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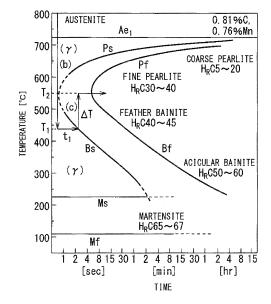
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(54) WIRE ROD, HYPEREUTECTOID BAINITE STEEL WIRE, AND METHOD FOR MANUFACTURING SAME

A wire rod according to the present invention includes a predetermined chemical composition, wherein a metal structure includes 90 area% to 100 area% of bainite, wherein when eight test pieces having a length of 400 mm, which are obtained by dividing a wire rod having a length of 3200 mm into eight components having a same length, are manufactured, an average tensile strength TS of each test pieces satisfies a relation of "[TS] < 810 × [C] +475" by N/mm², wherein a difference between a maximum value and a minimum value of the tensile strengths of each test pieces is 50 N/mm² or less, and wherein an average reduction of area RA of each pieces satisfies relation test "[RA]≥-0.083×[TS]+154" by %.

FIG. 1



Description

[Technical Field of the Invention]

[0001] The present invention relates to a wire rod for a hypereutectoid bainite steel wire having excellent drawing properties and delayed fracture resistance, a hypereutectoid bainite steel wire which is manufactured from the wire rod, and a method for manufacturing thereof.

[0002] Priority is claimed on Japanese Patent Application No. 2013-211365, filed on October 8, 2013, the contents of which are incorporated herein by reference.

[Related Art]

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[0003] Wire rods are used as the material to make various machined parts, such as steel wire. When various mechanical parts (hereinafter referred as final products) are manufactured from wire rods, the wire rods are usually subjected to wire drawing and annealing. The tensile strength of the final product is mainly affected by the chemical composition of the wire rod, in particular, by the C content of the wire rod. However, the metal structure of the wire is transformed during annealing. Therefore, when the final product is manufactured by the process including annealing, the metal structure of the wire rod does not affect the tensile strength of the final product. For the above reasons, when the final product is manufactured by a process including annealing, it is essential that the chemical composition of the wire rod correspond to the tensile strength which is required of the final product.

[0004] On the other hand, regardless of the tensile strength of the final product, it is preferable that the tensile strength of the wire rod be minimized. In a wire rod having high tensile strength, the machinability and drawing properties thereof are decreased. Furthermore, since a wire rod having high tensile strength has a high sensitivity to delayed fracture (fracture by the hydrogen embrittlement), breakages easily occur during manufacture, storage and transportation. Particularly, when the C content of the wire rod is 0.8 mass% or more (that is, in a case where the wire rod is hypereutectoid steel, since the C content of the wire rod is higher than the eutectoid point), there is a problem that the sensitivity to delayed fracture (the hydrogen embrittlement) of the wire rod increases. As a result, when the wire rod after manufacturing is bundled into a coil shape for storage and transportation, breakage in the wire rod may occur due to the stress during bundling. Breakage in wire rod leads to a reduction in machining efficiency of the wire rod. In addition, when the length of the wire rod in which the breakage occurs is shorter than the length that is required of the final product, the wire rod cannot be used as the material for the final product.

[0005] In order to prevent breakage due to delayed fracture (hydrogen embrittlement), it can be considered that the bundling conditions are relaxed, for example, such as reducing the power to bind the wire rod. However, when the bundling conditions are relaxed, the storage stability of the coil, the transportability of the coil, and safety and the like at the time of handling the coil are impaired.

[0006] Issues related to the delayed fracture and machinability can be solved by adjusting the chemical composition of the wire rod, for example, by decreasing the tensile strength of the wire rod by decreasing the C content. However, as described above, it is essential that the chemical composition of the wire rod correspond to the tensile strength which is required of the final product. Therefore, the adjustment of the chemical composition of the wire rod cannot be adopted as a means for preventing the delayed fracture.

[0007] The tensile strength of the wire rod can be decreased by changing the heat treatment conditions during manufacture the wire rod. The metal structure of general hypereutectoid wire rod (the wire rod in which the C content is higher than the eutectoid point) mainly includes pearlite. The method for manufacturing hypereutectoid wire rod according to the prior art includes a process of rolling the steel to obtain the wire rod and a process of cooling the wire rod. During cooling process, the metal structure of the wire rod becomes pearlite. In this manufacturing method, when the wire rod after rolling is heated to an austenite temperature region at first and then the wire rod is cooled at a relatively slow cooling rate, the tensile strength of the wire rod can be decreased. However, when the manufacturing condition in which the cooling rate is slow is applied to the manufacturing method of the wire rod in which the C content is higher than the eutectoid point, a large amount of proeutectoid cementite in addition to pearlite are generated during cooling. The proeutectoid cementite deteriorates the workability of the wire rod. Therefore, the slowing the cooling rate of the wire rod cannot be adopted as a means for preventing the delayed fracture.

[0008] In view of the above circumstances, the present inventors studied that an adjustment of the metal structure of the wire rod was adopted as a means of decreasing the tensile strength. As described above, when the final product is manufactured by the process including annealing, the metal structure of the wire rod does not affect the tensile strength of the final product. General wire rods according to the prior art mainly includes the pearlite structure, and these wire rods are referred as the pearlite wire rods. On the other hand, it is well known that the wire rod including bainite as a main metal structure (bainite wire rod) has excellent drawing properties compared with the pearlite wire rod (for example, see the patent documents 1 to 7). In addition, the tensile strength of the hypereutectoid bainite wire rod in which the C

content is higher than the eutectoid point is lower than the tensile strength of the pearlite wire rod which includes the same C content with the bainite wire rod. For example, the present inventors found that the average tensile strength of the bainite wire rod in which the C content is 1.1% is lower 200MPa to 300MPa than the average tensile strength of the pearlite wire rod in which the C content is 1.1%. When the metal structure of the wire rod is set to bainite, the tensile strength of the wire rod can decrease, regardless of the tensile strength required of the final product after annealing (that is, regardless of the C content required for steel wire). Therefore, an improvement in both drawing properties and suppression of delayed fracture can be achieved.

[0009] However, the bainite wire rod has a problem that the tensile strength is easy to vary. The state where the tensile strength of the wire rod is varied means the state where these measurements are varied, when the tensile strength is measured at a plurality of locations in a one wire rod. When the tensile strength of the wire rod is varied, the sensitivity to the delayed fracture (hydrogen embrittlement) increases at a place where the tensile strength is high, and the breakage occurs. Furthermore, when the tensile strength of the wire rod varies, since the workability of the wire rod varies, machining of the wire rod becomes difficult. The patent documents 1 to 7 disclose the method for manufacturing the bainite wire rod. However, the present inventors found that the tensile strength of the wire rod is greatly varied, when the bainite wire rod is manufactured based on the manufacturing methods specifically disclosed in these patent documents. Firstly, the present inventors cut the wire rod obtained by the above-described manufacturing method to a length of 3200 mm. Next, the present inventors made the eight test pieces having a length of 400 mm by dividing the wire rod into eight equal parts, and the tensile strength test was subjected to these test pieces. The difference between the maximum value and minimum value within the tensile strengths of these test pieces (hereinafter, referred as the variation in the tensile strength) was more than 100 N/mm². On the other hand, as a result of studying by the present inventors, it was found that the wire rod in which the variation in the tensile strength is more than 50 N/mm² is difficult to use industrially.

[Prior Art Document]

[Patent Document]

[0010]

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[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. H05-117762 [Patent Document 2] Japanese Unexamined Patent Application, First Publication No. 1106-017190 [Patent Document 3] Japanese Unexamined Patent Application, First Publication No. H06-017191 [Patent Document 4] Japanese Unexamined Patent Application, First Publication No. H06-017192 [Patent Document 5] Japanese Unexamined Patent Application, First Publication No. H06-073502 [Patent Document 6] Japanese Unexamined Patent Application, First Publication No. H06-330240 [Patent Document 7] Japanese Unexamined Patent Application, First Publication No. H08-003639

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0011] As described above, since the pearlite wire rod according to the prior art has high tensile strength, there is a problem that the delayed fracture easily occurs. In view of the required specifications of the final product obtained from the pearlite wire rod, it is difficult to decrease the tensile strength by reducing the C content of this pearlite wire rod. On the other hand, when the tensile strength is decreased due to the reducing the cooling rate in the method for manufacturing this pearlite wire rod, the amount of the proeutectoid cementite is increased. Therefore, it is not preferable. An increase in the amount of the proeutectoid cementite deteriorates the machinability of the wire rod. In addition, the bainite wire rod according to the prior art, particularly, the hypereutectoid bainite wire rod in which the C content is higher than the eutectoid point has a problem that the tensile strength is easy to vary. The variation in the tensile strength increases the occurrence frequency of the delayed fracture and deteriorates the machinability.

[0012] The problem of the present invention is to decrease the tensile strength of the wire rod and increase the ductility of the wire rod in which the C content is higher than the eutectoid point in order to enhance the drawing properties and delayed fracture resistance of the wire rod by being the main metal structure of bainite. Furthermore, the problem of the present invention is to suppress variation in the tensile strength of the wire rod. Accordingly, the aim of the present invention is to provide a wire rod for solving these problems, the hypereutectoid bainite steel wire manufactured by using the wire rod, and the method for stably manufacturing them.

[Means for Solving the Problem]

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[0013] The present inventors found that the above-described problem can be solved by manufacturing the wire rods based on the manufacturing conditions that the bainite structure, which can achieve both the suppression of the proeutectoid cementite and the low strength of the wire rod, can be generated.

[0014] The present invention has been made based on the findings, and the summary is as follows. [0015]

(1) A wire rod according to one aspect of the present invention includes, as a chemical composition, by mass%: C: more than 0.80% to 1.20%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%, S: 0% to 0.02%, Cr: 0% to 1.00%, Ni: 0% to 1.00%, Cu: 0% to 1.00%, Mo: 0% to 0.50%, Ti: 0% to 0.20%, Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to 0.0050%, Al: 0% to 0.10%, Ca: 0% to 0.05%; and a remainder including Fe and impurities; in which a metal structure includes 90 area% to 100 area% of a bainite; in which when eight test pieces having a length of 400 mm, which are obtained by dividing a wire rod having a length of 3200 mm into eight components having a same length, are manufactured, an average tensile strength TS of each test pieces satisfies a following equation 1, by N/mm², in which the difference between the maximum value and the minimum value of the tensile strengths of each test pieces is 50 N/mm² or less, in which and the average RA of the reduction of area of each test pieces satisfies a following equation 2, by %.

 $[TS] \le 810 \times [C] + 475$ (Equation 1)

 $[RA] \ge -0.083 \times [TS] + 154$ (Equation 2)

Here, [C] means the C content in the wire rod by mass%, [TS] means the average TS of the tensile strength by N/mm², and [RA] means the average RA of the reduction of area by %.

(2) A hypereutectoid bainite steel wire according to another aspect of the present invention, which is obtained by the wire drawing the wire rod according to (1).

(3) A method for manufacturing the wire rod according to one aspect of the present invention is the method for manufacturing the wire rod according to (1), the method includes: rolling a billet to obtain a wire rod, in which the billet includes, as a chemical composition, by mass%: C: more than 0.80% to 1.20%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%, S: 0% to 0.02%, Cr: 0% to 1.00%, Ni: 0% to 1.00%, Cu: 0% to 1.00%, Mo: 0% to 0.50%, Ti: 0% to 0.20%, Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to 0.0050%, Al: 0% to 0.10%, Ca: 0% to 0.05%, and a remainder including Fe and impurities; immersing the wire rod of 850°C to 1050°C into a first molten salt bath or a first molten lead bath of 350°C to 450°C, subsequently taking out the wire rod from the first molten salt bath or the first molten lead bath; immersing the wire rod into a second molten salt bath or a second molten lead bath of 530°C to 600°C at a time which is 5 seconds or less from the take-out and which is from t_s seconds before to t_s seconds after the start of the bainite transformation of the wire rod; and taking out the wire rod from the second molten salt bath or the second molten lead bath after the bainite transformation is completely finished.

 $t_s=0.05 \times t_{complete}$ (Equation 3)

 $t_{complete}$ represents a time from a start to a finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath.

(4) In the method for manufacturing the wire rod according to (3), in which the elapsed time between a time in which the wire rod is immersed in the first molten salt bath or the first molten lead bath and a time in which the wire rod is immersed in the second molten salt bath or second molten lead bath may be 10 seconds to 40 seconds.

(5) In the method for manufacturing the wire rod according to (3), in which the length of time when the bainite transformation starts in the wire rod in the first molten salt bath or a first molten lead bath may be determined by detecting the reheat of the wire rod.

(6) A method for manufacturing the hypereutectoid bainite steel wire according to another aspect of the present invention is the method for manufacturing the hypereutectoid bainite steel wire according to (2), the method includes: rolling a billet to obtain a wire rod, in which the billet includes, as a chemical composition, by mass%: C: more than 0.80% to 1.20%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0.02% or less, S: 0.02% or less, Cr: 0% to 1.00%, Ni: 0% to 1.00%, Cu: 0% to 1.00%, Mo: 0% to 0.50%, Ti: 0% to 0.20%, Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to

0.0050%, Al: 0% to 0.10%, Ca: 0% to 0.05%, and a remainder including Fe and impurities; immersing the wire rod of 850° C to 1050° C into a first molten salt bath or a first molten lead bath of 350° C to 450° C, subsequently taking out the wire rod from the first molten salt bath or the first molten lead bath; immersing the wire rod into a second molten salt bath or a second molten lead bath of 530° C to 600° C at a time which is 5 seconds or less from the takeout and which is t_s seconds before to t_s seconds after start of bainite transformation of the wire rod; taking out the wire rod from the second molten salt bath or the second molten lead bath after the bainite transformation is completely finished; and wire drawing of the wire rod taken out from the second molten salt bath or the second molten lead bath.

 $t_s = 0.05 \times t_{complete}$

 $t_{complete}$ represents a time from a start to a finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath.

- (7) In the method for manufacturing the hypereutectoid bainite steel wire according to (6), in which the immersion time that the wire rod is immersed into the first molten salt bath or the first molten lead bath may be 10 seconds to 40 seconds.
- (8) In the method for manufacturing the hypereutectoid bainite steel wire according to (6), in which the time when the bainite transformation starts in the wire rod in the first molten salt bath or the first molten lead bath may be determined by detecting a reheat of the wire rod.
- (9) A method for manufacturing the hypereutectoid bainite steel wire according to another aspect of the present invention is the method for manufacturing the hypereutectoid bainite steel wire according to (2), the method includes: wire drawing a wire rod obtained by rolling a billet to obtain a steel wire, in which the billet includes, as a chemical composition, by mass%: C: more than 0.80% to 1.20%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%, S: 0% to 0.02%, Cr: 0% to 1.00%, Ni: 0% to 1.00%, Cu: 0% to 1.00%, Mo: 0% to 0.50%, Ti: 0% to 0.20%, Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to 0.0050%, Al: 0% to 0.10%, Ca: 0% to 0.05%, and a remainder including Fe and impurities; immersing the steel wire of 850°C to 1050°C into a first molten salt bath or a first molten lead bath of 350°C to 450°C, subsequently taking out the steel wire from the first molten salt bath or the first molten lead bath; immersing the steel wire into a second molten salt bath or a second molten lead bath of 530°C to 600°C at a time which is 5 seconds or less from the take-out and which is t_s seconds before to t_s seconds after start of bainite transformation of the steel wire; and taking out the steel wire from the second molten salt bath or the second molten lead bath after the bainite transformation is completely finished.

$t_s = 0.05 \times t_{complete}$

 $t_{complete}$ represents a time from a start to a finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath.

- (10) In the method for manufacturing the hypereutectoid bainite steel wire according to (9), in which an elapsed time between a time when the steel wire is immersed into the first molten salt bath or the first molten lead bath and a time when the steel wire is immersed into the second molten salt bath or the second molten lead bath may be 10 seconds to 40 seconds.
- (11) In the method for manufacturing the hypereutectoid bainite steel wire according to (9), in which the time when the bainite transformation starts in the steel wire in the first molten salt bath or the first molten lead bath may be determined by detecting a reheat of the steel wire.
- (12) In the method for manufacturing the hypereutectoid bainite steel wire according to any one of (9) to (11), the method further may include: wire drawing to the steel wire taken out from the second molten salt bath or the second molten lead bath.

[Effects of the Invention]

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[0016] According to the present invention, the wire rod which has the lower tensile strength and higher ductility compared with traditional pearlite wire rod and in which the variation in the tensile strength is small compared with the traditional bainite wire rod can be obtained. During the wire rod according to the present invention is bundled, or in the state where the wire rod according to the present invention is bundled, the generation of the breakage is suppressed. Furthermore, the workability of the wire rod according to the present invention and the workability of the steel wire according to the present invention obtained by wire drawing the wire rod are favorable. Therefore, according to the present invention, the wire rod having excellent drawing properties and delayed fracture resistance for the hypereutectoid bainite steel

wire, the hypereutectoid bainite steel wire manufactured by using the wire rod, and the method for stably manufacturing them can be provided.

[Brief Description of the Drawings]

[0017]

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- FIG. 1 is a view showing heat treatment conditions in a method for manufacturing a wire rod according to an embodiment of the present invention.
- FIG. 2 is a view showing an example of a relationship between tensile strength TS (N/mm²) and C content (mass%) in a wire rod according to an embodiment of the present invention.
- FIG. 3 is a view showing a relationship between heat treatment conditions in a method for manufacturing a wire rod and a variation in tensile strength of a wire rod according to an embodiment of the present invention.
- FIG. 4 is a flowchart showing a method for manufacturing a wire rod or a steel wire according to an embodiment of the present invention.
- FIG. 5 is a flowchart showing a method for manufacturing a steel wire according to another embodiment of the present invention.
- FIG. 6 is a view showing a method for calculating an area ratio of bainite.
- FIG. 7 is a schematic view showing a wire shape when a wire rod is immersed into a molten salt bath or molten lead bath.

[Embodiments of the Invention]

[0018] Hereinafter, embodiments of the present invention will be described.

[0019] A wire rod for hypereutectoid bainite steel wire having excellent drawing properties and delayed fracture resistance according to the present embodiment will be described. Hereinafter, this wire rod is simply referred to as "wire rod according to the present embodiment".

[0020] A wire rod according to the present embodiment includes, as a chemical composition, by mass%: C: more than 0.80% to 1.20%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%, S: 0% to 0.02%, Cr: 0% to 1.00%, Ni: 0% to 1.00%, Cu: 0% to 1.00%, Mo: 0% to 0.50%, Ti: 0% to 0.20%, Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to 0.0050%, Al: 0% to 0.10%, Ca: 0% to 0.05%; and a remainder including Fe and impurities; in which when eight test pieces having a length of 400 mm, which are obtained by dividing a wire rod having a length of 3200 mm into eight components having a same length, are manufactured, an average tensile strength TS of each test pieces satisfies a following equation 1, by N/mm², a difference between the maximum value and the minimum value of the tensile strengths of each test pieces is 50 N/mm² or less, and the average RA of reduction of area of each test pieces satisfies a following equation 2, by %.

$$[TS] \le 810 \times [C] + 475$$
 (Equation 1)

 $[RA] \ge -0.083 \times [TS] + 154$ (Equation 2)

[0021] Here, [C] means C content in the wire rod by mass%, and [TS] means the average tensile strength TS by N/mm². [0022] At first, chemical composition of wire rod according to the present embodiment will be described. Hereinafter, "%" means "mass%".

C: more than 0.80% to 1.20%

[0023] C is an element to enhance the hardenability and tensile strength of a wire rod. Enhancing the hardenability of the wire rod causes the main structure thereof to become bainite. When the C content is more than 0.80%, the required hardenability and tensile strength can be obtained. On the other hand, when the C content is more than 1.20%, proeutectoid cementite is generated and breaking easily occurs during wire drawing of the wire rod. Therefore, in order to suppress generation of proeutectoid cementite, the upper limit of the C content is set to 1.20%. In order to further facilitate generation of bainite, the lower limit of the C content may be set to 0.85%, 0.90% or 0.95%. In addition, when the tensile strength is too high, the sensitivity of the wire rod to delayed fracture is increased. Therefore, the lower limit of the C content may be set to 1.15%, 1.10% or 1.05%.

Si: 0.10% to 1.50%

[0024] Si is an element which enhances the tensile strength of a wire rod. In addition, Si is an element which functions as a deoxidizer. When Si content is less than 0.10%, the above-described effect cannot be obtained. Therefore, the lower limit of the Si content is set to 0.10%. However, Si promotes precipitation of proeutectoid ferrite in hypereutectoid steel. There is a concern that the proeutectoid ferrite causes breaking during wire drawing of the wire rod. Furthermore, there is a concern that Si deteriorates the working limit of wire drawing in hypereutectoid steel. Therefore, the upper limit of the Si content is set to 1.50%. In order to further enhance the above-described effect, the lower limit of the Si content may be set to 0.15%, 0.20% or 0.25%. In addition, in order to further facilitate the wire drawing, the upper limit of the Si content may be set to 1.45%, 1.40% or 1.35%.

Mn: 0% to 1.00%

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[0025] It is not necessary for a wire rod according to the present embodiment to contain Mn. Therefore, the lower limit of Mn content in the wire rod according to the present embodiment is 0%. However, Mn has an effect for enhance the strength of the wire rod by enhancing hardenability of the wire rod. In addition, Mn is an element acting as a deoxidizer as well as Si. Therefore, Mn may be contained in the wire rod if necessary. When the Mn content is more than 1.00%, the hardenability is improved in a place where Mn is segregated and the time until the transformation is completed becomes longer. That is, in this case, the hardenability is not uniform in the wire rod and martensite is generated in a place where the hardenability is high. Then, this martensite causes breaking during wire drawing. Therefore, the upper limit of the Mn content is required to be 1.00%. In addition, in order to further enhance drawing properties, the upper limit of the Mn content may be set to 0.90% or 0.80%. Although the lower limit of Mn content is 0%, in order to obtain the above-described effect, the lower limit of the Mn content is preferably 0.20%, and more preferably 0.40%.

P: 0% to 0.02%

S: 0% to 0.02%

[0026] P and S are impurity elements. When large amounts of P and S are contained in the wire rod, ductility of the wire rod is deteriorated. Therefore, the upper limits of the P content and S content are both 0.02%. Preferably, the upper limits of the P content and S content are both 0.005%. Since the P content and S content are preferably as small as possible, the lower limits of the P content and S content are 0%. However, if the amounts of these elements are reduced to 0.001% or less, the manufacturing cost of the wire rod increases. Therefore, it is usual for the lower limits of the P content and S content to be 0.001% in practical steel.

[0027] In addition to the above elements, the wire rod according to the present embodiment may contain Cr, Ni, Cu, Mo, Ti, Nb, V, B, Al and Ca as appropriate within a range that does not inhibit the properties of the wire rod according to the present embodiment. However, it is not essential to contain these elements and the lower limits of the amounts of these elements are 0%.

Cr: 0% to 1.00%

[0028] Cr is an element to promote bainite transformation by improving the hardenability of wire rod. When Cr content is more than 1.00%, time required for transformation from start to finish becomes longer and the heat treatment time to complete the bainite transformation is increased, thereby undesirable. In addition, when the Cr content is more than 1.00%, there is a concern that martensite is generated in the wire rod as well as Mn. Therefore, the upper limit of the Cr content is set to 1.00%. The Cr content is preferably 0.50% or less, and more preferably 0.30% or less. Although the lower limit of the Cr content is 0%, in order to obtain the above-described effect, the amount of Cr contained is preferably 0.01% or more, and more preferably 0.05% or more.

Ni: 0% to 1.00%

[0029] Ni is an element to promote bainite transformation by improving the hardenability of wire rod as well as Cr. When the Ni content is more than 1.00%, the ductility of ferrite decreases. Therefore, the upper limit of the Ni content is set to 1.00%. The Ni content is preferably 0.70% or less, and more preferably 0.50% or less. Although the lower limit of the Ni content is 0%, in order to obtain the above-described effect, the amount of Ni contained is preferably 0.05% or more, and more preferably 0.10% or more.

Cu: 0% to 1.00%

[0030] Cu is an element to improve corrosion fatigue properties of wire rod. When the Cu content is more than 1.00%, ductility of ferrite in bainite decreases. Therefore, the upper limit of the Cu content is set to 1.00%. The Cu content is preferably 0.70% or less, and more preferably 0.50% or less. Although the lower limit of the Cu content is 0%, in order to obtain the above-described effect, the amount of Cu contained is preferably 0.05% or more, and more preferably 0.10% or more.

Mo: 0% to 0.50%

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[0031] Mo is an element to improve hardenability of wire rod. When the Mo content is more than 0.50%, hardenability of wire rod is excessively increased and there is a concern that micro-martensite precipitates at a place where Mo is segregated. The micro-martensite may deteriorate the ductility of the wire rod. Therefore, the upper limit of the Mo content is set to 0.50%. The Mo content is preferably 0.30% or less, and more preferably 0.10% or less. Although the lower limit of the Mo content is 0%, in order to obtain the above-described effect, the amount of Mo contained is preferably 0.01% or more, and more preferably 0.03% or more.

Ti: 0% to 0.20%

20 Nb: 0% to 0.20%

V: 0% to 0.20%

[0032] Ti, Nb and V refine the diameter of y grain of the heated wire rod. In this case, structure formed during cooling the wire rod is refined and toughness of the wire rod is improved. On the other hand, when the amounts of Ti, Nb and V are more than 0.20%, the properties of the wire rod according to the present embodiment are adversely affected. Therefore, the upper limits of each amount of Ti, Nb and V are set to 0.20%. Each amount of Ti, Nb and V is preferably 0.15% or less, and more preferably 0.10% or less. Although the lower limits of each amount of Ti, Nb and V is 0%, in order to obtain the above-described effect, the lower limits of each amount of Ti, Nb and V may be set to 0.01% preferably, 0.02% and more preferably.

B: 0% to 0.0050%

[0033] B improves the hardenability of a wire rod. When the B content is more than 0.0050%, the hardenability of the wire rod is too high and there is a concern that the ductility of the wire rod is deteriorated by the formation of martensite in the wire rod. Therefore, the upper limit of the B content is set to 0.0050%. The B content is preferably 0.0040% of less, and more preferably 0.0030% or less. Although the lower limit of the B content is 0%, in order to obtain the above-described effect, the amount of B contained is preferably 0.0005% or more, and more preferably 0.0010% or more.

40 AI: 0% to 0.10%

[0034] Al is an element functioning as a deoxidizer. When the Al content is more than 0.10%, hard alumina-based inclusions are generated and this inclusion deteriorates ductility and drawability of a wire rod. Therefore, the upper limit of the Al content is set to 0.10%. The Al content is preferably 0.07% or less, and more preferably 0.05% or less. Although the lower limit of the Al content is 0%, in order to obtain the above-described effect, the amount of Al of contained is preferably 0.01% or more, and more preferably 0.02% or more.

Ca: 0% to 0.05%

[0035] Ca improves delayed fracture resistance of wire rod by controlling form of MnS which is an inclusion in the wire rod. However, when the Ca content is more than 0.05%, Ca makes coarse inclusions and the delayed fracture resistance of the wire rod is deteriorated by this inclusion. Therefore, the upper limit of the Ca content is set to 0.05%. The Ca content is preferably 0.04% or less, and more preferably 0.03% or less. Although the lower limit of the Ca content is 0%, in order to obtain the above-described effect, the amount of Ca contained is preferably 0.001% or more, and more preferably 0.005% or more.

[0036] Remainder of the chemical composition of the wire rod according to the present embodiment including Fe and impurity. The impurity is a component which is incorporated from raw materials such as mineral or scrap or by various factors in a manufacturing process when the steel is industrially manufactured, and is accepted within a range that does

not adversely affect the property of the wire rod according to the present embodiment.

[0037] Next, metal structure of the wire rod according to the present embodiment will be described.

Bainite: 90 area% to 100 area%

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[0038] The metal structure of the wire rod according to the present embodiment includes 90 area% to 100 area% of bainite. The drawing properties of the wire rod in which the metal structure includes bainite of 90 area% to 100 area% (bainite wire rod) are excellent compared with the wire rod in which the metal structure mainly includes pearlite (pearlite wire rod). In addition, cementite included in bainite is finer than cementite included in pearlite. When the bainite wire rod is compared with the pearlite wire rod having the same chemical composition as the bainite wire rod, the tensile strength of the bainite wire rod is lower than the tensile strength of the pearlite wire rod. When the tensile strength of the wire rod is low, the ductility, drawing properties and workability of the wire rod and steel wire obtained by drawing this wire rod are high. In order to further improve these properties, the lower limit of the amount of bainite may be set to 95 area%, or 98 area%. In addition to bainite, for example, micro-martensite (MA), proeutectoid cementite and the like may be included in the metal structure of the wire rod. Inclusion of these structures is acceptable as long as the amount of bainite is 90 area% or more.

[0039] The amount of bainite can be obtained by observing a cross section of the wire rod perpendicular to a drawing direction. An example of the method for measuring the amount of bainite is as follows. Firstly, metal structure image is obtained at multiple locations on a cross section of the wire rod perpendicular to a drawing direction. Next, the average area ratio of bainite in each metal structure image is obtained. A photographing region to obtain the metal structure image is not particularly limited. For example, as shown in Fig. 6, each of a center portion 11 of the cross section 1 of the wire rod perpendicular to a drawing direction, a surface layer portion 12, and intermediate portion 13 where is a region of 1/4 depth of the wire diameter preferably includes four photographing region 2 in which they are spaced apart from each other as possible. Means for obtaining the metal structure image is not particularly limited. For example, it is preferable to take the metal structure image using SEM (Scanning Electron Microscope) at 1000 magnification. Means for discriminating bainite in the metal structure image is not particularly limited. In view of the chemical composition, it can be regarded that the wire rod according to the present embodiment does not include a structure other than pearlite, martensite (including micro-martensite), proeutectoid cementite and bainite. Therefore, in the metal structure image of the wire rod according to the present embodiment, a structure other than pearlite, martensite and proeutectoid cementite may be regarded as bainite.

[0040] Next, mechanical properties of wire rod according to the present embodiment will be described.

Average tensile strength TS of wire rod: 810×[C]+475 N/mm² or less

[0041] The mechanical properties of wire rod according to the present embodiment is evaluated by measuring the properties of the eight test pieces having a length of 400 mm, which can be obtained by dividing a wire rod having a length of 3200 mm into eight components having the same length. The average of tensile strength of the above-described eight test pieces is defined as the average tensile strength TS of the wire rod. The average tensile strength TS of the wire rod according to the present embodiment satisfies the following equation 1.

 $[TS] \le 810 \times [C] + 475$ (1)

[0043] Here, [C] means C content in the wire rod by mass%, and [TS] means the average tensile strength TS by N/mm². [0043] Main factors for increasing tensile strength of wire rod are C content of the wire rod and heat treatment condition during manufacturing the wire rod. An increase in tensile strength due to an increase in the C content of the wire rod does not disperse the tensile strength of the wire rod. The reason is that increase in the tensile strength which is caused by increasing C content occurs uniformly across the entire wire rod. On the other hand, if the tensile strength is increased by changing the heat treatment conditions during manufacture of the wire rod, there is a concern that the tensile strength of the wire rod may vary. Particularly, when a wire diameter is small, the heat capacity per unit length of the wire rod is small and temperature distribution in the longitudinal direction of the wire rod varies. Therefore, it is difficult to perform the heat treatment uniformly across the entire wire rod and it is easy to spread the variation in the tensile strength. The greater effect the heat treatment brings to the tensile strength, the larger the variation in the tensile strength is. When the tensile strength of the wire rod is varied, variation in workability of the wire rod and steel wire is occurred and it becomes difficult to perform machining for the wire rod and steel wire. Furthermore, in this case, the sensitivity to delayed fracture (hydrogen embrittlement) increases at a place where the tensile strength is high, and breakage occurs.

[0044] In view of the foregoing matters, the average tensile strength of the wire rod according to the present embodiment,

it is necessary to be below the upper limit that is only defined by C content. The present inventors limit the upper limit of the average tensile strength TS by the above equation 1.

[0045] Coefficients of "810" and "475" in the above equation 1 are coefficients that the present inventors have experimentally determined for the wire rod, in which the C content is more than 0.80%, that is, the C content is more than eutectoid point. When the average tensile strength TS of the wire rod is more than the upper limit defined by equation 1, (that is, when the average tensile strength is too high for the C content), an influence which the heat treatment brings to the tensile strength increases to inappropriate level and the variation in tensile strength of the wire rod is increased. Therefore, the present inventors found that the stability of the machining is impaired and the breakage is easy to occur. In this case, since the heat treatment condition during manufacturing the wire rod is not appropriate, therefore, it is considered that the tensile strength of the wire rod is increased unevenly.

[0046] An example of a relationship between the average tensile strength TS (N/mm²) and the C content (mass%) is showed in Fig. 2. From this figure, it can be understand that the average tensile strength TS of the wire rod according to the present embodiment is within a range of "[TS] \leq 810×[C]+475".

[0047] The lower limit of the tensile strength of the wire rod is not particularly limited. However, it is usual for the wire rod which is industrially used that a certain tensile strength is required. In addition, when the average tensile strength of the wire rod is too low for the C content, it is difficult to industrially use the wire rod. Therefore, the average tensile strength of the wire rod according to the present embodiment may be defined by the following equation 1', equation 1" or equation 1".

 $810 \times [C] + 425 \le [TS] \le 810 \times [C] + 475$ (Equation 1')

 $810 \times [C] + 435 \le [TS] \le 810 \times [C] + 475$ (Equation 1")

 $810 \times [C] + 445 \le [TS] \le 810 \times [C] + 475$ (Equation 1''')

Average reduction of area of wire rod: -0.083×TS+154 or more

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[0048] The mechanical properties of wire rod according to the present embodiment is evaluated by measuring the properties of the eight test pieces having a length of 400 mm, which can be obtained by dividing a wire rod having a length of 3200 mm into eight components having the same length. The average reduction of area of the above-described eight test pieces is defined as the average reduction of area RA of the wire rod. The average reduction of area RA of the wire rod according to the present embodiment satisfies the following equation 2.

$$[RA] \ge -0.083 \times [TS] + 154$$
 (Equation 2)

[0049] Here, [TS] means the average tensile strength TS by N/mm².

[0050] In addition, in the wire rod according to the present embodiment, the lower limit of the average reduction of area RA is limited by the lower limit calculated from the average tensile strength TS.

[0051] Coefficients of "-0.083" and "154" in the above equation 2 are coefficients that the present inventors have experimentally determined for the wire rod by investigating the average tensile strength and average reduction of area in various wire rods, in which C content is within a hypereutectoid region. As described later, reduction of area of the wire rod obtained by the method for manufacturing according to the present embodiment had the average reduction of area of "-0.083×[TS]+154" or more at least. This average reduction of area is higher than the average reduction of area of the conventional pearlite wire rod. On the other hand, the average reduction of area of the wire rod in which the metal structure does not have 90 area% to 100 area% of bainite was lower than the above-described lower limit. In addition, the average reduction of area of the wire rod, in which bainite was obtained by heating austenite in supercooled state before bainite the transformation was started although the metal structure mainly consisted of bainite, was lower than the above-described lower limit.

[0052] Variation range in tensile strength of wire rod: difference between maximum value and minimum value in each tensile strength of eight test pieces is 50 N/mm² or less

[0053] The mechanical properties of wire rod according to the present embodiment is evaluated by measuring the properties of the eight test pieces having a length of 400 mm, which can be obtained by dividing a wire rod having a length of 3200 mm into eight components having the same length. In the wire rod according to the present embodiment,

the difference between maximum value and minimum value in each tensile strength of the above-described each test pieces is defined as the variation range in the tensile strength of the wire rod. The variation range in the tensile strength of the wire rod according to the present embodiment is 50 N/mm² or less.

[0054] When the tensile strength of the wire rod is high, the workability of the wire rod and steel wire obtained by wire drawing the wire rod becomes small. When the variation range in the tensile strength of the wire rod is more than 50 N/mm², it is difficult to process the wire rod and steel wire obtained by wire drawing the wire rod under certain conditions. Furthermore, in this case, sensitivity to delayed fracture (hydrogen embrittlement) increases at a place where the tensile strength is high, and breakage occurs. In order to further process the wire rod and steel wire easily and suppress the generation of breakage of the wire rod, the variation range in the tensile strength of the wire rod may be 45 N/mm² or less, 40 N/mm² or less, 35 N/mm² or less or 30 N/mm² or less.

[0055] A wire diameter according to the present embodiment is not particularly limited. However, in order to further suppress the variation in the tensile strength of the wire rod, the wire diameter may be set to 3.5 mm to 16.0 mm. As described above, when a wire diameter is small, the heat capacity per unit length of the wire rod is small and the temperature distribution in the longitudinal direction of the wire rod varies. Therefore, it is difficult to perform the heat treatment uniformly across the entire wire rod and it is easy to spread the variation in the tensile strength. On the other hand, when the wire diameter is more than 16.0 mm, it is difficult to uniformly cool the center portion and surface layer portion of the wire rod and there is a concern that it is difficult to set the metal structure of the center portion of the wire rod to the predetermined structure.

[0056] Next, a method for manufacturing a wire rod and steel wire according to the present embodiment (hereinafter, may be referred to as "a manufacturing method according to the present embodiment") will described.

[0057] As shown in Fig. 4, a method for manufacturing a wire rod according to the present embodiment includes:

- (a) rolling a billet having the above-described chemical composition of the wire rod according to the present embodiment to obtain the wire rod;
- (b) immersing the wire rod of 850°C to 1050°C into a first molten salt bath or a first molten lead bath of 350°C to 450°C, subsequently taking out the wire rod from the first molten salt bath or the first molten lead bath;
- (c) immersing the wire rod into second molten salt bath or second molten lead bath of 530° C to 600° C at the time within 5 seconds from the take-out and at the time from t_s seconds before to t_s seconds after the bainite transformation of the wire rod starts; and
- (d) taking out the wire rod from the second molten salt bath or the second molten lead bath after the bainite transformation is completely finished. t_s is obtained by the following equation 3.

$$t_s = 0.05 \times t_{complete}$$
 (Equation 3)

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t_{complete} represents a time from the start to the finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath. As shown in Fig. 4, in addition to above (a) to (d), a method for manufacturing a hypereutectoid bainite steel wire according to the present embodiment further includes wire drawing to the wire rod before immersing the wire rod into the first molten salt bath or the first molten lead bath to obtain a steel wire. Furthermore, as shown in Fig. 5, in addition to above (a) to (d), a method for manufacturing a hypereutectoid bainite steel wire according to the another embodiment of the present invention further includes:

(e) wire drawing to the wire rod taken out from the second molten salt bath or the second molten lead bath.

[0058] In addition, "molten salt bath or molten lead bath" is simply referred as "bath" in Figs. 4 and 5. Hereinafter, the matter that the wire rod is immersed into the second molten salt bath or the second molten lead bath at the time from t_s seconds before to t_s seconds after the bainite transformation of the wire rod starts may be referred as "immersing the wire rod into the second molten salt bath or the second molten lead bath at substantially the same time as the start of the bainite transformation of the wire rod".

[0059] A heat treatment of a manufacturing method according to the present embodiment is showed in Fig. 1. The arrow labeled with symbol (b) in figure represents the wire rod of 850°C to 1050°C being immersed into the first molten salt bath or the first molten lead bath having a temperature T₁ within a range of 350°C to 450°C and subsequently the wire rod is taken out, that is, represents the above-described (b). In (b), the wire rod is hold at temperature T₁, taken out and subsequently transferred to the second molten salt bath or the second molten lead bath. t₁ in figure represents the sum of a time for immersing the wire rod into the first molten salt bath or the first molten lead bath and a time of transferring the wire rod from the first molten salt bath or the second molten salt bath or the second molten salt bath or the second molten salt bath or the

first molten lead bath to the wire rod is immersed into the second molten salt bath or the second molten lead bath). The arrow labeled with symbol (c) in figure represents the wire rod being immersed into the second molten salt bath or the second molten lead bath having a temperature $(T_1+\Delta T)$ within a range of 530°C to 600°C at substantially the same time as the start of the bainite transformation, that is, represents the above-described (c). The arrow labeled with symbol (d) in the figure represents the wire rod being held in the the second molten salt bath or the second molten lead bath until the bainite transformation is completely finished, that is, represents the above-described (d).

Temperature of wire rod before immersing into first molten salt bath or first molten lead bath: 850°C to 1050°C

[0060] In the method for manufacturing the wire rod according to the present embodiment, firstly, a billet having the above-described chemical composition of the wire rod according to the present embodiment is rolled to obtain the wire rod. Next, the wire rod is immersed into the first molten salt bath or the first molten lead bath. The wire rod may be cooled once between the rolling and immersing, and reheated, or the wire rod may not be cooled and reheated between the rolling and immersing. In addition, the wire drawing may be performed to the wire rod between the rolling and immersing. In any case, the temperature of the wire rod immersed into the first molten salt bath or the first molten lead bath is set to 850°C to 1050°C. Generally, since the temperature of the wire rod immediately after rolling is 1050°C or less, when the wire rod after rolling or the steel wire after wire drawing is directly immersed into the first molten salt bath or first molten lead bath (that is, immersing without performing cooling and reheating), the upper limit of the temperature of the wire rod or steel wire which is immersed becomes substantially 1050°C. In addition, even when the wire rod after rolling or the steel wire after wire drawing is cooled once and reheated, and immersed into the first molten salt bath or the first molten lead bath, the upper limit of the temperature of the wire rod or steel wire which is immersed may be set to 1050°C. The reason is that there is no advantage to heat the wire rod or steel wire to 1050°C or more. When the temperature of the wire rod or steel wire which is immersed into the first molten salt bath or the first molten lead bath is less than 850°C, hardening is not performed well to the wire rod or steel wire. Therefore, the lower limit of the temperature of the wire rod or steel wire which is immersed into the first molten salt bath or the first molten lead bath is set to 850°C. In addition, when the wire drawing is performed to the wire rod between the rolling and immersing, hereinafter, the mention of the "wire rod" in the description of the process can be suitably replaced with "steel wire".

Temperature of first molten salt bath or first molten lead bath: 350°C to 450°C

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[0061] In the method for manufacturing the wire rod according to the present embodiment, the wire rod having a temperature of 850° C to 1050° C is rapidly cooled by immersing into the first molten salt bath or the first molten lead bath ((b) in Fig. 1). The temperature T_1 of the first molten salt bath or the first molten lead bath is 350° C to 450° C. The metal structure of the wire rod becomes austenite being cooled to a supercooled state by rapid cooling. When the wire is isothermally held in this state, the bainite transformation of austenite being the supercooled state starts.

[0062] When the temperature T_1 of the first molten salt bath or the first molten lead bath is more than 450°C, the cooling rate of the wire rod decreases and the metal structure of the wire rod is transformed to bainite before austenite is formed in s supercooled state. In this case, although the tensile strength of the wire rod is deteriorated, proeutectoid cementite precipitates in the wire rod. The proeutectoid cementite deteriorates the drawing properties of the wire rod. Therefore, in order to rapidly cool the wire rod, the temperature T_1 of the first molten salt bath or the first molten lead bath is required to be 450°C or less. On the other hand, when the temperature T_1 of the first molten salt bath or the first molten lead bath will solidify. The length of time for the wire rod being immersed into the first molten salt bath or the first molten lead bath needs to be adjusted so that the wire rod can be immersed into the second molten salt bath or a second molten lead bath as desired.

[0063] At time of immersing wire rod into a second molten salt bath or a second molten lead bath: at time which is 5 seconds or less from take-out from a first molten salt bath or a first molten lead bath and which is from t_s seconds before to t_s seconds after start of bainite transformation of wire rod

[0064] In the method for manufacturing the wire rod according to the present embodiment, the wire rod is immersed into the second molten salt bath or the second molten lead bath having the temperature T_2 at the time within 5 seconds from when the wire rod is taken out from the first molten salt bath or the first molten lead bath having the temperature T_1 and at the time from t_s seconds before to t_s seconds after the bainite transformation of the wire rod starts.

[0065] The present inventors manufactured the wire rod under the various manufacturing conditions in which t_1 that is from the time immersing the wire rod into the first molten salt bath or the first molten lead bath to the time immersing the wire rod into the second molten salt bath or the second molten lead bath (that is, total length of time of time for immersing the wire rod into the first molten salt bath or the first molten lead bath and time for transferring the wire rod from the first molten salt bath or the first molten lead bath to the second molten salt bath or the second molten lead bath) and the temperature T_1 of the first molten salt bath or the first molten lead bath are changed, and measured the variation

range in the tensile strength of the wire rod. Using the obtained data by this, the present inventors investigated the relationship between the temperature T_1 , time t_1 , and the variation range in the tensile strength. As a result, results shown in Fig. 3 were obtained.

[0066] Curve attached with symbol "S" in Fig. 3 is the curve showing the temperature and the time when the bainite transformation starts (hereinafter, referred as S curve). This curve varies according to the chemical composition of the wire rod. Data points described in Fig. 3 represents the temperature T₁ and time t₁ when the wire rod according to data point is manufactured. The wire rod according to data point on the left side than the curve is the wire rod immersed into the second molten salt bath or the second molten lead bath before the bainite transformation starts, and the wire rod according to data point on the right side than the curve is the wire rod immersed into the second molten salt bath or the second molten lead bath after the bainite transformation starts. In Fig. 3, the dotted line described with respect to each data point represents the thermal history of the wire rod according to each data point. The variation range in the tensile strength of the wire rod in which type of data point is "BAD" is more than 50 N/mm², the variation range in the tensile strength of the wire rod in which type of data point is "VERY GOOD" is 40 N/mm² or less. [0067] As shown in Fig. 3, in the wire rod according to data point close to the curve (that is, the wire rod immersed into the second molten salt bath or the second molten lead bath at substantially the same time as the start of the bainite transformation), the variation range in the tensile strength was small.

[0068] The time t_1 is appropriately set so that the wire rod is immersed into the second molten salt bath or the second molten lead bath at the time from t_s seconds before to t_s seconds after the bainite transformation of the wire rod starts. The t_s is the value obtained by the following equation 3.

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$$t_s = 0.05 \times t_{complete}$$
 (Equation 3)

t_{complete} represents a time from the start to the finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath.

[0069] The time from when the wire rod is immersed into the first molten salt bath or the first molten lead bath to when the bainite transformation of the wire rod starts and the t_s are determined dependent on S curve corresponding to the chemical composition of the wire rod and the temperature of the first molten salt bath or the first molten lead bath. Therefore, the time t_1 can be obtained by the simulation based on the chemical composition and the temperature of the first molten salt bath or the first molten lead bath the wire, and/or by the preliminary experiment. In addition, as described later, because the reheat of the wire rod is detected, the time from when the wire rod is immersed into the first molten salt bath or the first molten lead bath to when the bainite transformation of the wire rod starts can be obtained. Therefore, before manufacturing the wire rod, a preliminary investigation may be carried out to determine the time t_1 using the above-described means.

[0070] The reason why the variation in the tensile strength of the wire rod is suppressed by immersing the wire rod into the second molten salt bath or the second molten lead bath at substantially the same time as the start of the bainite transformation of the wire rod is not clear. However, the reason explained below is estimated. When the bainite transformation of the wire rod occurs while immersing into the first molten salt bath or the first molten lead bath, or when the bainite transformation of the wire rod occurs while transferring to the second molten salt bath or the second molten lead bath, the temperature of the wire rod is increased during immersion into the first molten salt bath or the first molten lead bath or during transfer to the second molten salt bath or the second molten lead bath due to reheating (transformation heat). In this case, there is a concern that the rising in the temperature of the wire rod is non-uniform. The reason is that, when the heat treatment of the wire rod is performed in the molten salt bath or molten lead bath, for example as shown in Fig. 7, the wire rod in the state having the coil shape is immersed into the molten salt bath or molten lead bath and subsequently taken out. When the wire rod has a coil shape during heat treatment, the rising of the temperature due to reheating is increased in portions where the wire rods overlap, compared with other portions. The reason is that the cooling effect by the first molten salt bath or the first molten lead bath is difficult to reach to the portion where the wire rod is overlapped with each other. Therefore, since the above-described time t₁ becomes longer, when the start of the heating of the wire rod is delayed, variation in tensile strength of the wire rod occurs due to non-uniform rise in the temperature of the wire rod. In addition, it is essential that the wire rod have a coil shape during heat treatment in order to enhance the production efficiency thereof. As long as there is no special reason, the wire rod in a state where the wire rods do not overlap with each other is not immersed into the molten salt bath or molten lead bath. On the other hand, when the above-described time t₁ becomes shorter and the wire rod is immersed in the second molten salt bath or the second molten lead bath for more than ts seconds before the bainite transformation starts, the start of the transformation accelerates. Therefore, the transformation start temperature is increased. In this case, the strength of the wire rod increases and the ductility of the wire rod decreases.

[0071] For the above-described reasons, it is most preferable to immerse the wire rod into the second molten salt bath or the second molten lead bath at exactly the same time as the bainite transformation of the wire rod starts. However, the present inventors found from the experimental facts that the variation in tensile strength of the wire rod is sufficiently suppressed in a wire rod in which the bainite transformation proceeds rapidly and the temperature rise due to reheating is relatively large, when the time between the immersion of the wire rod and the start of the transformation of the wire rod is 5 seconds or less. Also, the present inventors found from the experimental facts that the variation is suppressed in the wire rod in which the bainite transformation proceeds slowly and the temperature rise due to reheating is relatively low, even when the time between the immersion of the wire rod and the start of the transformation of the wire rod is more than 5 seconds. Based on these findings, in the the method for manufacturing the wire rod according to the present embodiment, the time between the immersion of the wire rod and the start of the transformation of the wire rod is defined by the value $t_{\rm s}$ which is determined in accordance with the progression rate of the bainite transformation. In addition, in the wire rod according to the present embodiment, since $t_{\rm complete}$ is not less than 100 seconds, the upper limit of the $t_{\rm s}$ may be set to 5 seconds.

[0072] In many cases, the elapsed time t₁ between the time when the wire rod is immersed into the first molten salt bath or the first molten lead bath and the time when the wire rod is immersed into the second molten salt bath or the second molten lead bath is preferably 10 seconds to 40 seconds. In view of the chemical composition of the wire rod according to the present embodiment, when the time t₁ is less than 10 seconds or more than 40 seconds, it is difficult to properly perform the following immersing the wire rod into the second molten salt bath or the second molten lead bath. [0073] In addition to the above-mentioned provisions, it is essential that the wire rod is immersed into the second molten salt bath or the second molten lead bath within 5 seconds from being taken out of the first molten salt bath or the first molten lead bath. When the time from the take-out of the wire rod to the immersion of the wire, that is, when the transferring time of the wire rod, is more than 5 seconds, there is a concern that the temperature of the wire rod varies during transfer thereof. Therefore, it is extremely difficult to immerse the wire rod into the second molten salt bath or the second molten lead bath at substantially the same time the bainite transformation of the wire rod starts.

[0074] The start of the bainite transformation in the wire rod in the first molten salt bath or the first molten lead bath may be determined by detecting the reheat of the wire rod (transformation heat). The reheat in the present embodiment represents the phenomenon in which the temperature of the wire rod is increased by starting of the bainite transformation therein. The reheat can be detected, for example, by comparing the temperature of the wire rod, which is immersed into and taken out from the first molten salt bath or the first molten lead bath, with the temperature of the first molten salt bath or the first molten lead bath. When the temperature of the wire rod is higher than the temperature of the first molten salt bath or the first molten lead bath, it can be judged that the reheat is generated in the wire rod. In each wire rod in which the immersion time of the first molten salt bath or the first molten lead bath is variously changed, the shortest immersion time t_{min} that the reheat can be generated in the wire rod can be obtained by examining the presence or absence of reheat. The time passed for t_{min} from when the wire rod is immersed into the first molten salt bath or the first molten lead bath can be regarded as the time when the bainite transformation starts in the wire rod. In this way, the time when the bainite transformation starts in the wire rod based on the obtained time.

[0075] In addition, when the time immersed into the first molten salt bath or the first molten lead bath is less than 5 seconds, even if the temperature of the wire rod is higher than the first molten salt bath or the first molten lead bath, it cannot be judged whether the reheat is generated in the wire rod, or not. The reason is that there is a case where the temperature of the wire rod is increased due to insufficient immersion time, and not by reheating.

Temperature of second molten salt bath or second molten lead bath: 530°C to 600°C

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Time when wire rod is taken out from second molten salt bath or the second molten lead bath: Time after bainite transformation is completely finished

[0076] The wire rod is immersed into the second molten salt bath or the second molten lead bath having a temperature T_2 at substantially the same time as the start of the bainite transformation of the wire rod. The temperature T_2 is 530°C to 600°C. In this way, the wire rod is rapidly heated to the temperature of 530°C to 600°C ((c) in Fig. 1), and the wire rod can be held at that temperature until the bainite transformation is completely finished. When the wire rod is rapidly heated to a temperature of 530°C to 600°C at substantially the same time as the start of the bainite transformation of the wire rod, cementite spacing in the bainite is widened. As a result, the strength of the wire rod is decreased compared with a case in which the rapidly heating is not performed. When the temperature of the second molten salt bath or the second molten lead bath is less than 530°C or more than 600°C, it takes a long time until the end of the bainite transformation. Therefore, the temperature of the second molten salt bath or the second molten lead bath is set to 530°C to 600°C in order to certainly complete the bainite transformation in a short time. The heating rate during heating the wire rod to the above temperature range is not particularly limited. However, in order to reduce the time for completing the

bainite transformation, the heating rate is preferably faster, specifically, the heating rate is preferably 10 °C/second to 50 °C/second. By immersing the wire rod into the molten salt bath or molten lead bath having a temperature of 530°C to 600°C, such a heating rate can be obtained. When the wire rod is taken out from the second molten salt bath or the second molten lead bath before the bainite transformation is not completed, MA is generated in the wire rod, and there is a concern that this MA deteriorates the workability of the wire rod.

[0077] When the wire rod is continuously held after the bainite transformation starts during immersing the wire rod into the first molten salt bath or the first molten lead bath, fine bainite structure grows. The strength of the wire rod in which the fine bainite structure is grown is higher than the strength of the wire rod in which is rapidly heated at substantially the same time as the start of the bainite transformation. Therefore, in the wire rod according to the present embodiment, the strength is decreased by rapidly heating the wire rod and widening the interval of cementite which precipitates.

[0078] A hypereutectoid bainite steel wire having excellent delayed fracture resistance according to the present embodiment (hereinafter may be referred as "steel wire according to the present embodiment") is obtained by wire drawing the wire rod having excellent drawing properties according to the present embodiment. Wire drawing may be a conventional wire drawing, and area reduction rate is not particularly limited. Since the steel wire according to the present embodiment has excellent delayed fracture resistance, applications of steel wire are greatly expanding.

[Examples]

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[0079] Next, examples of the present invention will be described, but the conditions of the examples are exemplary examples adopted to confirm the practicability and effect of the present invention. The present invention is not limited to the examples. The present invention can adopt various conditions to accomplish the object of the present invention without departing from the gist of the present invention.

(Example 1)

[0080] Hypereutectoid billets having chemical compositions as shown in Table 1 were rolled to obtain wire rods having wire diameters as shown in Table 2, and the bainite transformation was completed under the temperature conditions as shown in Table 2. The average tensile strength of the wire rods (N/mm²), the average reduction of area of the wire rods (%), and variation range in the tensile strength of the wire rods (N/mm²) after the bainite transformation was completed were measured. The average tensile strength of the wire rod is obtained by averaging the tensile strength of each of the eight test pieces having a length of 400 mm, which can be obtained by dividing a wire rod having a length of 3200 mm into eight components having the same length. The average reduction of area of the wire rod is obtained by dividing a wire rod having a length of 3200 mm into eight test pieces having a length of 400 mm, which can be obtained by dividing a wire rod having a length of 3200 mm into eight components having the same length. The variation range in the tensile strength of the wire rod is the difference between the maximum value and minimum value within the tensile strengths of each of the eight test pieces having a length of 400 mm, which can be obtained by dividing a wire rod having a length of 3200 mm into eight components having the same length. The measurement results are also shown in Table 2. In addition, the heating rate during immersing the wire rod into the second molten salt bath or the second molten lead bath was 10 °C/second to 50 °C/second.

40 **[0081]** [Table 1]

		_									
5		LOWER LIMIT OF RA	39.3	59.4	52.7	48.7	46.7	42.6	58.0	58.3	55.8
10		UPPER LIMIT OFTS	1382	1139	1220	1269	1293	1342	1156	1153	1183
		Ca (0	0	0	0	0	0	0	0	0
20		A	0.001	0.001	0.001	0.001	0.001	0.001	0.001	0.026	0.001
25		В	0.0009	0	0	0	0	0	0	0	0
		^	0.00	0.00	0.00	0.07	0.00	0.00	0.00	0.00	0.00
30 E Y L 35 40	TABLE 1	qN	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00	00.00
	—	Мо	0.05	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00
		ïZ	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
		Cu	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
		Ξ	0.00	00.00	0.00	0.00	0.00	0.00	0.00	00.00	0.00
		Cr	0.20	0.01	0.19	0.19	0.19	0.19	0.04	0.02	0.01
		S	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.01
		۵	0.01	0.01	0.01	0.01	0.01	0.01	0.01	0.02	0.01
50		Mn	0.30	0.52	0.29	0.30	0.29	0.30	0.48	69.0	0.48
		Si	0.20	0.18	0.19	0.19	0.19	0.19	0.17	0.19	0.18
55		O	1.12	0.82	0.92	0.98	1.01	1.07	0.84	0.84	0.87
			∢	В	ပ	Ω	Ш	ш	Д	Ø	2

EP 3 056 580 A1

		ВЕМАРКЗ			EXAMPLE							COMPARATIVE EXAMPLE			
5		ВВЕРКРСЕ			NOT OCCURRED	NOT OCCURRED	NOT OCCURRED	NOT OCCURRED	NOT OCCURRED	NOT OCCURRED	NOT OCCURRED	OCCURRED	NOT OCCURRED	NOT OCCURRED	
10		RA	AA NOITAIRAV ЭDNAЯ	%	4.6	4.7	5.2	5.7	9.0	3.2	5.9	6.4	7.0	7.1	
15			MINIMUM OF RA	%	41.5	29.5	52.9	49.7	43.6	45.8	42.2	24.9	57.0	51.8	
			MUMIXAM AЯ 70	%	46.1	63.9	58.1	55.4	52.6	49.0	48.1	31.3	64.0	58.9	
20			AA AVERAGE	%	44.4	61.8	56.2	53.1	49.8	47.7	45.7	28.5	61.8	56.1	
			LOWER LIMIT OF RA	%	39.3	59.4	52.7	52.7	48.7	46.7	42.6	39.3	59.4	52.7	
25	TABLE 2		ST NOITAIЯAV ЭДИАЯ	N/mm ²	39	37	35	24	20	43	40	28	34	37	
30		TS		MINIMUM OF TS	N/mm ²	1337	1101	1193	1195	1231	1271	1298	1573	1161	1246
			MUMIXAM 2T 70		1376	1138	1228	1219	1251	1314	1338	1631	1195	1283	
35			ST BDARBVA	N/mm ² N/mm ²	1356	1120	1210	1207	1242	1283	1310	1595	1177	1269	
40			UPPER LIMIT OF TS	N/mm ²	1382	1139	1220	1220	1269	1293	1342	1382	1139	1220	
40		T ₂		ပွ	550	550	550	550	550	550	550	550	550	550	
		ΔΤ		ပွ	125	150	125	150	125	125	125	0	150	150	
45		T ₁ t ₁		sec	26	30	20	35	25	30	30	20	009	009	
	e 2]			ပ	425	400	425	400	425	425	425	550	400	400	
50		MIRE DIAMETER F _C		ပ	950	980	980	980	980	950	980	920	980	980	
				E	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.5	5.0	5.0	
55	Table 2]		SJAIRETAM		∢	В	၁	ပ	О	Ш	ш	∢	В	ပ	
		S O			-	2	3	4	5	9	7	8	6	10	

[0082] In Table 2, To represents the temperatures of the wire rods immersed into the first molten salt bath or the first molten lead bath, T₁ represents the temperatures of the first molten salt bath or the first molten lead bath, t₁ represents the time from when the wire rods are immersed into the first molten salt bath or the first molten lead bath to when the wire rods are immersed into the second molten salt bath or the second molten lead bath, ΔT represents the temperatures that were increased by immersing the wire rods into the second molten salt bath or the second molten lead bath, T2 represents the temperatures of the second molten salt bath or the second molten lead bath, the upper limit of TS represents the upper limit of the average tensile strengths calculated by the C contents and equation 1, TS average represents the average tensile strengths (N/mm2), maximum of TS represents the maximum value of the tensile strengths (N/mm²), minimum of TS represents the minimum value of the tensile strengths (N/mm²), TS variation range represents the difference between the maximum of TS and the minimum ofTS (N/mm2), the lower limit of RA represents the upper limit of the average reduction of area calculated by the upper limit of the average tensile strengths and equation 2, RA average represents the average reduction of area (%), the maximum of RA represents the maximum value of the average reduction of area (%), the minimum of RA represents the minimum value of the average reduction of area (%), and the RA variation range represents the difference between maximum of RA and minimum of RA (%). Immersion time t of the wire rods immersed into the first molten salt bath or the first molten lead bath during manufacturing the Nos. 1 to 7 examples were appropriately selected so that the wire rods were immersed into the second molten salt bath or the second molten lead bath at substantially the same time as the start of the bainite transformation. In the comparative example No. 8, the wire rod was not immersed into the second molten salt bath or the second molten lead bath. In the comparative examples Nos. 9 and 10, the wire rods were immersed into the second molten salt bath or the second molten lead bath after a long time passed since the bainite transformation started. In addition, in the examples Nos. 1 to 7 and comparative examples Nos. 9 and 10, the wire rods were immersed into the second molten salt bath or the second molten lead bath within 5 seconds when the wire rods were taken out from the first molten salt bath or the first molten lead bath.

[0083] As shown in Table 2, in the examples Nos. 1 to 7, TS average satisfied equation 1 and RA average satisfied equation 2, in addition, TS variation range was 50 N/mm² or less. From these results, in the examples Nos. 1 to 7, it can be found that the delayed fracture resistance was improved and the breakages were not generated during bundling the wire rods and in the state where the wire rods were bundled.

[Industrial Applicability]

[0084] As mentioned above, according to the present invention, the wire rod has lower strength and higher ductility compared with pearlite steel and the wire rod, in which the breakage is suppressed during bundling operation of the wire rod or in the state where the wire rod is bundled, has excellent drawing properties and delayed fracture resistance, the hypereutectoid bainite steel wire manufactured by using the wire rod, and the method for stably manufacturing them can be provided. Therefore, the present invention has high availability in the steel industry.

[Brief Description of the Reference Symbols]

[0085]

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- 1 Cross section of wire rod
- 11 Center portion
- 12 Surface layer portion
- 13 Intermediate portion
- ⁴⁵ 2 Photographing region

Claims

1. A wire rod comprising, as a chemical composition, by mass%:

C: more than 0.80% to 1.20%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%, S: 0% to 0.02%,

Cr: 0% to 1.00%, Ni: 0% to 1.00%,

Cu: 0% to 1.00%, Mo: 0% to 0.50%, Ti: 0% to 0.20%, Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to 0.0050%, Al: 0% to 0.10%,

Ca: 0% to 0.05%, and

a remainder including Fe and impurities,

wherein a metal structure includes 90 area% to 100 area% of a bainite;

wherein when eight test pieces having a length of 400 mm, which are obtained by dividing a wire rod having a length of 3200 mm into eight components having a same length, are manufactured, an average tensile strength TS of each test pieces satisfies a following equation 1, by N/mm²,

wherein a difference between a maximum value and a minimum value of the tensile strengths of each test pieces is 50 N/mm² or less, and

wherein an average RA of reduction of area of each test pieces satisfies a following equation 2, by %.

 $[TS] \le 810 \times [C] + 475$ (equation 1)

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 $[RA] \ge -0.083 \times [TS] + 154$ (equation 2)

Here, [C] means C content in the wire rod by mass%, [TS] means the average TS of the tensile strengths by N/mm², and [RA] means the average RA of the reduction of area by %.

2. A hypereutectoid bainite steel wire,

which is obtained by the wire drawing the wire rod according to claim 1.

30 **3.** A method for manufacturing the wire rod according to claim 1, the method comprising:

rolling a billet to obtain a wire rod,

wherein the billet includes, as a chemical composition, by mass%:

35 C: more than 0.80% to 1.20%,

Si: 0.10% to 1.50%, Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%, S: 0% to 0.02%,

Cr: 0% to 1.00%, Ni: 0% to 1.00%,

Cu: 0% to 1.00%,

Mo: 0% to 0.50%,

Ti: 0% to 0.20%, Nb: 0% to 0.20%,

V: 0% to 0.20%,

B: 0% to 0.0050%, AI: 0% to 0.10%,

Ca: 0% to 0.05%, and

a remainder including Fe and impurities;

immersing the wire rod of 850°C to 1050°C into a first molten salt bath or a first molten lead bath of 350°C to 450°C, subsequently taking out the wire rod from the first molten salt bath or the first molten lead bath; immersing the wire rod into a second molten salt bath or a second molten lead bath of 530°C to 600°C at a time which is 5 seconds or less from the take-out and which is t_s seconds before to t_s seconds after start of bainite transformation of the wire rod; and

taking out the wire rod from the second molten salt bath or the second molten lead bath after the bainite

transformation is completely finished.

 $t_s = 0.05 \times t_{complete}$ (equation 3)

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 t_{complete} represents a time from a start to a finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath.

- **4.** The method for manufacturing the wire rod according to claim 3, wherein an elapsed time between a time when the wire rod is immersed into the first molten salt bath or the first molten lead bath and a time when the wire rod is immersed into the second molten salt bath or the second molten lead bath is 10 seconds to 40 seconds.
- 5. The method for manufacturing the wire rod according to claim 3, wherein the time when the bainite transformation starts in the wire rod in the first molten salt bath or the first molten lead bath is determined by detecting a reheat of the wire rod.
- 6. A method for manufacturing the hypereutectoid bainite steel wire according to claim 2, the method comprising:
- rolling a billet to obtain a wire rod,
 wherein the billet includes, as a chemical composition, by mass%:

C: more than 0.80% to 1.20%,

Si: 0.10% to 1.50%,

Mn: 0% to 1.00%,

P: 0% to 0.02%,

S: 0% to 0.02%,

Cr: 0% to 1.00%,

Ni: 0% to 1.00%,

Cu: 0% to 1.00%,

Mo: 0% to 0.50%,

Ti: 0% to 0.20%,

Nb: 0% to 0.20%,

ND. 0% to 0.207

 $V{:}\;0\%$ to 0.20%,

B: 0% to 0.0050%, A1: 0% to 0.10%,

A1. 0 % to 0.10 %,

Ca: 0% to 0.05%, and

a remainder including Fe and impurities;

immersing the wire rod of 850°C to 1050°C into a first molten salt bath or a first molten lead bath of 350°C to 450°C, subsequently taking out the wire rod from the first molten salt bath or the first molten lead bath; immersing the wire rod into a second molten salt bath or a second molten lead bath of 530°C to 600°C at a time which is 5 seconds or less from the take-out and which is t_s seconds before to t_s seconds after start of bainite transformation of the wire rod;

taking out the wire rod from the second molten salt bath or the second molten lead bath after the bainite transformation is completely finished; and

wire drawing to the wire rod taken out from the second molten salt bath or the second molten lead bath.

$$t_s = 0.05 \times t_{complete}$$

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t_{complete} represents a time from a start to a finish of the bainite transformation of the wire rod in seconds, when continuing an immersion of the wire rod into the first molten salt bath or the first molten lead bath.

7. The method for manufacturing the hypereutectoid bainite steel wire according to claim 6, wherein the immersion time that the wire rod is immersed into the first molten salt bath or the first molten lead bath is 10 seconds to 40 seconds.

- **8.** The method for manufacturing the hypereutectoid bainite steel wire according to claim 6, wherein the time when the bainite transformation starts in the wire rod in the first molten salt bath or the first molten lead bath is determined by detecting a reheat of the wire rod.
- 9. A method for manufacturing the hypereutectoid bainite steel wire according to claim 2, the method comprising:

wire drawing a wire rod obtained by rolling a billet to obtain a steel wire, wherein the billet includes, as a chemical composition, by mass%:

10 C: more than 0.80% to 1.20%,

Si: 0.10% to 1.50%, Mn: 0% to 1.00%, P: 0% to 0.02%,

S: 0% to 0.02%, Cr: 0% to 1.00%.

Ni: 0% to 1.00%,

Cu: 0% to 1.00%, Mo: 0% to 0.50%,

Ti: 0% to 0.20%,

Nb: 0% to 0.20%, V: 0% to 0.20%, B: 0% to 0.0050%, Al: 0% to 0.10%,

Ca: 0% to 0.05%. and

a remainder including Fe and impurities;

immersing the steel wire of 850°C to 1050°C into a first molten salt bath or a first molten lead bath of 350°C to 450°C, subsequently taking out the steel wire from the first molten salt bath or the first molten lead bath; immersing the steel wire into a second molten salt bath or a second molten lead bath of 530°C to 600°C at a time which is 5 seconds or less from the take-out and which is t_s seconds before to t_s seconds after start of bainite transformation of the steel wire; and

taking out the steel wire from the second molten salt bath or the second molten lead bath after the bainite transformation is completely finished.

 $t_s = 0.05 \times t_{complete}$

 $t_{complete}$ represents a time from a start to a finish of the bainite transformation of the steel wire in seconds, when continuing an immersion of the steel wire into the first molten salt bath or the first molten lead bath.

- **10.** The method for manufacturing the hypereutectoid bainite steel wire according to claim 9, wherein an elapsed time between a time when the steel wire is immersed into the first molten salt bath or the first molten lead bath and a time when the steel wire is immersed into the second molten salt bath or the second molten lead bath is 10 seconds to 40 seconds.
- 45 11. The method for manufacturing the hypereutectoid bainite steel wire according to claim 9, wherein the time when the bainite transformation starts in the steel wire in the first molten salt bath or the first molten lead bath is determined by detecting a reheat of the steel wire.
- 12. The method for manufacturing the hypereutectoid bainite steel wire according to any one of claims 9 to 11, the method further comprising:

 a wire drawing to the steel wire taken out from the second molten salt bath or the second molten lead bath.

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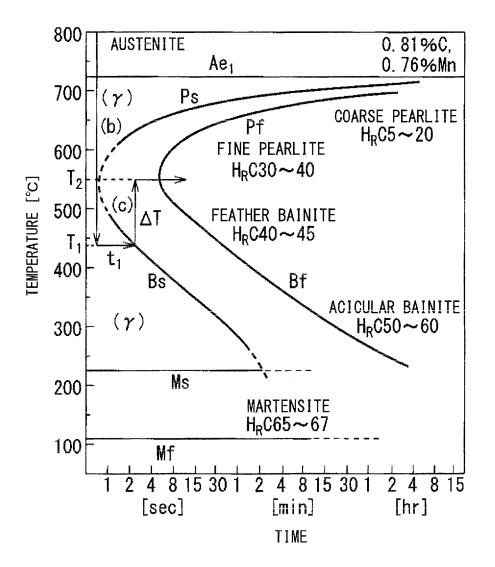
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FIG. 1





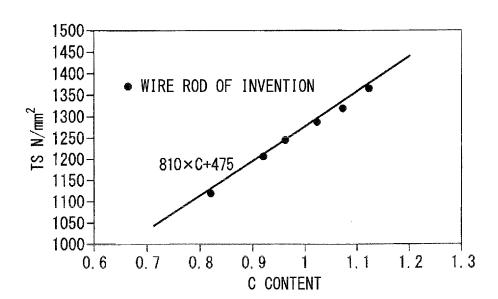
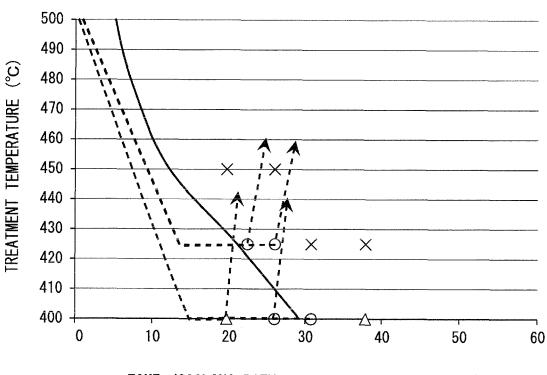


FIG. 3



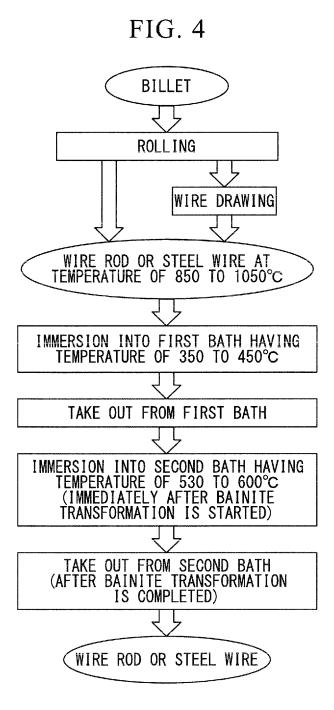
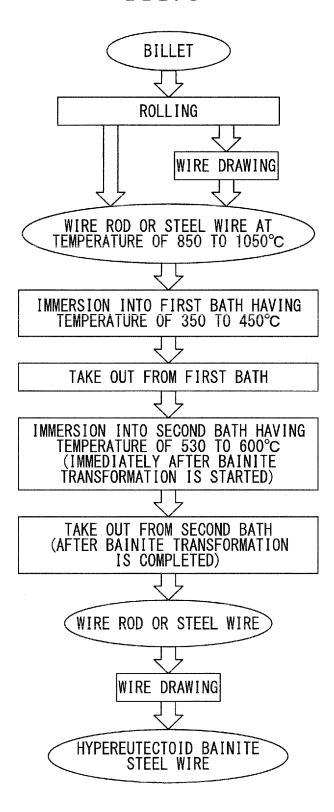


FIG. 5



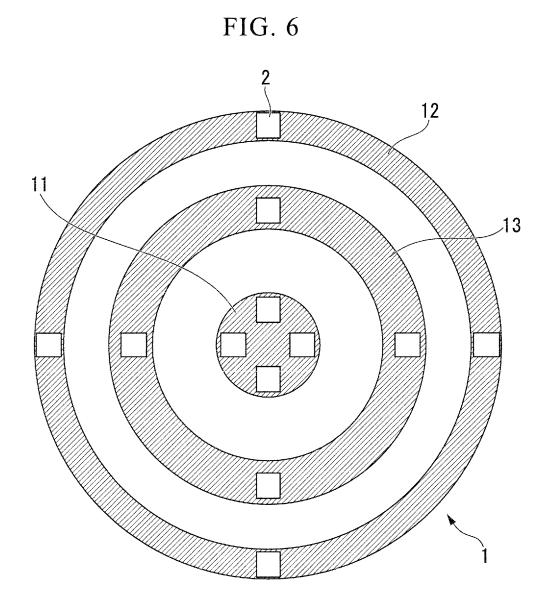
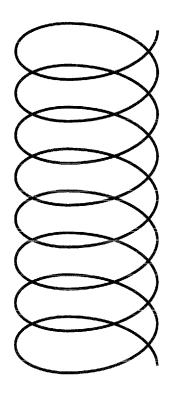


FIG. 7



International application No.

INTERNATIONAL SEARCH REPORT

PCT/JP2014/076938 A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01)i, C21D1/20(2006.01)i, C21D1/607(2006.01)i, C21D8/06 5 (2006.01)i, C21D9/52(2006.01)i, C21D9/58(2006.01)i, C22C38/54(2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC Minimum documentation searched (classification system followed by classification symbols) 10 C22C1/00-49/14, C21D1/20, C21D1/607, C21D8/06, C21D9/52, C21D9/58 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 1996-2014 15 Kokai Jitsuyo Shinan Koho 1971-2014 Toroku Jitsuyo Shinan Koho 1994-2014 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) C. DOCUMENTS CONSIDERED TO BE RELEVANT 20 Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Α JP 6-340950 A (Nippon Steel Corp.), 1 - 1213 December 1994 (13.12.1994) & US 5725689 A & EP 708182 A1 25 & WO 1995/026422 A1 & DE 69429810 D & CA 2163894 A & KR 10-0230523 B & CN 1126501 A JP 11-293400 A (Nippon Steel Corp.), Α 1-12 26 October 1999 (26.10.1999), 30 (Family: none) Α JP 2001-220650 A (Sumitomo Electric Industries, 1-12 Ltd.), 14 August 2001 (14.08.2001), (Family: none) 35 Further documents are listed in the continuation of Box C. See patent family annex. 40 Special categories of cited documents: later document published after the international filing date or priority date and not in conflict with the application but cited to understand "A" document defining the general state of the art which is not considered — to be of particular relevance the principle or theory underlying the invention "E" earlier application or patent but published on or after the international filing 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 "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 of particular relevance; the claimed invention cannot be 45 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 "O" document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the "P" "&" document member of the same patent family Date of the actual completion of the international search Date of mailing of the international search report 05 December, 2014 (05.12.14) 16 December, 2014 (16.12.14) 50 Name and mailing address of the ISA/ Authorized officer Japanese Patent Office Telephone No. Facsimile No Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT International application No. PCT/JP2014/076938 C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT 5 Category* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. JP 2002-241899 A (Kobe Steel, Ltd.), 28 August 2002 (28.08.2002), (Family: none) 1-12 Α 10 15 20 25 30 35 40 45 50

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REFERENCES CITED IN THE DESCRIPTION

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