plural times in the final step. With the effects of applying the appropriate residual compressive stress to the surface and removing the carbon fixed to dislocation, the amount of locally solid-solved carbon can be easily reduced, and decomposition of the cementite in the outermost layer can be suppressed.

[0042] A2: Shot peening is performed after the wire drawing.

[0043] The shot peening is a method of manufacturing a worked layer or strain layer only in the surface region of the steel wire by discharging the spherical shot having a specific size to the entire steel wire under a specific press and for a specific time. Preferably, the shot peening is performed, for example, such that the air blasting type is used; air pressure is 4-5$\times10^5$ Pa; a period of time is 5-10 seconds; and the size of the shot ball is 10-100 μm. It is effective to perform sufficient amount of discharge to the entire surface of the steel wire.

[0044] The compressive residual stress is applied to the surface of the steel wire, and the lamella structure on the surface is made further uniform by performing the shot peening after the wire-drawing working. With the effects of applying the appropriate residual compressive stress to the surface and removing the carbon fixed to dislocation, the amount of locally solid-solved carbon can be easily reduced, and decomposition of the cementite in the outermost layer can be suppressed.

(Processes in B group)

[0045] B1: In the final step, a wire-drawing speed is set at a low wire-drawing speed of 200 m/min or lower, preferably, 50 m/min or lower.

[0046] By performing the wire-drawing at the low speed, the amount of heat generated during the drawing working due to friction or plastic deformation can be made smaller. This makes it possible to suppress the decomposition of the cementite in the pearlite structure, whereby the amount of carbon diffused in the ferrite phase can be reduced.

[0047] B2: Between drawing passes in the wire-drawing working, heat treatment at a temperature range of 40-400°C is applied for 0.5 second to 5 minutes, preferably, at a temperature range of 100-300°C for 1 second to 3 minutes. During the wire-drawing working, the temperature of the wire rapidly rises and immediately drops. In addition to this, by applying heat treatment at an appropriate temperature between drawing passes in the wire-drawing working, the supersaturated carbon dissolved in the ferrite phase due to the decomposition of the cementite during the wire-drawing working is discharged from the ferrite phase by the heat treatment between the drawing passes, whereby the C concentration in the ferrite phase can be reduced, and at the same time, unnecessary point defects (atom vacancy and the like) or dislocations can be prevented. This makes it possible to recover the ductility, and perform drawing working with high strain, that is, make the distance between the ferrite phases finer. However, this treatment is not applied to all the pass-to-pass sections in the wire-drawing working, and is only effective when applied between a specified pass-to-pass section.

[0048] B3: In the final step including the skin pass, and the wire-drawing process immediately therebefore, a die having an approach angle of 8-12°, and coefficient of dynamic friction of 0.1, preferably, 0.05 or lower is employed.

By employing the die having the small approach angle and small dynamic friction coefficient, the generated heat due to the friction during the wire-drawing working can be suppressed, and an increase in C concentration in the ferrite phase caused by the decomposition of the cementite due to the temperature rise in the outermost layer can be suppressed. This process is effective when employed in the step close to the final step.

(Processes in C group)

[0049] C1: After the wire-drawing working, heating at a temperature of 60-300°C is held for 0.1 minute to 24 hours, more preferably, heating at a temperature of 180-260°C is held for 20 seconds to 15 minutes.

[0050] By the aging during the wire-drawing working or after the drawing working, the supersaturated carbon dissolved in the ferrite phase due to the decomposition of the cementite during the wire-drawing working is discharged from the ferrite phase, and the carbon concentration in the ferrite phase is decreased. However, when the temperature is too high, the spherical cementite or transition carbide is formed, and on the other hand, when the temperature is too low, the effect is small. It is necessary to set the appropriate temperatures according to types of steel materials, and conditions for wire drawing.

[0051] C2: During the wire-drawing working except for the final three steps, a process with a large area reduction rate of 20% or more is inserted one time, preferably, plural times.

[0052] By inserting the process with the large area reduction rate of 20% or more one time, preferably, plural times, the strain of the wire can be introduced uniformly into the wire, and does not exist unbalancedly in the surface. This is effective when performed before the final three steps.

[0053] The C concentration in the ferrite phase of the steel wire can be accurately measured by the three-dimensional atom probe technique (3DAP). Conventionally, however, the C concentration of the ferrite phase in the pearlite structure of the drawn wire in the outermost layer of the steel wire was not able to be measured. By developing a technique of manufacturing a needle specimen such that small pieces are cut out from a surface of the steel wire and the cut out pieces are processed using the focused ion beam (FIB) device, it becomes possible to accurately measure the carbon concentration in the outermost layer.

[0054] The C concentration in the form of a solid solution may take different values according to the positions in the ferrite phase, and hence attention should be paid to it. In general, when cementite is decomposed and C is diffused in the ferrite phase, the C concentration is high at an interfacial position between the ferrite phase and the cementite phase, and is minimum at the center of the ferrite phase. In the present embodiment, the average C concentration is defined in the region (region of half of the ferrite phase width) from the center plane of the ferrite phase to a portion located at one-fourth of a width of the ferrite phase toward both ends thereof.

[0055] Through analysis with the 3DAP, the C concentration in the ferrite phase including the interface between the ferrite phase and the cementite phase can be measured. Thus, it is possible to obtain the C concentration in the ferrite phase by atom% by allocating a box having a specified size to a region to be investigated on the basis of the measured data, cutting out the box, and calculating a ratio of the C atoms to all the atoms in the box. The obtained value can be converted into mass% by multiplying by 12/56. The measurement described above is performed on plural portions in the center portion of the ferrite phase to obtain the average value, and the thus obtained value is defined as the average C concentration at the center portion in the ferrite phase.

[0056] As examples, FIG. 2A through FIG. 2F show a method of preparing a needle specimen for measuring the C concentration at the center portion of the ferrite phase located at a position 1 μm below the surface of the steel wire, and FIG. 3 shows the C distribution measured by the 3DAP and the C concentration at the center portion of the ferrite phase using the prepared needle specimen.

[0057] To prepare the needle specimen of the region 1 μm inside from the surface of the steel wire, for example, a rod-like block having the surface of the steel wire on one side thereof is cut out from the surface region of the steel wire using the FIB, as shown in FIG. 2A. This block is fixed on a needle mount as shown in FIG. 2B through vapor deposition (deposition) using, for example, tungsten. This fixed block is processed using FIB so as to have a thin top end position as shown in FIG. 2C. FIG. 2D is a diagram showing the processed block as viewed from above, and from FIG. 2D, it can be understood that the top end portion is the rod-like block having the surface of the steel wire. Thereafter, the top end portion is processed to be a needle-like portion by irradiating a ring-like beam from above. FIG. 2F is a diagram showing the thus prepared needle specimen as viewed from the side. As shown in FIG. 2E, the needle top end is prepared such that the position thereof corresponds to 1 μm inside from the surface of the steel wire. With the needle-specimen creating technique as described above, the needle specimen in the outermost layer of the steel wire can be prepared.

[0058] Further, in FIG. 3, a thick-colored portion indicates that the C concentration is high, and a thin-colored portion indicates that the C concentration is low. Therefore, the thick-colored band-like regions indicate the cementite phase having been subjected to the wire-drawing working, and the thin-colored region between the thick-colored band-like regions indicates the ferrite phase having been subjected to the wire-drawing working. FIG. 3 shows that C is solid-solved in the ferrite phase.

[0059] The carbon concentration at the center portion of the ferrite phase can be estimated such that the box is cut out from the center of the ferrite phase as shown in FIG. 3, and the number of C atoms contained in the box is divided by the total number of atoms. In this example, the C concentration is 0.18 mass%. The center portion of the ferrite phase is located at the midway point between two cementite phases, and corresponds to the region (region of half of the ferrite phase width) from the center plane of the ferrite phase to a portion located at one-fourth of a width of the ferrite phase toward both ends thereof.

[0060] The width of the ferrite phase is not necessarily constant and depends on the amount of working or position in the specimen, and there exists a region having a width as narrow as 10 nm or lower. If the box contains the cementite region, the resulting value may be higher than the actual C concentration in the ferrite phase. For this reason, the box position to be analyzed is set at the center portion of the ferrite phase, and the box width is half of the width of the ferrite phase. Further, the average C concentration is an average of five or more, preferably, ten or more different values of the C concentration measured at the center portion of the ferrite phase.

[0061] The residual stress in the outermost layer of the steel wire can be measured accurately, for example, using the X-ray diffraction method. The measurement can be made accurately, in particular, through debye-ring fitting method using the micro-region X-ray diffractometer that can measure the local region. This method is performed by a fitting operation using the reflection of the crystal grain of the steel wire as the debye ring, and investigating the size and orientation of the residual stress on the basis of distortion of the debye ring. The depth-region including the surface is determined from the depth of penetration of X-rays. For example, when Cr is used as the X-ray source, the integrated value of several μm depth below the surface is obtained. Further, another method of investigating the residual stress at the surface of the steel wire is a method of dissolving as needed (Heyn method). This method is a method for measuring the difference in length of the steel wire before and after the outermost layer to be investigated is dissolved, and investigating the residual stress in the longitudinal direction of the steel wire. These methods make it possible to accurately obtain the residual stress of the high-strength steel wire in which aggregated structures are developed.

[Example]

[0062] Hereinbelow, the operability and effect of the present invention will be specifically described through an example.

[0063] A high-strength ultrathin steel wire with brass plate having the wire diameter of 0.04-0.40 mm and having a pearlite structure was prepared such that a sample material having chemical components shown in Table 1 is processed to be a predetermined wire diameter through hot rolling; then patenting treatment is applied using a lead bath; and, the wire-drawing working are performed to make the wire have the tensile strength of 4500 MPa or more. The brass plating was performed after the final patenting treatment was performed and the acid cleaning was performed.

[0064] Table 2 shows: the real strain of the ultrathin steel wire at the time of wire-drawing working; manufacturing method; wire diameter; average C concentration at the center portion of the ferrite phase in the outermost layer of the steel wire; residual stress in the outermost layer of the steel wire; tensile strength; and, twisting number until break at the time of twisting test. In Table 2, the manufacturing method is represented by characters indicating contents described above. In the twisting test, the test specimen was fixed at a holding interval 100 times larger than the wire diameter at both ends of the test specimen, and the number of twistings until breakage was investigated. The evaluation was made such that the ductility is favorable when the tensile strength is 4500 MPa or more and the twisting number is 20 or more, and the ductility is extremely favorable when the twisting number is 25 or more. The C concentration in the ferrite phase in the outermost layer of the steel wire was measured at a position 1 μm below the surface of the steel wire by the method described above using the 3DAP. The residual stress in the outermost layer of the steel wire in the longitudinal direction of the steel wire was measured using the debye-ring fitting method described above. The compressive stress is indicated when the residual stress is negative, and the tensile stress is indicated when the residual stress is positive.

[0065] [Table 1]

[0066] [Table 2]

[0067] In Table 2, test Nos. 1-6 are the present invention examples, and the other test examples are comparative examples. As shown in Table 2, all the present invention examples exhibit the tensile strength of 4500 MPa or more, the average C concentration at the center portion of the ferrite phase in the outermost layer of 0.2 mass% or lower, and the residual stress of -600MPa or lower (residual compressive stress of 600 MPa or more). As a result, the ultrathin steel wire having the large twisting number and sufficient ductility can be realized. In particular, test Nos. 1-2 exhibit the twisting number of 25 or more, and are extremely favorable.

[0068] On the other hand, test Nos. 7-20 are comparative examples, and exhibit the tensile strength of 4500 MPa or more but an insufficient twisting number.

[0069] Nos. 7-9 are comparative examples whose components in the steel wire are outside the range according to the present invention. As for No. 7, as the C concentration of the steel wire is too low or the amount of strain of the steel wire is made higher, the C concentration at the center portion of the ferrite phase becomes the specified value or more, which results in the decrease in ductility. No. 8 and No. 9 are comparative examples, in which the amount of Si in the steel wire and the amount of of C in the steel wire are higher than the range according to the present invention, respectively. In those comparative examples, although the residual stress and the C concentration at the center portion of the ferrite phase are within the specified range, the ductility deteriorates.

[0070] Further, Nos. 10-13 are comparative examples, in which components in the steel wire and the residual stress are within the range according to the present invention, but the C concentration is the specified value or more. In these comparative examples, the ductility deteriorates. Nos. 14-16 are comparative examples, in which components in the steel wire and the C concentration at the center portion of the ferrite phase are within the range according to the present invention, but the residual stress is outside the range. In these comparative examples, the ductility deteriorates. Nos. 17-20 are comparative examples, in which the C concentration at the center portion of the ferrite phase in the outermost layer and the residual stress are outside the range. In these comparative examples, the ductility deteriorates.

[Industrial Applicability]

[0071] According to the present invention, it is possible to provide a high-strength steel wire having sufficient ductility that will contribute to future industrial development.

Table 1

Steel type	Chemical components (wt%)												
	C	Si	Mn	P	S	Al	N	Cr	Ni	V	Nb	Mo	B
A	1.16	0.19	0.33	0.008	0.007	0.001	0.0031	-	-	-	-	-	-
B	0.85	1.63	0.42	0.011 1	0.005	0.002	0.0035	0.32	-	-	-	-	-
C	0.88	0.26	0.40	0.009	0.008	0.003	0.0039	-	-	-	0.005	0.03	-
D	1.01	0.15	0.27	0.007	0.009	0.001	0.0028	0.25	-	0.11	-	-	-
E	0.78	1.78	0.38	0.008	0.006	0.002	0.0033	0.19	-	-	-	-	0.0018
F	0.88	0.33	1.46	0.005	0.007	0.001	0.0035	0.22	0.33	-	0.028	-	-
G	0.69	0.28	0.50	0.007	0.006	0.002	0.0028	-	-	-	-	-	-
H	0.90	2.40	0.39	0.008	0.008	0.003	0.0030	-	-	-	-	-	0.0030
I	1.23	0.35	0.45	0.010	0.0010	0.003	0.0042	-	-	-	0.004	-	-

Table 2

Test No.	Material		Manufacturing condition		Property of ultrathin steel wire					Remarks
	Steel type	Strength of patenting material (MPa)	Real strain of wire drawing working	Manufacturing method	Steel wire diameter (mm)	Average C concentration at center portion of ferrite phase in outermost layer of steel wire (mass%)	Residual stress (MPa)	Tensile strength (MPa)	Number of twisting (turn)	
1	A	1520	4.46	A1+B1+C1	0.17	0.07	-1040	4520	27	Present invention example
2	B	1480	4.61	A1+B2+C2	0.16	0.04	-700	4530	26	Present invention example
3	C	1460	4.73	A1+B3+C1	0.15	0.14	-1080	4550	22	Present invention example
4	D	1500	4.61	A1+B2+C2	0.16	0.18	-940	4510	23	Present invention example
5	E	1450	4.73	A2+B3+C2	0.15	0.10	-850	4600	24	Present invention example
6	F	1460	4.87	A2+B1+C1	0.14	0.12	-620	4620	20	Present invention example
7	G	1450	5.02	A1+B1+C1	0.13	0.60	-650	4500	17	Comparative example
8	H	1510	4.48	A2+B3+C2	0.18	0.18	-620	4520	19	Comparative example
9	I	1550	4.15	A1+B3+C1	0.20	0.13	-720	4620	14	Comparative example

(continued)

Test No.	Material		Manufacturing condition		Property of ultrathin steel wire					Remarks
	Steel type	Strength of patenting material (MPa)	Real strain of wire drawing working	Manufacturing method	Steel wire diameter (mm)	Average C concentration at center portion of ferrite phase in outermost layer of steel wire (mass%)	Residual stress (MPa)	Tensile strength (MPa)	Number of twisting (turn)	
10	A	1500	4.61	A1+C2	0.16	0.32	-1200	4550	19	Comparative example
11	B	1480	4.61	A1+B3+C1+C2	0.16	0.21	-740	4560	14	Comparative example
12	B	1480	4.87	A2	0.14	0.26	-900	4630	16	Comparative example
13	C	1460	4.61	A2+B2	0.16	0.42	-650	4510	18	Comparative example
14	D	1530	4.48	A1+A2+B3+C1	0.17	0.15	-450	4630	16	Comparative example
15	C	1460	4.87	B1+C1	0.14	0.05	210	4530	15	Comparative example
16	E	1450	4.73	B1+B2+C1	0.16	0.09	820	4600	18	Comparative example
17	E	1380	4.73	A1+A2+B3	0.15	0.25	-350	4500	19	Comparative example
18	F	1460	4.87	-	0.14	0.50	-170	4730	8	Comparative example
19	A	1500	4.61	B2+C1	0.16	0.35	-60	4620	19	Comparative example
20	D	1500	4.37	C2	0.18	0.36	540	4540	14	Comparative example

Claims

1. A steel wire including the chemical components of:

C: 0.7-1.2 mass%;
Si: 0.05-2.0 mass%; and
Mn: 0.2-2.0 mass%,
with a balance including Fe and inevitable impurities, wherein
the steel wire has a pearlite structure,
an average C concentration at a center portion of a ferrite phase in an outermost layer of the steel wire is 0.2 mass% or lower, and
a residual compressive stress in a longitudinal direction of the steel wire in the outermost layer is 600 MPa or more.

2. The steel wire according to claim 1, further including one or more chemical components of:

Cr: 0.05-1.0 mass%;
Ni: 0.05-1.0 mass%;
V: 0.01-0.5 mass%;
Nb: 0.001-0.1 mass%;
Mo: 0.01-0.1 mass%; and
B: 0.0001-0.01 mass%.

3. The steel wire according to claim 1 or 2, wherein
the steel wire is a high-strength ultrathin steel wire having a tensile strength of 4500 MPa or more.

4. The steel wire according to claim 3, wherein
the high-strength ultrathin steel wire is a steel cord.

5. The steel wire according to claim 3, wherein
the high-strength ultrathin steel wire is a saw wire.

6. A method of manufacturing a steel wire having a tensile strength of 4500 MPa or more, the steel wire including the chemical components of:

C: 0.7-1.2 mass%;
Si: 0.05-2.0 mass%; and
Mn: 0.2-2.0 mass%,
with a balance including Fe and inevitable impurities,
the method including:

applying a patenting treatment to the steel wire to generate a pearlite structure,
drawing the steel wire so as to control an average C concentration at a center portion of a ferrite phase in the pearlite structure in an outermost layer of the steel wire to be 0.2 mass% or lower, and
applying a residual compressive stress of 600 MPa or more to the steel wire.

FIG. 1

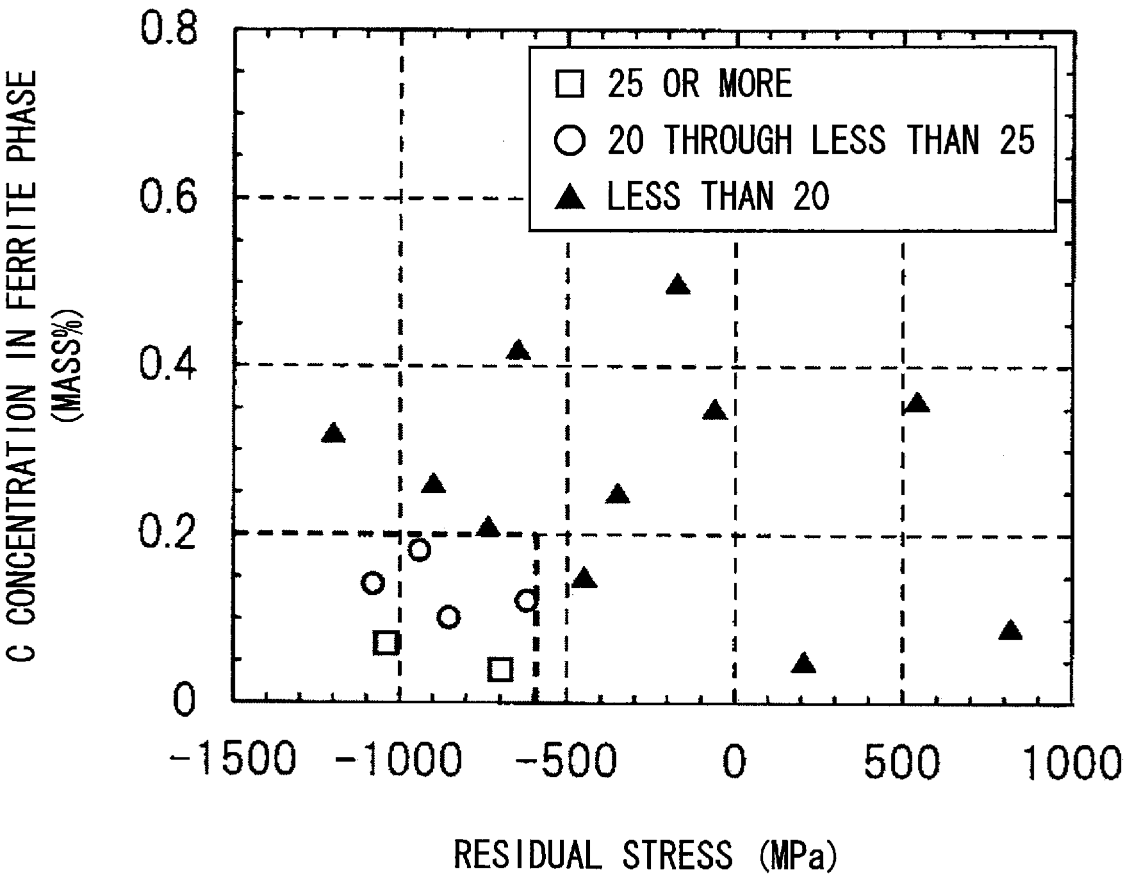

0.8
0.6
0.4
0.2
0
C CONCENTRATION IN FERRITE PHASE (MASS%)
25 OR MORE
20 THROUGH LESS THAN 25
LESS THAN 20
-1500
-1000
-500
0
500
1000
RESIDUAL STRESS (MPa)

FIG. 2A

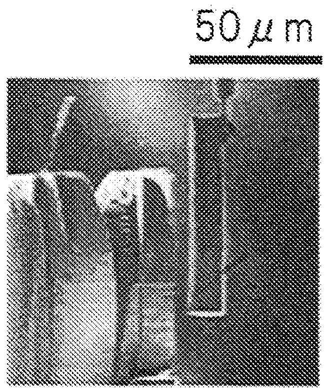


FIG. 2B

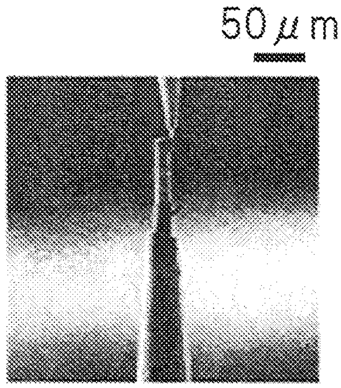


FIG. 2C

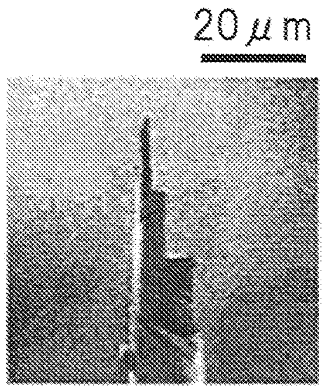


FIG. 2D

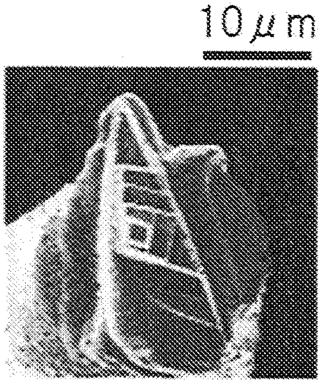


FIG. 2E

FIG. 2F

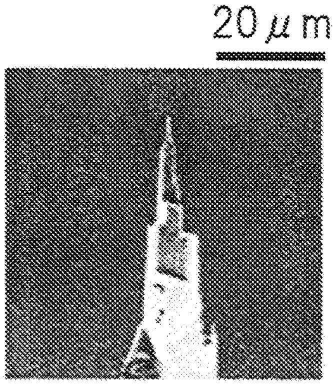
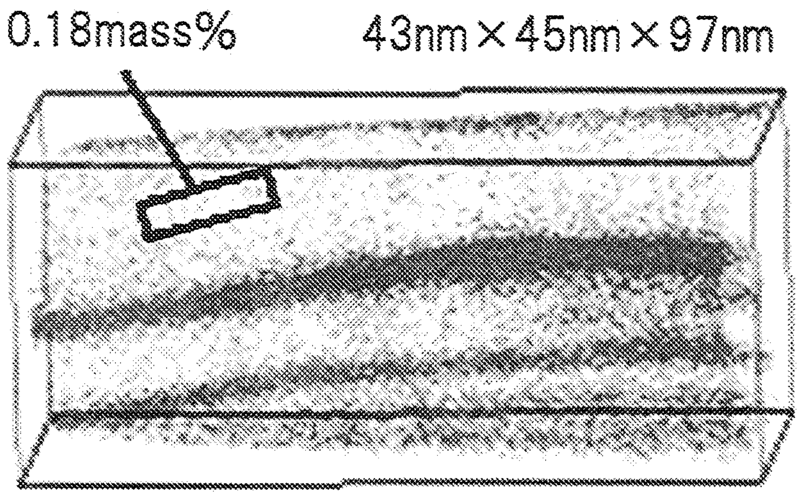


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/002859

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C21D7/06*(2006.01)i, *C21D8/06*(2006.01)i, *C21D9/52*(2006.01)i, *C22C38/04*(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, C21D7/06, C21D8/06, C21D9/52, C22C38/04, C22C38/58

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	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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.
Y	JP 11-199980 A (Nippon Steel Corp.), 27 July 1999 (27.07.1999), claims; paragraphs [0001], [0006], [0022] to [0029]; examples; tables 1, 2 (Family: none)	1-6
Y	JP 2006-249561 A (Nippon Steel Corp.), 21 September 2006 (21.09.2006), claims; paragraphs [0001], [0008], [0018] to [0038]; examples; tables 1, 2 (Family: none)	1-6
Y	JP 2001-279381 A (Kobe Steel, Ltd.), 10 October 2001 (10.10.2001), claims; paragraphs [0005], [0010], [0012], [0015], [0032] to [0033]; examples; table 1 (Family: none)	1-6

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

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"&" document member of the same patent family

Date of the actual completion of the international search	Date of mailing of the international search report
22 July, 2010 (22.07.10)	03 August, 2010 (03.08.10)

Name and mailing address of the ISA/	Authorized officer
Japanese Patent Office	
Facsimile No.	Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

REFERENCES CITED IN THE DESCRIPTION

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