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(71) Applicant: Nippon Steel & Sumitomo Metal Corporation

Corporation Tokyo 100-8071 (JP) (72) Inventors:

 OOBA Hiroshi Tokyo 100-8071 (JP)

ISO Arata

Tokyo 100-8071 (JP)

 TADA Tatsusei Tokyo 100-8071 (JP)

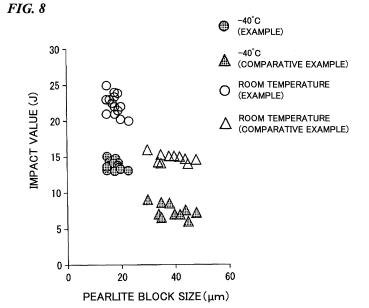
 MANABE Toshiyuki Tokyo 100-8071 (JP)

(74) Representative: Vossius & Partner Patentanwälte Rechtsanwälte mbB Siebertstrasse 3 81675 München (DE)

## (54) WIRE ROD AND METHOD FOR MANUFACTURING SAME

(57) A wire rod according to the present invention includes a predetermined chemical composition and the remainder thereof includes Fe and impurity, wherein the average value of a grain size of a pearlite block in a cross section perpendicular to a wire rod axial direction is  $23\mu m$ 

or less, and wherein a number density of the pearlite blocks having a grain size of  $40\mu m$  or more in the cross section perpendicular to the wire rod axial direction is 0 to 20 pieces/mm<sup>2</sup>.



#### Description

[Technical Field]

**[0001]** The present invention relates to a wire rod which is raw material of PC steel stranded wire for reinforcing a PC structure used for LNG (Liquefied Natural Gas) Tank of energy relating facility, and which has excellent low-temperature elongation and low-temperature toughness.

**[0002]** Priority is claimed on Japanese Patent Application No. 2013-092782, filed on April 25, 2013 and on Japanese Patent Application No. 2013-092775, filed on April 25, 2013, the content of which is incorporated herein by reference.

[Related Art]

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**[0003]** LNG tank is categorized as ground type and underground type. The present invention relates to a wire rod for ground type LNG tank and method for manufacturing the same. As the conventional art of the ground type LNG tank, Patent document 1 proposes metal double shell type LNG tank including a metal inner tank and a metal outer tank.

[0004] Generally, in the metal double shell type LNG tank, refrigerant is filled with clearance between the inner tank and the outer tank to limit increases in the temperature in the LNG tank and vaporization of LNG associated therewith. However, the structure includes the possibility of causing damage such as outflow of a lot of LNG, if a defect occurs at both of the inner tank and the outer tank. Therefore, in recent years, in order to further enhance safety, a technique in which a PC dike including PC structure (Prestressed Concrete Structure) is deployed outside the LNG tank and the inside of the PC dike is combined with the conventional metal double shell type LNG tank appears.

[0005] The PC dike in the technique includes concrete forming circular dike enclosing the LNG tank and PC steel stranded wire embedded in the concrete. Prestress is provided to the PC dike by tensioning the concrete along circumferential direction using the PC steel stranded wire. If LNG outflows from the LNG tank inside the PC dike, although tensile stress is applied to the PC dike along the circumferential direction thereof by the fluid pressure of the outflowing LNG, the prestress provided to the PC dike relieves the tensile strength.

[Prior Art Document]

30 [Patent Document]

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[0006] [Patent Document 1] Japanese Unexamined Patent Application, First Publication No. 2006-234137

[Disclosure of the Invention]

[Problems to be Solved by the Invention]

[0007] On the other hand, the PC dike is continuously in a low-temperature state since heat is drawn by the LNG in the LNG tank. In addition, if outflow of LNG occurs as described above, LNG having temperature of -162°C or lower contacts with the concrete, and thus, the temperature around the PC steel stranded wire reinforcing the PC dike at the inner portion of the concrete may be greatly reduced. If low-temperature elongation and low-temperature toughness of the PC steel stranded wire are not sufficiently high, the PC steel stranded wire may break and the PC dike may fracture. Therefore, a wire rod which has better low-temperature elongation and better low-temperature toughness than the conventional wire rod for the PC steel stranded wire is needed. An object of the present invention is to provide a wire rod which has more excellent low-temperature elongation and more excellent low-temperature toughness than the conventional wire rod for the PC steel stranded wire in order to meet the needs of the markets.

[Means for solving the Problem]

[0008] The inventors performed factual survey of use environment of the PC dike in order to enhance the tension providing effect in the PC dike constructing the PC type LNG tank (LNG tank including PC dike). As a result, in the actual use environment, it was found that there were cases in which the wire rod was exposed to an environmental temperature of about -40°C by heat transfer to the LNG in the LNG tank.

**[0009]** Therefore, various examinations with regard to a method for obtaining a wire rod having higher low-temperature elongation and higher low-temperature toughness as compared with the conventional PC steel stranded wire was performed. Specifically, in order to consider about the low-temperature elongation at first, a tensile test piece having especial shape shown in Figure 3 was manufactured from the wire rod and tensile test was performed with the tensile test piece. In addition, in order to consider about the low-temperature toughness, a 5mm subsize charpy impact test piece defined

in JIS Z 2202 was manufactured from the wire rod and 2mm U-notch test was performed to the test piece to examine a relationship between the aspect of fracture surface and the charpy absorbed energy obtained by the test. As a result of the tests, it was found that the average grain size of pearlite block of the wire rod and a number density of coarse pearlite block affected to the low-temperature elongation at -40°C and fracture facet, which improve the low-temperature elongation and the low-temperature toughness.

**[0010]** Moreover, it was found that it was possible to provide the wire rod which had more excellent low-temperature elongation and more excellent low-temperature toughness as compared with the conventional wire rod for the PC steel stranded wire rod based on the above-described findings.

[0011] That is, the gist of the present invention of which the object is to solve the above-described problems is as follows.
[0012]

- (1) In a wire rod according to one embodiment of the present invention, a chemical composition includes, in terms of mass%: C :0.60 to 1.20%; Si:0.30 to 1.30%; Mn:0.30 to 0.90%; P :0.020% or less; S :0.020% or less; N :0.0025 to 0.0060%; Cr:0 to 1.00%; V :0 to 0.800%; one or more selected from the group consisting of A1:0.005 to 0.100%, Ti:0.003 to 0.050%, and B :0.0005 to 0.0040%; and remainder including Fe and impurity, wherein an average value of a grain size of a pearlite block in a cross section perpendicular to a wire rod axial direction is 23  $\mu$ m or less, and wherein a number density of the pearlite blocks having  $40\mu$ m or more of the grain size in the cross section perpendicular to the wire rod axial direction is 0 to 20 pieces/mm².
- (2) In the wire rod according to (1), the chemical composition may include one or more selected from the group consisting of, in terms of mass%:Cr: 0.10 to 1.00%, and V: 0.005 to 0.800%.
- (3) In the wire rod according to (1), the chemical composition may include, in terms of mass%: C: 0.70 to 0.90%; Si: 0.80 to 1.30%; Mn: 0.60 to 0.90%; and V: 0 to 0.500%.
- (4) In the wire rod according to (3), the chemical composition may include one or more selected from the group consisting of, in terms of mass%: Cr: 0.50 to 1.00%, and V: 0.300 to 0.500%.
- (5) A method for manufacturing the wire rod according to the other embodiment of the present invention, comprising: heating a steel piece having the chemical composition according to claim 3 or 4 to a rough-rolling temperature of 950 to 1040°C and rough-rolling; finish-wire-rolling at a finish-rolling temperature of 750 to 950°C; then, coiling at a coiling temperature of 730 to 840°C; and thereafter, air blast cooling to a normal temperature with a cooling rate of 15°C/sec or more, wherein the finish-rolling temperature and a strain rate in the finish-wire-rolling satisfy an expression A.

$$13.7 \le \log_{10} \{ (d\epsilon / dt) \times \exp(63800 / (1.98 \times (T + 273.15)) \} \le$$

## 16.5 : expression A,

and wherein  $d\epsilon$  / dt expresses the strain rate in the finish-wire-rolling in terms of s<sup>-1</sup> and T expresses the finish-rolling temperature in terms of °C.

40 [Advantageous Effects of Invention]

**[0013]** According to the above-described embodiments of the present invention, a wire rod for PC steel stranded wire which is favorable to usage as tendon of PC dike of PC-type LNG tank and which has more excellent elongation and toughness at about -40°C as compared with the conventional material can be provided by reducing the grain size of pearlite block and limiting the number density of coarse pearlite block.

[Brief Description of Drawings]

## [0014]

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Figure 1 is a graph indicating a relationship between an average grain size of pearlite block of the wire rod and reduction of area of the wire rod.

Figure 2 is a graph indicating a relationship between Z value in manufacturing the wire rod and the grain size of the pearlite block of the wire rod.

Figure 3 indicates a shape of low temperature tensile test piece.

Figure 4 indicates a collection position of 5mm subsize charpy impact test piece defined in JIS Z 2202.

Figure 5A indicates a grain size of the pearlite block of the example manufactured with a stelmor method.

Figure 5B indicates the grain size of the pearlite block of the comparative example.

Figure 6 indicates elongation of an example (No. 6) and a comparative example (No. 17) at -40°C.

Figure 7A indicates a grain size of the pearlite block of the example manufactured with DLP method.

Figure 7B indicates a grain size of the pearlite block of the comparative example.

Figure 8 indicates a relationship between pearlite block size ( $\mu$ m) and an absorbed energy (Charpy impact value) (J). Figure 9A is a photograph indicating an observation result of a fracture surface of the impact test piece of the example with SEM.

Figure 9B is a photograph indicating an observation result of a fracture surface of the impact test piece of the comparative example with SEM.

Figure 10 is a flow chart indicating an example of a method for manufacturing the wire rod with a stelmor method.

[Description of Embodiments]

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[0015] In a wire rod for PC steel stranded wire according to the present embodiment (hereinafter "a wire rod according to the present embodiment") having excellent low-temperature elongation and low-temperature toughness, a chemical composition includes, in terms of mass%: C :0.60 to 1.20%; Si:0.30 to 1.30%; Mn:0.30 to 0.90%; P :0.020% or less; S :0.020% or less; N :0.0025 to 0.0060%; Cr:0 to 1.00%; V :0 to 0.800%; one or more selected from the group consisting of A1:0.005 to 0.100%, Ti:0.003 to 0.050%, and B :0.0005 to 0.0040%; and remainder including Fe and impurity, wherein an average value of a grain size of a pearlite block is  $23\mu m$  or less in a cross section perpendicular to a wire rod axial direction, and wherein the number density of the pearlite block having  $40\mu m$  or more of the grain size is 0 to 20 pieces/mm² in the cross section perpendicular to the wire rod axial direction.

**[0016]** At first, a reason for limiting the chemical composition of the wire rod according to the present embodiment will be described. Hereinafter, "%" expresses "mass%".

(C: 0.60 to 1.20%)

**[0017]** C is an element having an effect of increasing a cementite ratio in the wire rod to increase strength of the wire rod. A lamellar spacing of the pearlite can be controlled by adjusting a patenting condition, and the strength of the wire rod can be increased by working. On the other hand, if an amount of C is less than 0.60%, a strength which can sufficiently tension a PC dike of a PC-type LNG tank cannot be obtained even if the above-described adjusting the patenting condition is performed.

**[0018]** If the amount of C in the wire rod is more than 1.20%, a mesh-shaped cementite forms in a structure in the wire rod. The mesh-shaped cementite may frequently cause breaking during wire drawing and may interfere production activity of the wire rod.

**[0019]** As a method for manufacturing the wire rod according to the present embodiment, both of DLP (Direct in-Line Patenting) method and stelmor method can be employed as follows. If the wire rod is manufactured with the stelmor method, it is preferable that the amount of C be 0.70 to 0.90%. If the wire rod is manufactured with the stelmor method, a cooling rate of the wire rod is lower than that in the manufacturing with the DLP method, and thus, the elongation and the toughness of the wire rod is relatively low. In order to compensate for the decrease in the strength, it is preferable that the lower limit of the amount of C be 0.70%. In addition, if the amount of C excessively increases, a pro-eutectoid cementite forms in the mesh shape at a grain boundary of prior austenite during cooling the wire rod, since the wire rod becomes a hyper-eutectoid steel (a steel having a structure containing both of pearlite and cementite). The mesh-shaped pro-eutectoid cementite significantly deteriorates the drawability of the wire rod. In order to prevent the mesh-shaped pro - eutectoid cementite from forming, it is preferable that the upper limit of the amount of C be 0.90%. It is more preferable that the amount of C be 0.80 to 0.90%.

(Si: 0.30 to 1.30%)

**[0020]** Si is an element which acts as a deoxidizing element during refining. When 0.30% or more of Si is included, the deoxidizing effect is sufficiently expressed. Therefore, the lower limit of the amount of Si of the wire rod according to the present embodiment is 0.30%. Si also includes an effect for enhancing the strength of the wire rod. When 0.80% or more of Si is included, the effect of enhancing the strength is expressed. Therefore, the lower limit of the amount of Si of the wire rod according to the present embodiment may be 0.80%. In addition, although Si solid-solute strengthen ferrite, Si has an effect for rising a nose of isothermal transformation during heat treatment. Therefore, an excessive amount of Si increases cost for the heat treatment. Accordingly, in view of a capacity of the manufacturing equipments, the upper limit of the amount of Si is 1.30%.

**[0021]** As the method for manufacturing the wire rod according to the present embodiment, both of the DLP method and the stelmor method can be employed. If the wire rod is manufactured with the stelmor method, it is preferable that the amount of Si be 0.80 to 1.30%. If the wire rod is manufactured with the stelmor method, a cooling rate of the wire

rod is lower than that in the manufacturing with the DLP method, and thus, the elongation and the toughness of the wire rod is relatively low. In order to compensate the decreasing of the strength, it is preferable that the lower limit of the amount of Si be 0.80%. It is more preferable that the amount of Si be 0.90 to 1.25%.

(Mn: 0.30 to 0.90%)

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[0022] Mn is an solid-solute strengthening element and has an effect of enhancing elongation and toughness of the wire rod and an effect of enhancing hardenability. In order to secure elongation and toughness of the wire rod, it is necessary that 0.30% or more of Mn be included. In addition, in order to further enhance the elongation of the wire rod, the lower limit of the amount of Mn may be 0.60%. On the other hand, if the amount of Mn is higher than 0.90%, a delay of transformation occurs in a center portion of the wire rod to cause a formation of micro martensite at a portion of untransformed austenite during manufacturing the wire rod. The micro martensite at the center portion of the wire rod causes breaking during drawing of the wire rod. Therefore, it is necessary that the upper limit of the amount of Mn is 0.90%. [0023] As the method for manufacturing the wire rod according to the present embodiment, both of the DLP method and the stelmor method can be employed. If the wire rod is manufactured with the stelmor method, it is preferable that the amount of Mn be 0.60 to 0.90%. If the wire rod is manufactured with the stelmor method, the cooling rate of the wire rod is lower than that in the manufacturing with the DLP method, and thus, the elongation and the toughness of the wire rod is relatively low. In order to compensate the decreasing of the strength, it is preferable that the lower limit of the amount of Mn be 0.60%. It is more preferable that the amount of Mn be 0.70 to 0.90%.

(P: 0.020% or lower)

(S: 0.020% or lower)

[0024] P has an effect of embrittling the steel. Therefore, it is necessary that an upper limit an amount of P is 0.020%. When the wire rod is further securely prevented from low-temperature embrittlement, the upper limit of the amount of P may be 0.010%, 0.005%, or 0.001%.

**[0025]** S is an element which combines with Mn in the wire rod to form MnS. Since S segregates at a center portion of the steel during refining and solidifying the steel, MnS accumulates at the center portion of the steel. MnS deteriorates the low-temperature elongation of the steel. If an amount of S is more than 0.020%, the low-temperature elongation significantly deteriorates, and thus, the amount of S is 0.020% or lower. When the wire rod is further securely prevented from the low-temperature embrittlement, the upper limit of the amount of S may be 0.010%, 0.005%, or 0.001%.

[0026] In the wire rod according to the present embodiment, the lower the amount of P and the amount of S are, the better it is. Therefore, both of the lower limit of the amount of P and the lower limit of the amount of S is 0%.

(N: 0.0025 to 0.0060%)

[0027] N is an element which combines with AI, Ti, and B to form nitrides. The nitrides act as a nucleuses of precipitation of the austenite, and thus, the grain size of the austenite can be controlled during heating the steel by controlling the number of the nitrides. If the amount of the nitrides increase, the grain is refined. If the amount of N is less than 0.0025%, the nitrides do not sufficiently form and the effect of refining the grain size cannot be sufficiently obtained. On the other hand, If the amount of N is more than 0.0060%, free N, which does not combine with AI, Ti, and B, become excess. The excess amount of free N causes age hardening to deteriorate the elongation and the toughness of the wire rod. Therefore, it is necessary that the amount of N be 0.0025 to 0.0060%. It is preferable that the amount of N be 0.0025 to 0.0040%. [0028] In addition to the above-described elements, the wire rod according to the present embodiment further includes one or more selected from the group consisting of AI: 0.005 to 0.100%, Ti: 0.003 to 0.050%, and B: 0.0005 to 0.0040%.

(AI: 0.005 to 0.100%)

**[0029]** All acts as a deoxidizing agent during refining the steel. In addition, since All forms composition with N in the steel, All has an effect of fixing N. Due to fixing N, the steel can be prevented from age hardening. Furthermore, when B is included together with Al, due to fixing N, the amount of solute B can be increased.

**[0030]** However, if an amount of Al is less than 0.005%, the effect of fixing N by Al cannot be sufficiently obtained. On the other hand, if the amount of Al is more than 0.100%,  $Al_2O_3$ , which is formed by Al combining with oxygen in the steel, forms clusters. The clusters act as origins of cracking during drawing. Therefore, the amount of Al may be 0.005 to 0.100%. It is preferable that the amount of Al be 0.020 to 0.050%.

(Ti: 0.003 to 0.050%)

**[0031]** Ti acts as the deoxidizing agent of the steel, similar to Al. In addition, since Ti forms chemical compound with N in the steel, Ti has an effect of fixing N. Due to fixing N, the steel can be prevented from age hardening. Furthermore, when B is included together with Ti, due to fixing N, the amount of solute B can be increased.

**[0032]** However, if the amount of Ti is less than 0.003%, the effect of fixing N by Ti cannot be sufficiently obtained. On the other hand, if the amount of Ti is more than 0.050%, TiC, which is formed by Ti combining with carbon in the steel, increase. TiC act as an origins of cracking during drawing. Therefore, the amount of Ti may be 0.003 to 0.050%. It is preferable that the amount of Ti be 0.020 to 0.040%.

[0033] As described above, Al and Ti have similar effects. Therefore, the amount of Al can be decreased by including Ti. In this case, a similar effect can be obtained.

(B: 0.0005 to 0.0040%)

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- **[0034]** When B exists as the solute B in the austenite, B has an effect of enhancing the hardenability of the wire rod. If the amount of B is less than 0.0005%, the effect of enhancing the hardenability cannot be sufficiently obtained. On the other hand, if the amount of B is more than 0.0040%, B forms chemical compound with Fe and C to form a precipitates such as Fe<sub>23</sub> (C, B)<sub>6</sub>, and the like. The precipitates act as the origins of cracking during drawing. Therefore, the amount of B may be 0.0005 to 0.0040%. It is preferable that the amount of B be 0.0009% to 0.0030%.
- [0035] In addition to the above-described elements, the wire rod according to the present embodiment may further include, in terms of mass%, Cr: 0 to 1.00% or V: 0 to 0.800%.

(Cr: 0 to 1.00%)

- [0036] In the wire rod according to the present embodiment, it is not necessary to include Cr. Therefore, a lower limit of an amount of Cr is 0%. However, Cr has an effect of reducing lamellar spacing of the pearlite to enhance the strength of the wire rod. Due to the effect, the degree of increasing of the strength of the wire rod during drawing is enhanced. The effect is obtained in a case in which the amount of Cr is 0.10% or more, and thus, it is preferable that the amount of Cr be 0.10% or more. In addition, when the strength is further enhanced, it is preferable that 0.50% or more of Cr be included. If the amount of Cr is more than 1.00%, a termination time of pearlite transformation becomes long, and thus, a supercooled structure forms during cooling the wire rod to deteriorate the elongation of the wire rod. Therefore, it is preferable that an upper limit of the amount of Cr be 1.00%.
  - **[0037]** As the method for manufacturing the wire rod according to the present embodiment, both of the DLP method and the stelmor method can be employed. If the wire rod is manufactured with the stelmor method, it is more preferable that the amount of Cr be 0.50 to 1.00%. If the wire rod is manufactured with the stelmor method, the cooling rate of the wire rod is lower than that in the manufacturing with the DLP method, and thus, the elongation and the toughness of the wire rod is relatively low. In order to compensate the decreasing of the strength, it is more preferable that the lower limit of the amount of Cr be 0.50%. It is further preferable that the amount of Cr be 0.50 to 0.90%.
- 40 (V: 0 to 0.800%)
  - [0038] In the wire rod according to the present embodiment, it is not necessary to include V. Therefore, a lower limit of an amount of V is 0%. However, V is an element which combines with C to precipitate as carbide in ferrite. Due to the precipitation of the carbide, the ferrite can be hardened and the wire rod can be high-strengthened. The effect can be obtained if 0.005% or more of V is included. However, if the amount of V is more than 0.800%, a coarse carbides precipitate. The coarse carbides act as the origins of cracking in working the wire rod. Therefore, it is preferable that the amount of V be 0.005 to 0.800%.
  - [0039] As the method for manufacturing the wire rod according to the present embodiment, both of the DLP method and the stelmor method can be employed. If the wire rod is manufactured with the stelmor method, it is more preferable that the amount of V be 0.300 to 0.500%. If the wire rod is manufactured with the stelmor method, the cooling rate of the wire rod is lower than that in the manufacturing with the DLP method, and thus, the elongation and the toughness of the wire rod is relatively low. In order to compensate the decreasing of the strength, it is more preferable that the lower limit of the amount of V be 0.300%. In addition, since micro cracks form at boundary portions of VC precipitates and base iron when a processing strain occurs, it is more preferable that an upper limit of the amount of V be 0.500%. It is further preferable that the amount of V be 0.300 to 0.400%.

(remainder: Fe and impurity)

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**[0040]** Remainder of the wire rod according to the present embodiment includes Fe and impurity. The impurity is a component which is incorporated by raw materials such as mineral or scrap or various factors of 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.

(The average value of the grain size of a pearlite block in a cross section perpendicular to a wire rod axial direction: 23µm or less.)

[0041] In the present embodiment, a pearlite block boundary is defined as a boundary of adjacent two pearlites between which a difference in crystal orientation is  $9^{\circ}$  or higher, a pearlite block is defined as an area surrounded by the pearlite block boundary, and PBS (Pearlite Block Size) is defined as an equivalent circle diameter of the pearlite block. In the wire rod according to the present embodiment, in addition to the above-described definition of the chemical composition, an average PBS (Pearlite Block Size) in a cross section perpendicular to a wire rod axial direction is defined to  $23\mu m$  or less.

[0042] If the average PBS (Pearlite Block Size) is more than  $23\mu m$ , a reduction of area of the wire rod deteriorates. It is necessary that the wire rod according to the present embodiment has 30% or more of the reduction of area. In view of the past production result, it was found that 30% or more of the reduction of area was necessary to prevent breaking from causing during drawing in the drawing working of the wire rod. As a result of the inventor's consideration, it was found that there was a relationship indicated by a graph of Figure 1 between the average pearlite block size and the reduction of area. Figure 1 indicates that 30% or more of the reduction of area can be obtained when the average PBS (Pearlite Block Size) is  $23\mu m$  or less. In addition, when the average PBS (Pearlite Block Size) is more than  $23\mu m$ , frequency of branching of the crack end decreases. Since a branch of the crack end has an effect of suppressing crack propagation, decreasing the frequency of branching of the crack end enlarges a fracture facet to deteriorate the low-temperature elongation and the low-temperature toughness. Therefore, the average PBS (Pearlite Block Size) is  $23\mu m$  or less. It is preferable that the average pearlite block size be  $18\mu m$  or less.

[0043] The average value of the equivalent circle diameter of the pearlite block in any size of field of view at any position of the cross section perpendicular to the wire rod axial direction can be obtained by using EBSD device. The average PBS in the cross section perpendicular to the wire rod axial direction according to the present embodiment can be obtained by the following procedures. At first, average values (primary average values) of equivalent circle diameters of pearlite blocks in  $300\mu m \times 180\mu m$  of fields of view in each of five area consisting of

- (1) a surface part (an area of which a depth from a surface of the wire rod is  $30\mu m$ ),
- (2) a 1/4D part (an area of which a depth from the surface of the wire rod is 1/4 of a diameter D of the wire rod),
- (3) a center part,
- (4) a 3/4D part (an area of which a depth from the surface of the wire rod is 3/4 of a diameter D of the wire rod, i.e. an area opposite to the (2) with respect to the center part of the wire rod), and
- (5) an opposite surface part (i.e. an area opposite to the (1) with respect to the center part of the wire rod),

are measured by using the EBSD device. Then, the average value (secondary average value) of the each primary average values is calculated. The secondary average value is the average PBS in the cross section perpendicular to the wire rod axial direction according to the present embodiment.

 $^{45}$  (The number density of the pearlite block having  $40\mu m$  or more of grain size in the cross section perpendicular to the wire rod axial direction is 0 to 20 pieces/mm<sup>2</sup>.)

[0044] In the wire rod according to the present embodiment, in addition to the above-described definition of the chemical composition and the average value of the grain size of the pearlite block, the number density of the pearlite block having a grain size of  $40\mu m$  or more in the cross section perpendicular to the wire rod axial direction is defined to 0 to 20 pieces/mm<sup>2</sup>.

[0045] Since the pearlite blocks having  $40\mu m$  or more of grain size act as fracture origins, the pearlite blocks having  $40\mu m$  or more of grain size deteriorate the elongation and the toughness of the wire rod even if the number of the pearlite blocks having  $40\mu m$  or more of grain size is small. In addition to controlling the average value of the grain size of the pearlite block, in the wire rod according to the present embodiment, it is necessary that a coarse pearlite block is prevented from forming. For these reasons, the number density of the coarse pearlite blocks is limited. Hereinafter, "pearlite block having a grain size of  $40\mu m$  or more" may be referred to as "coarse pearlite block" or "coarse PB".

[0046] If the number density of the coarse pearlite blocks in the cross section perpendicular to the wire rod axial

direction is more than 20 pieces/mm², the elongation and the toughness of the wire rod do not satisfy required levels. Therefore, it is necessary that the number density of the coarse pearlite blocks in the cross section perpendicular to the wire rod axial direction is limited to 0 to 20 pieces/mm². It is preferable that an upper limit of the number density of the coarse pearlite blocks in the cross section perpendicular to the wire rod axial direction be 18 pieces/mm². The less the amount of the coarse pearlite blocks are, the more preferable it is, and therefore, the lower limit of the number density of the coarse pearlite blocks in the cross section perpendicular to the wire rod axial direction is 0 pieces/mm².

[0047] The number density of the pearlite blocks having a grain size of  $40\mu m$  or more in any size of field of view at any position of the cross section perpendicular to the wire rod axial direction can be obtained by using EBSD device. The number density of the pearlite blocks having  $40\mu m$  or more of grain size in the cross section perpendicular to the wire rod axial direction according to the present embodiment can be obtained by the following procedures. At first, the number densities of the pearlite blocks having a grain size of  $40\mu m$  or more in  $300\mu m \times 180\mu m$  of fields of view in each of five areas of

- (1) a surface part (an area of which a depth from a surface of the wire rod is 30μm),
- (2) a 1/4D part (an area of which a depth from the surface of the wire rod is 1/4 of a diameter D of the wire rod),
- (3) a center part,

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- (4) a 3/4D part (an area of which a depth from the surface of the wire rod is 3/4 of a diameter D of the wire rod, i.e. an area opposite to the (2) with respect to the center part of the wire rod), and
- (5) an opposite surface part (i.e. an area opposite to the (1) with respect to the center part of the wire rod),

are measured by using the EBSD device. Then, the average value of the number densities in each areas is calculated. The average value is the number density of the pearlite block having a grain size of  $40\mu m$  or more in the cross section perpendicular to the wire rod axial direction according to the present embodiment.

[0048] Then, a method for manufacturing the wire rod according to the present embodiment will be described.

**[0049]** There are DLP method and stelmor method as the method for manufacturing the wire rod according to the present embodiment.

**[0050]** When the wire rod according to the present embodiment is manufactured by the stelmor method, as shown in Figure 10, (1) heating a steel piece having a chemical composition including, in terms of mass%, C: 0.70 to 0.90%; Si: 0.80 to 1.30%; Mn: 0.60 to 0.90%; P: 0.020% or less; S: 0.020% or less; N: 0.0025 to 0.0060%; Cr: 0 to 1.00%; V: 0 to 0.500%; one or more selected from the group consisting of Al: 0.005 to 0.100%, Ti: 0.003 to 0.050%, and B: 0.0005 to 0.0040%; and remainder including Fe and impurity to a rough-rolling temperature of 950 to 1040°C and then rough-rolling, (2) finish-wire-rolling at a finish-rolling temperature of 750 to 950°C, (3) coiling at a coiling temperature of 730 to 840°C, and (4) air blast cooling to a normal temperature with a cooling rate of 15°C/sec or more are performed. In this case, it is necessary that the finish-rolling temperature and a strain rate satisfy a relation of following expression 1.

$$13.7 \le \log_{10} \{ (d\epsilon / dt) \times \exp(63800 / (1.98 \times (T + 273.15))) \} \le$$

## 16.5 : expression 1

[0051]  $d\epsilon$  / dt expresses the strain rate during the finish-wire-rolling in terms of s<sup>-1</sup> and T expresses the finish-rolling temperature in terms of °C.

**[0052]** When manufacturing with stelmor method is performed, the steel piece may further include, in terms of mass%, one or more selected from the group consisting of Cr. 0.50 to 1.00%, and V: 0.300 to 0.500%.

(The chemical composition of a steel piece used for rough-rolling: within defined range as described above.)

**[0053]** When the wire rod according to the present embodiment is manufactured by the stelmor method, it is necessary that the chemical composition of a steel piece used for rough-rolling is within defined range as described above. The defined range is narrower than the above-described defined range of the chemical composition of the wire rod according to the present embodiment. The stelmor method is a manufacturing method in which air blast cooling is performed after coiling, and the cooling rate by the air blast cooling is lower than a cooling rate of a direct heat treatment by a molten salt in a DLP method described below. When the cooling rate is low, the elongation and the toughness of the wire rod finally obtained are relatively low.

[0054] Therefore, in a case in which the wire rod according to the present embodiment is manufactured by the stelmor method, it is necessary that the amount of C, Mn, and Si which are alloy elements for enhancing the elongation and the toughness are more than that in a case of performing the direct heat treatment by the molten salt in the DLP method. In addition, in a case in which Ca and V are included in order to enhance the property of the wire rod when the wire rod

according to the present embodiment is manufactured with stelmor method, it is preferable that the amount of Cr and V be also more than that in the case of performing the direct heat treatment by the molten salt in the DLP method.

(heating temperature of the steel piece before rough-rolling)

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[0055] In the method for manufacturing the wire rod according to the present embodiment with stelmor method, a heating temperature of the steel piece before the rough-rolling (rough-rolling temperature) is 950 to 1040°C. If the heating temperature of the steel piece before rough-rolling is lower than 950°C, roll reaction forth in wire rod rolling may rapidly increase to cause trouble of the equipment such as cracking of roll. Therefore, the heating temperature of the steel piece before the rough-rolling is 950°C or more. On the other hand, if the heating temperature of the steel piece before the rough-rolling is more than 1040°C, solutionizing of aluminum nitride (AIN) precipitated in the steel piece progresses excessively. As described above, AIN act as the nucleuses of precipitation of the austenite to contribute to refine the grain size of the austenite. The grain size of the pearlite of the wire rod finally obtained can be refined by refining the grain size of the austenite of the wire rod during manufacturing stage. However, if the solutionizing of AIN progresses excessively, coarsening the grain size of the austenite progresses. In this case, PBS of the wire rod is coarsened after manufacturing the wire rod. In this case, the average value of the grain size of the pearlite block in the cross section perpendicular to the wire rod axial direction becomes more than 23 $\mu$ m, and/or the number density of the pearlite block having 40 $\mu$ m or more of the grain size becomes more than 20 pieces/mm². In order to avoid such phenomenon from causing, the heating temperature of the steel piece before the rough-rolling is 1040°C or lower.

(a temperature in finish-wire-rolling: 750 to 950°C)

[0056] In the method for manufacturing the wire rod according to the present embodiment with stelmor method, finish-wire-rolling is performed at a temperature range of 750 to 950°C. If the temperature in the finish-wire-rolling (finish-rolling temperature) is less than 750°C, roll reaction forth during rolling may increase to cause trouble of the equipment such as cracking of roll, and thus, the temperature in the finish-wire-rolling is 750°C or more. On the other hand, if the temperature during the finish-wire-rolling is more than 900°C, the grain size of the austenite coarsens. In this case, the average value of the grain size of the pearlite block in the cross section perpendicular to the wire rod axial direction becomes more than  $23\mu m$ , and/or the number density of the pearlite blocks having  $40\mu m$  or more of the grain size becomes more than 20 pieces/mm². The elongation of the wire rod is deteriorated by coarsening the pearlite block. In order to avoid such phenomenon, the temperature during the finish-wire-rolling is 900°C or lower.

[0057] (relation between the finish-rolling temperature and a strain rate in the finish-wire-rolling:  $13.7 \le \log_{10} Z \le 16.5$ ) [0058] In addition, in the method for manufacturing the wire rod according to the present embodiment with stelmor method, it is necessary that a relation between the finish-rolling temperature and a strain rate in the finish-wire-rolling is defined. Specifically, it is necessary that common logarithm ( $\log_{10} Z$ ) of Z value (Zener-Hollomon parameter) is 13.7 to 16.5, in which the Z value is obtained by substituting a strain rate of the wire rod at the finish-wire-rolling  $d_{\rm E}$  / dt, an activation energy of plastic deformation of the wire rod Q, and the finish-rolling temperature at the finish-wire-rolling T into the following expression 2 which indicates Zener-Hollomon expression.

$$Z = (d\epsilon / dt) \times exp(Q/RT)$$
 (expression 2)

[0059] " $d\epsilon$  / dt" expresses the strain rate in terms of s<sup>-1</sup>. "R" is gas constant and the value thereof is 1.98 cal/mol·deg. "T" expresses the finish-rolling temperature in terms of K. If the term of the finish-rolling temperature is °C, it is necessary that "T" in the expression 2 is replaced by "(T + 273.15)". "Q" expresses the activation energy of the plastic deformation of the wire rod. It is assumed that the activation energy of the plastic deformation of the wire rod according to the present embodiment having the above-described chemical composition is 63800 cal/mol.

**[0060]** In the method for manufacturing according to the present embodiment, the strain rate of the wire rod at the finish-wire-rolling  $d\epsilon$  / dt can be obtained by the following expression.

$$d\varepsilon / dt = \varepsilon \times 2 \times \pi \times (N/60) \times L_d (expression 3)$$

$$\varepsilon = \ln (h2/h1)$$
 (expression 4)

 $L_d = (r / \Delta h)^{1/2}$  (expression 5)

 $\Delta h = h1 - h2$  (expression 6)

[0061] "¿" is an amount of strain during the finish-wire-rolling and is a dimensionless parameter. "h1" is a diameter of the wire rod before the finish-wire-rolling in terms of mm, and "h2" is a diameter of the wire rod after the finish-wire-rolling in terms of mm. "N" is a number of revolution of a roll performing the finish-wire-rolling in terms of rpm. "L<sub>d</sub>" is a projected roll contact length during the finish-wire-rolling in terms of mm. The projected roll contact length is the length of an area, at which the roll contacts with a rolled material (wire rod) during the rolling, along the rolling direction. "r" is a radius of the roll at the finish-wire-rolling in terms of mm. "Ah" is a rolling reduction during the finish-wire-rolling in terms of mm. As shown in expressions 3 to 6, the strain rate is a rolling condition depending on both of rolling speed and rolling reduction. [0062] As a result of the inventor's consideration, it was found that there was a relationship indicated in Figure 2 between the Z value at the finish-wire-rolling and the average pearlite block size of the wire rod finally obtained. As shown in Figure 2, in order to control the average pearlite block size in the cross section perpendicular to the wire rod axial direction to 23 µm or less, it is necessary that log 10 Z be 13.7 or more. In addition, in order to control the number density of the coarse pearlite blocks having 40 µm or more of grain size to 0 to 20 pieces/mm<sup>2</sup>, as is the case with that, it is necessary that log 10 Z is 13.7 or more. On the other hand, in view of the equipment capacity, it is difficult to set log <sub>10</sub> Z to more than 16.5. As shown in the Zener-Hollomon expression, in order to increase Z value, it is necessary to decrease the rolling temperature and increase the strain rate. Therefore, in the method for manufacturing the wire rod according to the present embodiment with stelmor method, the upper limit of log 10 Z is 16.5. It is preferable that log 10 Z be 14.0 to 16.0. If log 10 Z is lower than above-described range, the average value of the grain size of the pearlite block in the cross section perpendicular to the wire rod axial direction becomes more than 23 µm, and/or the number density of the pearlite block having 40 µm or more of the grain size becomes more than 20 pieces/mm<sup>2</sup>.

[0063] The speed of the finish-wire-rolling (finish rolling speed) is not limited as long as  $\log_{10}$  Z is within the range of 13.7 to 16.5. It is preferable that, if a wire rod having a diameter of 12mm or more is manufactured, the speed of the finish-wire-rolling be 15.5 to 25.2 m/sec. If the speed of the finish-wire-rolling is less than 15.5 m/sec, the strain rate decreases. In this case, PBS may not be sufficiently reduced. Therefore, it is preferable that the speed of the finish-wire-rolling be 15.5 m/sec or more. On the other hand, if the speed of the finish-wire-rolling is more than 25.2 m/sec, exotherm during working may increase to coarsen the grain size of austenite. Also in this case, PBS cannot be refined. As shown in above-described expressions 3 to 6, when a wire rod of which the diameter is not 12 mm, it is necessary that the speed of the finish-wire-rolling is arbitrarily changed from the above-described range so that  $\log_{10}$  Z is within the range of 13.7 to 16.5.

(coiling temperature: 730 to 840°C)

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(air blast cooling rate after coiling: 15°C/sec or more)

[0064] In the method for manufacturing the wire rod according to the present embodiment with stelmor method, after the finish-wire-rolling, the wire rod is coiled at a temperature of 730 to 840°C, and then, air blast cooling is performed with a cooling rate of  $15^{\circ}$ C/sec or more. If the coiling temperature is lower than  $730^{\circ}$ C, the amount of scale decreases to deteriorate mechanical descalability, and thus, the coiling temperature is  $730^{\circ}$ C or more. If the coiling temperature is higher than  $840^{\circ}$ C, the grain size of the austenite increases. In this case, the grain size of the pearlite block of the wire rod finally obtained cannot be controlled to  $23\mu m$  or less, and/or the number density of the pearlite blocks having  $40\mu m$  or more of the grain size becomes more than 20 pieces/mm². Therefore, the coiling temperature is  $840^{\circ}$ C or lower. It is preferable that the coiling temperature be 750 to  $820^{\circ}$ C.

[0065] The wire rod after the coiling is cooled by air blast cooling to a normal temperature. The normal temperature basically indicates a temperature range of 5 to 35°C as defined in JIS Z 8703. In the case, if the cooling rate is lower than 15°C/sec (i.e. slow cooling), the grain size of austenite increases, and thus, the average value of the grain size of the pearlite block in the cross section perpendicular to the wire rod axial direction becomes more than  $23\mu m$ , and/or the number density of the pearlite block having  $40\mu m$  or more of the grain size becomes more than 20 pieces/mm². As a result, the elongation of the wire rod finally obtained deteriorates. Therefore, the cooling rate at the air blast cooling is  $15^{\circ}$ C/sec or more. It is preferable that the cooling rate at the air blast cooling be  $25^{\circ}$ C/sec or more. Although it is not necessary to define the upper limit of the cooling rate at the air blast cooling, in view of the equipment capacity, the upper limit is about  $50^{\circ}$ C/sec.

[0066] When the wire rod according to the present embodiment is manufactured by the DLP method, (1) heating a

steel piece having a chemical composition including, in terms of mass%, C: 0.60 to 1.20%; Si: 0.30 to 1.30%; Mn: 0.30 to 0.90%; P: 0.020% or less; S: 0.020% or less; N: 0.0025 to 0.0060%; Cr: 0 to 1.00%; V: 0 to 0.500%; one or more selected from the group consisting of Al: 0.005 to 0.100%, Ti: 0.003 to 0.050%, and B: 0.0005 to 0.0040%; and remainder including Fe and impurity to a temperature of 950 to 1040°C and wire rod rolling, (2) coiling at a temperature range of 750 to 800°C, and (3) direct heat treating with 500 to 600°C of a molten salt just after termination of the coiling are performed.

**[0067]** When the wire rod according to the present embodiment is manufactured with DLP method, the steel piece, which is raw material, may further include, in terms of mass%, one or more selected from the group consisting of Cr: 0.10 to 1.00%, and V: 0.005 to 0.800%.

(a chemical composition of a steel piece used for wire rod rolling: within defined range as described above)

**[0068]** When the wire rod according to the present embodiment is manufactured by the DLP method, it is necessary that a chemical composition of a steel piece used for wire rod rolling is within defined range as described above. The defined range is equal to the above-described defined range of the chemical composition of the wire rod according to the present embodiment. A method for manufacturing with DLP method has an advantage that a wire rod having excellent elongation and toughness can be obtained from a steel piece of which alloy elements for enhancing the elongation and the toughness is relatively low. However, direct heat treatment with molten salt is essential the for the method for manufacturing with the DLP method, and thus, in order to bring the method for manufacturing with the DLP method into operation, much more equipment is required than that with the stelmor method.

(heating temperature in wire rod rolling: 950 to 1040°C)

[0069] When the wire rod according to the present embodiment is manufactured by the DLP method, the heating temperature of the wire rod before wire rod rolling the steel piece is 950 to  $1040^{\circ}$ C. If the heating temperature is lower than 950°C, roll reaction forth during the wire rod rolling may considerably increase to cause troubles in equipments such as cracking of roll, and thus, the heating temperature before the wire rod rolling is  $950^{\circ}$ C or more. On the other hand, if the heating temperature before the wire rod rolling is higher than  $1040^{\circ}$ C, solutionizing of aluminum nitride (AIN) precipitated in the steel piece progresses, and thus, coarsening the grain size of the austenite progresses to coarsen the pearlite block size (PBS) of the wire rod finally obtained. In this case, the average value of the grain size of the pearlite block in the cross section perpendicular to the wire rod axial direction becomes more than  $23\mu m$ , and/or the number density of the pearlite blocks having  $40\mu m$  or more of the grain size becomes more than  $20 \text{ pieces/mm}^2$ . In order to avoid such phenomenon from causing, the heating temperature before the wire rod rolling is  $1040^{\circ}$ C or lower. It is preferable that the heating temperature before the wire rod rolling be 980 to  $1030^{\circ}$ C. The finish temperature at the wire rod rolling is not limited, and thus, a reasonable temperature can be arbitrarily selected.

(coiling temperature: 750 to 850°C)

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[0070] When the wire rod according to the present embodiment is manufactured by the DLP method, coiling temperature after the wire rod rolling is 750 to  $850^{\circ}$ C. If the coiling temperature is lower than  $750^{\circ}$ C, unevenness along longitudinal direction of the wire rod regarding tensile strength increases after isothermal transformation in the following isothermal transformation treating. Therefore, the coiling temperature is  $750^{\circ}$ C or higher. If the coiling temperature is higher than  $800^{\circ}$ C, the grain size of austenite increases. In this case, the grain size of the pearlite block of the wire rod finally obtained cannot be controlled to  $23\mu m$  or less and the number density of the pearlite block having  $40\mu m$  or more of the grain size cannot be controlled to be 20 pieces/mm² or less, and thus, the coiling temperature is  $800^{\circ}$ C or lower.

(method for isothermal transformation treating: direct heat treating)

(isothermal transformation treating temperature: 500 to 600°C)

[0071] When the wire rod according to the present embodiment is manufactured by the DLP method, immediately after coiling the wire rod, the wire rod is immersed into 500 to 600°C of molten salt to perform isothermal transformation treating. If the isothermal transformation treating temperature is lower than 500°C, many amount of non-pearlite structure forms at the surface part of the wire rod. In this case, unevenness of processing strain occurs at boundary between pearlite structure forming at internal part of the wire rod and the non-pearlite structure at the surface part, and the unevenness may cause breaking during wire drawing stage. Therefore, the isothermal transformation treating temperature is 500°C or higher. If the isothermal transformation treating temperature is higher than 600°C, operational problems such as increasing heat deformation of the equipment occurs, and thus, the isothermal transformation treating temper-

ature is 600°C or lower. In addition, it is necessary that the isothermal transformation treatment is performed with direct heat treatment (online heat treatment). If the direct heat treatment is not performed (i.e. the isothermal transformation treatment is performed with offline heat treatment), reheating included in the offline heat treatment causes growth of y grain. The phenomenon prevents the grain size of PBS of the wire rod from being controlled to 23µm or less.

[Examples]

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**[0072]** Hereinafter, examples of the present invention will be described. The conditions in manufacturing the examples are an example condition employed to confirm the operability and the effects of the present invention, so the present invention is not limited to the example condition. The present invention can employ various types of conditions as long as the conditions do not depart from the scope of the present invention and can achieve the object of the present invention.

(Example)

[0073] Hereinafter, examples by a method for manufacturing with stelmor method will be described.

[0074] At first, molten steel having chemical composition shown in Table 1-1 was continuously casted so as to be a cast bloom of  $300 \text{mm} \times 500 \text{mm}$ , and the cast bloom is rolled so as to be a steel billet of 122 mm square by blooming. Then, the steel billet was heated to a heating temperature shown in Table 1-2 and rolled under a condition shown in the Table 1-2 to obtain a wire rod of  $12 \text{mm} \phi$ . A radius of a roll in finish-wire-rolling was 75.5mm. No. S1 to S16 are examples which satisfy the condition according to the present invention and No. S 17 to S41 are comparative examples which do not satisfy the condition according to the present invention.

**[0075]** A tensile test pieces shown in Figure 3 were manufactured from the rolled wire rods. Tensile test was performed to the tensile test pieces at a low temperature atmosphere of -40°C while controlling the temperature using dry ice and alcohol to measure tensile strength and elongation at -40°C of the wire rod.

**[0076]** In addition, a charpy impact test pieces defined in JIS Z 2202 were extracted from the above-described wire rods in a manner of extracting shown in Figure 4 to manufacture 5mm subsize 2mm U-notch charpy impact test pieces. Charpy impact test at -40°C was performed to the charpy impact test pieces to obtain impact value of the wire rods at a temperature of -40°C, which was similar to actual using environment temperature of PC dike of PC-type LNG tank.

[0077] The average PBS (Pearlite Block Size) of the wire rod was obtained by the following procedures. At first, average values (primary average values) of an equivalent circle diameter of a pearlite block in  $300\mu\text{m} \times 180\mu\text{m}$  of fields of view in each of five area of

- (1) a surface part (an area of which a depth from a surface of the wire rod was 30μm),
- (2) a 1/4D part (an area of which a depth from the surface of the wire rod was 1/4 of a diameter D of the wire rod),
- (3) a center part,
- (4) a 3/4D part (an area of which a depth from the surface of the wire rod was 3/4 of a diameter D of the wire rod,
- i.e. an area opposite to the (2) with respect to the center part of the wire rod), and
- (5) an opposite surface part (i.e. an area opposite to the (1) with respect to the center part of the wire rod),
- were measured by using the EBSD device. Then, the average value (secondary average value) of the each primary average values was calculated. The secondary average value was assumed as the average PBS in the cross section perpendicular to the wire rod axial direction. During measuring with EBSD device, a boundary of adjacent two pearlites between which a difference in crystal orientation was 9° or higher was judged as a pearlite block boundary.
- [0078] The number density of the coarse pearlite blocks of the wire rod was obtained by the following procedures. At first, number densities of the pearlite block having  $40\mu m$  or more of grain size in  $300\mu m \times 180\mu m$  of fields of view in each of five area of
  - (1) a surface part (an area of which a depth from a surface of the wire rod was  $30\mu m$ ),
  - (2) a 1/4D part (an area of which a depth from the surface of the wire rod was 1/4 of a diameter D of the wire rod),
  - (3) a center part,
  - (4) a 3/4D part (an area of which a depth from the surface of the wire rod was 3/4 of a diameter D of the wire rod,
  - i.e. an area opposite to the (2) with respect to the center part of the wire rod), and
  - (5) an opposite surface part (i.e. an area opposite to the (1) with respect to the center part of the wire rod),
- were measured by using the EBSD device. Then, the average value of the each number densities was calculated. The average value was assumed as the number density of the pearlite blocks having 40μm or more of grain size in the cross section perpendicular to the wire rod axial direction.

[Table 1-1]

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	С	Si	Mn	Р	S	Al	Ti	В	N	Cr	V
S1	0.70	0.80	0.76	0.017	0.010	0.020	0.038	0.0024	0.0031	0.50	-
S2	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-
S3	0.88	0.90	0.72	0.008	0.006	-	0.048	-	0.0047	-	-
S4	0.88	1.00	0.73	0.006	0.009	0.025	0.005	0.0035	0.0041	0.50	0.320
S5	0.90	0.90	0.80	0.009	0.007	0.042	0.010	0.0019	0.0060	0.50	0.310
S6	0.85	0.85	0.90	0.010	0.010	0.032	-	0.0020	0.0045	-	0.400
S7	0.90	0.85	0.72	0.012	0.000	0.033	0.025	0.0040	0.0035	0.60	-
S8	0.87	1.30	0.70	0.015	0.005	0.040	0.035	0.0036	0.0025	-	-
S9	0.87	0.95	0.71	0.015	0.006	0.060	-	0.0028	0.0036	-	-
S10	0.87	0.96	0.74	0.011	0.009	0.060	-	-	0.0025	-	0.500
S11	0.87	0.98	0.75	0.020	0.007	-	0.015	0.0030	0.0042	0.66	-
S12	0.90	1.30	0.60	0.016	0.009	0.005	0.011	0.0029	0.0036	0.56	-
S13	0.90	0.82	0.70	0.009	0.008	0.035	0.005	-	0.0039	-	-
S14	0.90	0.82	0.70	0.009	0.008	-	-	0.0035	-	-	-
S15	0.90	0.85	0.74	0.007	0.010	0.028	0.023	0.0033	0.0029	0.80	0.400
S16	0.90	0.85	0.74	0.007	0.010	0.028	0.023	0.0033	0.0029	0.80	0.400
S17	0.70	0.85	0.35	0.020	0.022	0.005	-	-	-	-	-
S18	0.82	0.75	0.81	0.022	0.019	0.030	-	-	-	-	-
S19	0.50	0.80	0.76	0.017	0.010	0.020	0.038	0.0024	0.0031	0.50	-
S20	1.03	0.85	0.74	0.007	0.010	0.028	0.023	0.0033	0.0029	0.80	0.400
S21	0.92	0.91	0.75	0.035	0.023	0.033	ı	-	-	-	-
S22	0.82	1.38	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-
S23	0.82	0.85	<u>1.10</u>	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-
S24	0.82	0.85	0.30	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-
S25	0.82	0.85	0.72	0.042	0.010	0.060	0.040	0.0037	0.0036	1.00	-
S26	0.82	0.85	0.72	0.015	0.038	0.060	0.040	0.0037	0.0036	1.00	-
S27	0.82	0.85	0.72	0.015	0.010	<u>0.120</u>	0.040	0.0037	0.0036	1.00	-
S28	0.82	0.85	0.72	0.015	0.010	0.060	<u>0.120</u>	0.0037	0.0036	1.00	-
S29	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0055	0.0036	1.00	-
S30	0.82	0.85	0.72	0.015	0.010	0.001	0.040	0.0037	0.0036	1.00	-
S31	0.82	0.85	0.72	0.015	0.010	0.060	0.001	0.0037	0.0036	1.00	-
S32	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0002	0.0036	1.00	-
S33	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	<u>1.50</u>	-
S34	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	0.620
S35	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-
S36	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-

(continued)

					CHEM	ICAL CO	//POSITIO	N						
No						UNIT: ma	ıss%							
	С	Si	Mn	Р	S	Al	Ti	В	N	Cr	V			
S37	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	ı			
S38														
S39	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00				
S40	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00				
S41	0.82	0.85	0.72	0.015	0.010	0.060	0.040	0.0037	0.0036	1.00	-			
UNDE	RLINED	VALUE	IS OUT	OF RAN	GE OF P	RESENT	INVENTIO	NC						

5		REMARKS																									
10		COOLING RATE	°C/s	15	15	22	20	15	16	17	15	15	20	20	22	20	20	25	25	5	<u>10</u>	15	25	<u>12</u>	15	15	15
15		COILING TEMPERATURE	J.	730	750	730	780	790	800	062	785	800	062	790	795	730	730	830	830	880	850	730	800	006	750	750	750
20		log	104	16.5	15.8	16.5	15.8	15.8	15.2	14.7	15.2	15.2	15.2	15.8	15.8	16.5	16.5	14.7	14.7	13.2	13.6	16.3	14.5	12.8	15.8	15.8	15.8
25 30	[Table 1-2]	STRAIN RATE IN THE FINISH- WIRE-ROLLING	s-1	607	209	209	607	209	209	209	209	209	209	209	607	209	209	209	209	371	371	371	371	371	209	209	607
35 40		FINISH-ROLLING TEMPERATURE	J.	750	800	750	800	800	850	006	850	850	850	800	800	750	750	006	006	1050	1000	750	006	1100	800	800	800
<ul><li>45</li><li>50</li><li>55</li></ul>		HEATING TEMPERATURE BEFORE ROUGH-ROLLING	J <sub>o</sub>	026	920	096	026	086	086	1000	1000	1000	1020	1030	1030	1040	1040	1040	1040	1080	1080	920	1040	1100	026	096	950
		o Z		S1	S2	83	84	S5	98	22	88	88	S10	S11	S12	S13	S14	S15	S16	S17	S18	S19	S20	S21	S22	S23	S24

5		REMARKS							!	COMPARATIVE											
10		COOLING RATE	s/J。	15	15	15	15	15	15	15	15	15	15	15	15	15	15	7	15	15	
15		COILING TEMPERATURE	°C	750	750	750	750	750	750	750	750	750	750	750	750	750	068	750	750	750	
20		log	104	15.8	15.8	15.8	15.8	15.8	15.8	15.8	15.8	15.8	15.8	15.8	16.9	12.6	15.8	15.8	14.2	13.5	
25 30	(continued)	STRAIN RATE IN THE FINISH- WIRE-ROLLING	s-1	209	209	209	209	209	209	209	209	209	209	209	209	209	209	209	209	42	
35 40		FINISH-ROLLING TEMPERATURE	o.C	800	800	800	800	800	800	800	800	800	800	800	720	1150	800	800	096	006	UNDERLINED VALUE IS OUT OF RANGE OF PRESENT INVENTION FINAL DIAMETER: 12mm ACTIVATION ENERGY OF PLASTIC DEFORMATION: 63800cal/mol
45		PERATURE 3H-ROLLING		(										OI			(				OUT OF RANGE I OF PLASTIC DEF
50 55		HEATING TEMPERATURE BEFORE ROUGH-ROLLING	O.	026	950	096	096	096	950	096	026	096	096	1150	096	026	096	026	096	096	UNDERLINED VALUE IS FINAL DIAMETER: 12mm ACTIVATION ENERGY OI
		o <sub>N</sub>		S25	S26	S27	S28	S29	830	S31	S32	S33	S34	S35	836	S37	838	839	S40	S41	UNDE FINAL ACTIV.

[Table 2]

No	AVERAGE PBS	NUMBER DENSITY OF COARSE PB	TENSILE STRENGTH AT -40°C		CHARPY IMPACT VALUE AT -40°C	CHARPY IMPACT VALUE AT ROOM TEMPERATURE	REMARKS
	μm	CUARSE PD	MPa	%	J	J	Œ
S1	15	0	1201	17.0	16.1	24.5	
S2	18	2	1265	15.2	14.8	24.2	
S3	19	0	1295	16.2	15.1	23.2	
S4	18	3	1430	17.0	14.6	23.1	
S5	15	3	1450	13.3	13.9	23.0	
S6	16	12	1460	14.2	13.4	22.0	
<b>S7</b>	17	15	1410	15.1	13.2	21.9	
S8	15	12	1400	15.6	13.5	22.0	
S9	18	11	1410	15.5	14.9	21.7	щ
S10	20	6	1460	13.0	14.0	21.2	ΜΡΙ
S11	19	4	1400	14.3	13.4	21.6	EXAMPLE
S12	18	5	1490	12.5	13.2	21.0	Щ
S13	20	0	1390	15.6	13.1	20.7	
S14	20	0	1390	14.0	13.2	20.7	
S15	23	18	1420	13.0	13.0	20.5	
S16	23	18	1420	13.0	13.0	20.1	
S17	<u>33</u>	<u>142</u>	1255	9.9	8.9	5.3	
S18	<u>37</u>	<u>85</u>	1280	6.3	7.1	8.2	
S19	<u>25</u>	19	980	10.0	13.2	13.5	
S20	<u>29</u>	<u>22</u>	1530	8.0	2.9	3.6	
S21	<u>48</u>	<u>180</u>	1390	5.1	3.2	4.2	
S22	18	2	1298	8.0	5.0	5.8	
S23	18	2	1105	15.2	14.8	15.2	
S24	18	2	1390	4.5	4.2	5.6	
S25	18	2	1281	7.6	3.8	4.5	VE
S26	18	2	1265	5.6	8.2	9.3	ATT LE
S27	18	2	1235	7.0	9.0	9.5	MPARATIVE EXAMPLE
S28	18	2	1265	6.2	14.8	15.0	MP. XX
S29	18	2	1260	8.1	8.9	9.5	COI
S30	18	2	1235	7.0	4.3	5.2	
S31	18	2	1265	6.9	8.1	9.3	
S32	18	2	1260	8.1	8.9	9.0	
S33	18	2	1320	7.2	6.3	6.5	
S34	18	2	1336	9.5	4.3	4.8	
S35	<u>25</u>	<u>95</u>	1390	3.2	3.1	3.5	
S36	MILL LO	AD INCREASED	TO PREVENT	ROLLING FRO	M PERFORMING	_	
S37	<u>32</u>	<u>80</u>	1265	15.2	6.3	6.9	
S38	<u>27</u>	2	1265	8.0	11.0	11.3	
S39	18	<u>55</u>	1220	3.6	4.2	5.3	
S40	20	<u>75</u>	1270	8.0	7.2	7.5	
S41	<u>35</u>	<u>68</u>	1262	6.8	6.0	6.8	

UNDERLINED VALUE IS OUT OF RANGE OF PRESENT INVENTION

[0079] The heating temperature, the finishing temperature, and the coiling temperature of the examples were within the adequate temperature range. Therefore, the pearlite block of the example was refined and the average PBS and the number density of the coarse PB of the example were controlled in the adequate level. On the other hand, the average PBS and the number density of the coarse PB of the comparative examples of which the heating temperature, the finishing temperature, and/or the coiling temperature were higher than the adequate temperature range were out of range defined by the present invention. The examples demonstrated better property than the comparative examples in low-temperature strength, low-temperature toughness, and room-temperature toughness. In example S36, the finish-rolling temperature was lower than the adequate temperature range, and thus, mill load increased to prevent rolling from performing.

**[0080]** Figure 5A shows SEM picture of the pearlite block of the example and Figure 5B shows SEM picture of the pearlite block of the comparative example. It could be found from the SEM pictures that the grain size of the pearlite block of the example was smaller than the grain size of the pearlite block of the comparative example.

[0081] Figure 6 shows a result of tensile test at -40°C of the example (No. S6) and the comparative example (No. S17). It could be found that the elongation of the example was higher and better than the elongation of the comparative example in low-temperature atmosphere of -40°C. In addition, it could be found from Table 2 that the elongation of the example tended to be higher than the elongation of the comparative example. It was assumed that the difference in elongation was caused by the difference in the grain size of the pearlite block shown in Figure 5A and Figure 5B.

[0082] Next, examples by a method for manufacturing with DLP method will be described hereinafter.

[0083] At first, molten steel having chemical composition shown in Table 3 was continuously casted so as to be a cast bloom of  $300 \text{mm} \times 500 \text{mm}$ , and the cast bloom was rolled so as to be a steel billet of 122 mm square. Then, the steel billet was heated to a heating temperature shown in Table 3 and rolled, coiled and heat treated using molten salt under a condition shown in the Table 3 to obtain a wire rod of  $12 \text{mm} \phi$ . No. D1 to D16 and No. D30 to D36 were manufactured with a heat treatment (direct heat treatment) in which they were immersed into the molten salt without reheating after coiling. No. D17 to D29 were coiled under conditions shown in the Table 3, and then, subjected to a heat treatment (offline heat treatment) in which they were reheated to  $950^{\circ}\text{C}$  and subjected to lead patenting treatment.

**[0084]** Tensile strength at -40°C, elongation at -40°C, and impact value at -40°C of the above-described wire rods were obtained. The test methods for obtaining the values were same to each test methods performed to the above-described No. S1 to No. S41. In addition, charpy impact test at room temperature was performed to the above-described wire rods to obtain impact value of the wire rods at the room temperature. The method for performing the charpy impact test at the room temperature was same to the above-described method for performing the charpy impact test at -40°C except test temperature. The average PBS and the number density of the coarse pearlite blocks of the above-described wire rod were measured.

5		T C C C C C C C C C C C C C C C C C C C	KEMAKKO									EXAMPLE								
10		ONLINE HEAT	IREALMENI TEMPERATURE	J.	200	009	520	520	520	520	099	250	099	099	260	260	275	275	260	929
15		COILING TEM-	PERATURE	ပ့	750	750	780	780	790	800	790	785	800	790	790	795	800	800	790	800
20 25		HEATING TEM- PERATURE BE-	FORE WIRE ROD ROLLING	ပံ	950	026	096	970	086	086	1000	1000	1000	1020	1030	1030	1040	1040	1030	1040
	1]			>		0.120		0.320	0.210	0.030	1	1	1	0.120		ı	ı	0.010	-	0.010
30	[Table 3-1]			ပ်	ı	-		0.27	0.23		0.15	ı	ı		0.16	0.41	ı	0.48	0.16	0.48
	<u> </u>			z	0.0031	0.0036	0.0047	0.0041	0900'0	0.0045	0.0025	0.0035	0.0036	0.0025	0.0042	0.0036	0.0039	0.0029	0.0042	0.0029
35		N O		В	0.0024	0.0037	0.0039	0.0035		0.0020	0.0040	0.0036	0.0028	ı	0.0030	0.0029	1	0.0033	0.0030	0.0038
40		MPOSITION	%ss#	ï	0.038	0.040	0.048	0.005	0.010	0.018	ı	0.035	0.031			0.011	0.005	0.023	0.040	
		CHEMICAL COMPO	UNIT: mass%	A	0.020	090'0	0.030	0.025	0.042	0.032	0.033	ı	0.085	090.0	0.032	0.005	0.035	0.028	0.032	•
45		CHEMIC	٦	s	0.010	0.010	900.0	0.009	0.007	0.010	0.000	0.005	900.0	600.0	0.007	600.0	0.008	0.010	0.007	0.010
				Ь	0.017	0.015	0.008	900'0	600.0	0.010	0.012	0.015	0.015	0.011	0.013	0.016	600.0	0.020	0.013	0.020
50				Mn	92.0	0.72	0.72	0.73	0.80	06.0	0.72	0.70	0.71	0.74	0.75	0.40	0.38	0.35	0.75	0.35
				Si	08.0	98.0	06'0	1.00	06.0	98.0	98.0	1.30	96.0	96'0	96.0	1.00	0.82	0.85	86.0	98.0
55				ပ	09.0	0.82	0.88	0.88	06.0	0.92	0.92	0.95	0.95	0.98	0.98	0.98	1.00	1.18	0.98	1.00
			Š		7	D2	D3	D4	D5	90	D7	D8	60	D10	D11	D12	D13	D14	D15	016

5			REMARKS								COMPAKATIVE								REMARKS				
10		ONLINE HEAT	TREATMENT TEMPERATURE	<b>ွ</b>	200	200	520	260	565	250	250	563	270	570	570	575	280	ONLINE HEAT	TREATMENT TEMPERATURE	J.	200	520	420
15 20		COLING TEM-	PERATURE	ပွ	750	750	780	850	850	850	850	850	860	860	850	860	860		TEMPERATURE	J.	750	780	860
25		HEATING TEM- PERATURE BE-	FORE WIRE ROD ROLLING	ပ <del>ွ</del>	920	950	096	1080	1080	1100	1100	1120	1120	1130	1130	1130	1135	HEATING	BEFORE WIRE ROD ROLLING	J.	950	960	1135
	[Table 3-2]			>	-	0.120	-	-	0.520	-	-	-	-	0.100	-	0.250	0.330			^	0.120	-	0.250
30	[Tabl			Cr	-	-	-	0.22	-	-	0.32	0.61	0.41	0.32	-	-	-			JO	-	ı	ı
35				z	0.0031	0.0036	0.0047	0.0045	0.0040	-	0.0035	0.0045	0.0051	0.0023	0.0015	0.0037	0.0073			Z	0.0036	0.0047	0.0037
		NO NO		В	0.0024	0.0037	0.0039	-	-	-	0.0030	0.0025	-	-	0.0036	0.0054	-	NOI		В	0.0037	0.0039	0.0054
40		APOSIT	%ssı	F	0.038	0.040	0.048	0.110	0.160	-	0.060	0.210	0.340	0.110	0.035	0.190	0.230	APOSIT	%ssı	Τi	0.040	0.048	0.190
		AL CO	UNIT: mass%	₹	0.020	090.0	0.030	0.024	0.030	-	0.041	0.120	0.027	0.023	-	0.027	0.025	AL COI	UNIT: mass%	A	090.0	0.030	0.027
45		CHEMICAL COMPOSITION	ے	S	0.010	0.010	900.0	0.022	0.019	0.023	0.032	0.026	0.011	0.015	0.005	0.019	0.011	CHEMICAL COMPOSITION	n	S	0.010	900.0	0.019
				۵	0.017	0.015	0.008	0.020	0.022	0.035	0.018	0.023	0.032	0.025	0.015	0.027	0.019			Ь	0.015	0.008	0.027
50				Mn	92.0	0.72	0.72	0.35	0.81	0.75	0.73	0.25	09.0	0.45	0.70	0.85	62.0			Mn	0.72	0.72	0.85
				Si	08'0	0.32	0.63	0.85	0.75	0.91	0.92	98'0	88.0	1.31	1.30	1.20	96'0			Si	0.85	06.0	1.20
55				ပ	0.64	0.82	0.88	0.83	0.87	0.88	0.91	0.92	0.95	0.98	0.95	1.05	1.10			C	0.50	1.25	1.05
			<u>8</u>		D17	D18	D19	D20	D21	D22	D23	D24	D25	D26	D27	D28	D29		<sub>S</sub>		D30	D31	D32

5			REMARKS			COMPARATIVE					
10		ONLINE HEAT	TREATMENT TEMPERATURE	ပ <del>ွ</del>	450	520	520	520	250	250	
15 20		COILING	TEMPERATURE	٦°	<u>850</u>	780	735	880	062	785	
25		HEATING TEMPERATIIRE	BEFORE WIRE ROD ROLLING	<sup>သ</sup>	1130	1080	086	086	1000	1000	
	(continued)			>	-	-	0.210	0.210	-	-	
30	(conti			Ö	ı	1	0.23	0.23	0.15	-	
35				z	0.0015	0.0047	0900.0	0900'0	0.0025	9800'0	NC
		NOIL		В	0.0036	0.0039			0.0040	0.0036	UNDERLINED VALUE IS OUT OF RANGE OF PRESENT INVENTION
40		MPOSIT	ass%	F	0.035	0.048	0.010	0.010		0.035	ESENT
		CHEMICAL COMPOSI	UNIT: mass%	¥	ı	0.030	0.042	0.042	0.033	ı	OF PR
45		СНЕМІС	٦	S	0.005	0.006	200'0	0.007	0.000	0.005	RANGE
				Ф	0.015	0.008	600'0	600.0	0.012	0.015	OUT OF
50				Mn	0.70	0.72	08.0	08.0	0.72	0.20	UE IS (
				Si	1.30	06.0	06.0	06'0	0.24	1.30	ED VAL
55				ပ	0.95	0.88	06.0	06.0	0.92	0.95	ERLINE
			2		D33	D34	D35	D36	D37	D38	UNDE

5		REMARKS																	
10 15		CHARPY IMPACT VALUE AT ROOM TEMPERATURE	٦	25.0	24.0	23.9	23.4	23.0	23.0	22.5	21.0	22.0	22.0	21.5	21.0	20.3	20.0	21.0	20.0
20 25		CHARPY IMPACT VALUE AT -40°C	ſ	15.0	14.7	14.0	13.0	13.2	13.8	13.5	13.6	14.0	13.2	13.6	13.0	13.2	13.0	13.0	13.0
30	[Table 4-1]	ELONGATION AT -40°C	%	18.0	17.8	17.1	16.8	16.6	16.2	16.3	15.9	15.6	15.5	14.8	14.5	13.4	13.1	13.7	13.5
35		TENSILE STRENGTH AT -40°C	MPa	1201	1265	1295	1380	1390	1430	1410	1490	1460	1530	1540	1530	1540	1580	1530	1542
40		SITY OF PB																	
45		NUMBER DENSITY OF COARSE PB		0	0	0	0	0	0	0	0	0	0	0	0	20	18	0	0
50 55		AVERAGE PBS	mπ	15	18	19	18	15	16	17	15	18	20	19	18	20	23	22	23
		o N		D1	D2	D3	D4	D2	9Q	D7	D8	60	D10	D11	D12	D13	D14	D15	D16

5		REMARKS								COMPARATIVE							REMARKS					L :	COMPARATIVE	
10 15		CHARPY IMPACT VALUE AT ROOM TEMPERATURE	٦	17.0	15.0	16.0	16.0	15.3	15.1	15.1	14.7	14.6	14.3	15.0	14.1	14.0	CHARPY IMPACT VALUE AT ROOM TEMPERATURE	J	22.0	9.0	14.0	14.3	14.0	13.0
20		CHARPY IN ROOM T															CHARPY IN ROOM T							
25		CHARPY IMPACT VALUE AT -40°C	Ŋ	10.1	10.0	9.5	9.0	8.6	8.5	7.0	7.5	7.2	7.0	6.9	6.5	6.0	CHARPY IMPACT VALUE AT -40°C	J	18.2	3.0	6.2	6.0	8.5	7.8
<i>30</i>	[Table 4-2]	ELONGATION AT -40°C	%	9.7	9.5	9.2	8.7	8.6	8.0	7.0	7.5	0.9	5.4	5.6	5.4	5.4	ELONGATION AT -40°C	%	11	5.1	6.3	6.9	6.2	5.1
40		TENSILE STRENGTH AT -40°C	МРа	1100	1210	1230	1255	1280	1310	1420	1400	1480	1580	1525	1540	1570	TENSILE STRENGTH AT -40°C	МРа	1010	1590	1310	1300	1375	1250
<b>4</b> 5		NUMBER DENSITY OF COARSE PB		44	51	<del>20</del>	<u>76</u>	120	09	140	160	180	<u>120</u>	100	170	160	NUMBER DENSITY OF COARSE PB		20	<u>23</u>	40	<u>09</u>	<u>56</u>	<u>65</u>
55		AVERAGE PBS	mπ	28	27	<u>28</u>	30	35	38	40	44	48	34	42	35	45	PBS	mπ	21	23	41	39	<u>25</u>	30
		o N	<u>I</u>	D17	D18	D19	D20	D21	D22	D23	D24	D25	D26	D27	D28	D29	o <sub>N</sub>		D30	D31	D32	D33	D34	D35

5		REMARKS					
10		VALUE AT RATURE					
15		CHARPY IMPACT VALUE AT ROOM TEMPERATURE	ר	15.2	9.5	13.2	
20		C C					
25		CHARPY IMPACT VALUE AT -40°C	7	8.6	4.2	5.3	
30	(continued)	ELONGATION AT -40°C	%	9.2	3	4.9	NO
35							T INVENTION
40		TENSILE STRENGTH AT -40°c	МРа	1385	1380	1490	
<i>45 50</i>		NUMBER DENSITY OF COARSE PB		<u>70</u>	0	<u>52</u>	UNDERLINED VALUE IS OUT OF RANGE OF PRESEN
30							√LUE
55		PBS	ωm	45	15	39	ERLINED V
		S S		D36	D37	D38	UNDE

[0085] No. D1 to D16 of the Table 3 were examples satisfying the condition according to the present invention. On the other hand, No. D17 to D38 of the Table 4 were comparative examples which did not satisfy the conditions according to the present invention. Although the grain size of the pearlite block and the number density of the coarse PB of the example were controlled to the adequate level, the grain size of the pearlite block and the number density of the coarse PB of the comparative example were out of the range defined by the present invention. The examples demonstrated more excellent low-temperature strength, low-temperature toughness, and room-temperature toughness as compared with the comparative examples.

[0086] Figure 7A shows SEM picture of the pearlite block of the example and Figure 7B shows SEM picture of the pearlite block of the comparative example. It could be found from the SEM pictures that the grain size of the pearlite block of the example was clearly different from that of the comparative example.

[0087] Figure 8 shows a relationship between the grain size of the pearlite block (µm) and the impact value based on the impact value shown in Table 4. It could be found from the Figure 8 that the impact value of the example (PBS: 15 to 23μm) was higher than the impact value of the comparative example (PBS: 30 to 45μm) in both of room temperature and -40°C.

15 [0088] Figure 9A and Figure 9B show SEM observation result of the fracture surface of the charpy impact test piece of the example and comparative example. Figure 9A shows fracture facet of the example and Figure 9B shows fracture facet of the comparative example. The fracture facet of the example was finer than the fracture facet of the comparative example. This indicates that the example had more excellent toughness than the comparative example. In view of the point, the effect of refining PBS could be found.

[0089] Accordingly, it was found that the toughness of the example was higher than the toughness of the comparative example at both of room temperature and the environment of -40°C, to which the wire rod was exposed when the wire rod was used as additional PC of LNG tank.

#### [Industrial Applicability]

[0090] According to the present invention, a wire rod for PC steel stranded wire which is used as tendon of PC dike of PC-type LNG tank and which has more excellent elongation at about -40°C as compared with the conventional material can be provided by reducing grain size of pearlite block. Therefore, the present invention contributes to enhancing reliability of the PC steel stranded wire, which is a member constructing equipments concerning LNG tank which is much in demand these days, under low-temperature usage environment, and thus, the present invention has significant industrial applicability.

[Brief Description of the Reference Symbols]

#### 35 [0091]

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- 1: wire rod
- 2mm U-notch charpy impact test piece 2:
- 2mm U-notch

## **Claims**

1. A wire rod, wherein

a chemical composition comprises, in terms of mass%:

C: 0.60 to 1.20%; Si: 0.30 to 1.30%; Mn: 0.30 to 0.90%; P: 0.020% or less; S: 0.020% or less; N: 0.0025 to 0.0060%; Cr: 0 to 1.00%; V: 0 to 0.800%: Al: 0.005 to 0.100%,

55 one or more selected from the group consisting of

Ti: 0.003 to 0.050%, and B: 0.0005 to 0.0040%; and

remainder including Fe and impurity,

wherein an average value of a grain size of a pearlite block in a cross section perpendicular to a wire rod axial direction is  $23\mu m$  or less, and

wherein a number density of the pearlite blocks having  $40\mu m$  or more of the grain size in the cross section perpendicular to the wire rod axial direction is 0 to 20 pieces/mm<sup>2</sup>.

2. The wire rod according to claim 1, wherein

the chemical composition includes one or more selected from the group consisting of, in terms of mass%:

Cr: 0.10 to 1.00%, and V: 0.005 to 0.800%.

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3. The wire rod according to claim 1, wherein

the chemical composition includes, in terms of mass%:

C: 0.70 to 0.90%; Si: 0.80 to 1.30%; Mn: 0.60 to 0.90%; and V: 0 to 0.500%.

4. The wire rod according to claim 3, wherein

the chemical composition includes one or more selected from the group consisting of, in terms of mass%:

Cr: 0.50 to 1.00%, and V: 0.300 to 0.500%.

5. A method for manufacturing the wire rod, the method comprising:

heating a steel piece having the chemical composition according to claim 3 or 4 to a rough-rolling temperature of 950 to 1040°C and rough-rolling;

finish-wire-rolling at a finish-rolling temperature of 750 to 950°C;

then, coiling at a coiling temperature of 730 to 840°C; and thereafter,

air blast cooling to a normal temperature with a cooling rate of 15°C/sec or more,

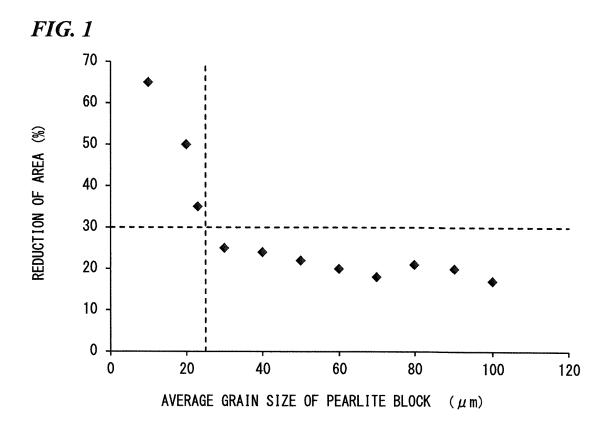
wherein the finish-rolling temperature and a strain rate in the finish-wire-rolling satisfy an expression A,

 $13.7 \le \log_{10} \{ (d\epsilon/dt) \times \exp(63800/(1.98 \times (T + 273.15)) \} \le$ 

16.5 :expression A,

and

wherein d $\epsilon$  / dt expresses the strain rate in the finish-wire-rolling in terms of s<sup>-1</sup> and T expresses the finish-rolling temperature in terms of °C.



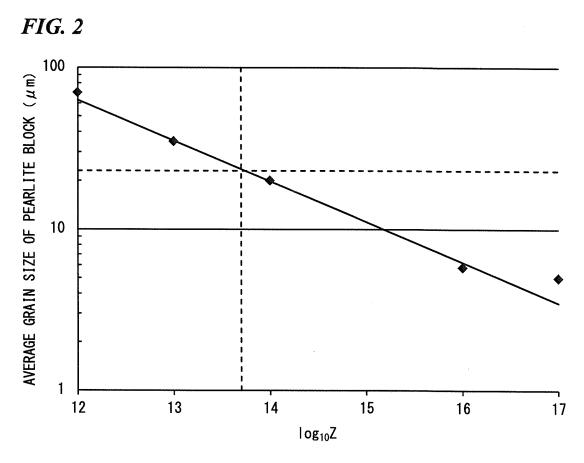


FIG. 3

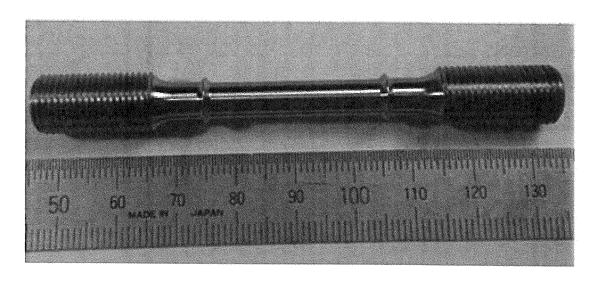
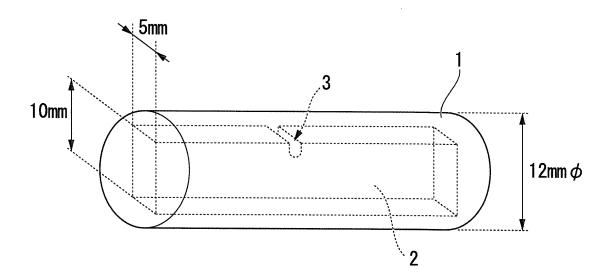
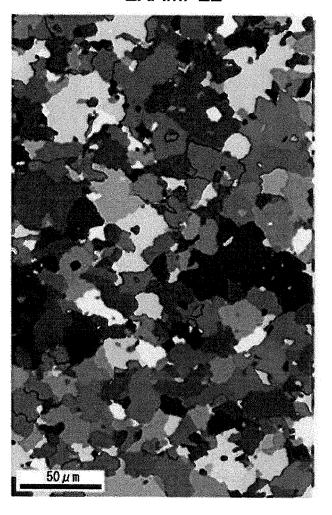


FIG. 4



# FIG. 5A

# **EXAMPLE**

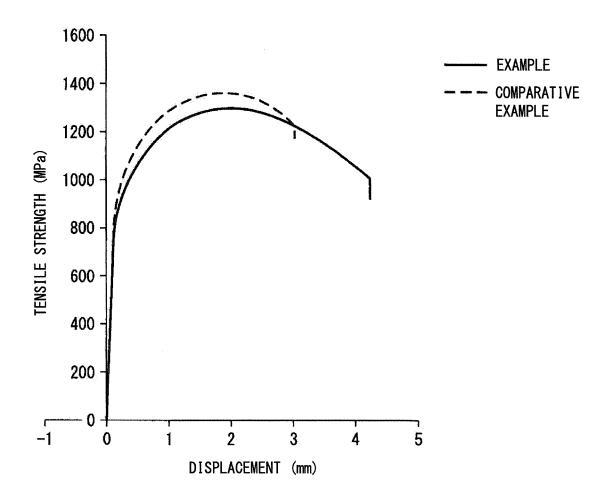


# FIG. 5B

# COMPARATIVE EXAMPLE

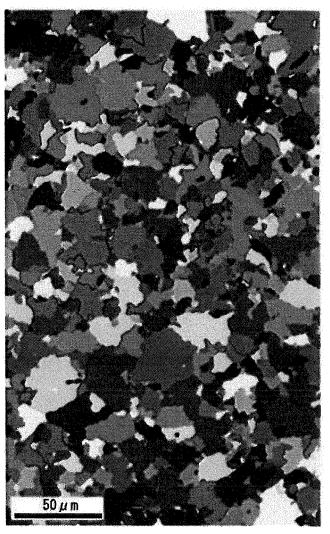


FIG. 6



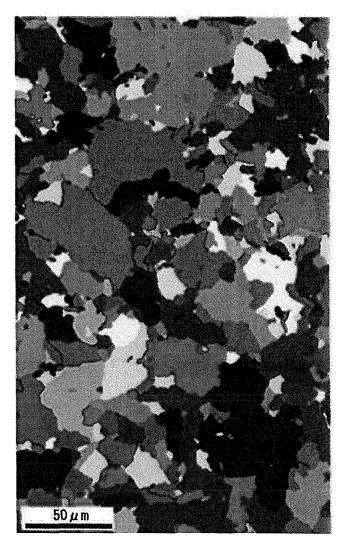
# FIG. 7A



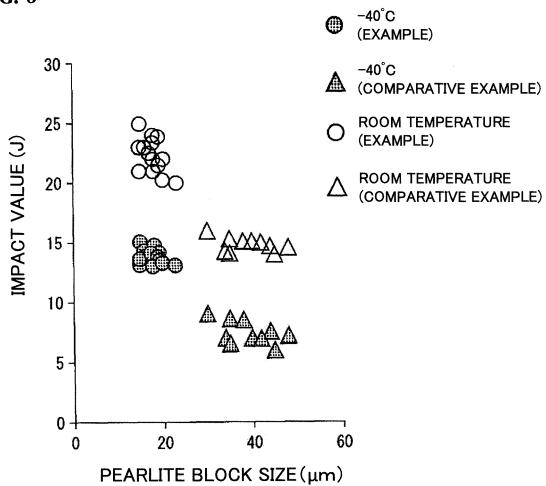


# FIG. 7B

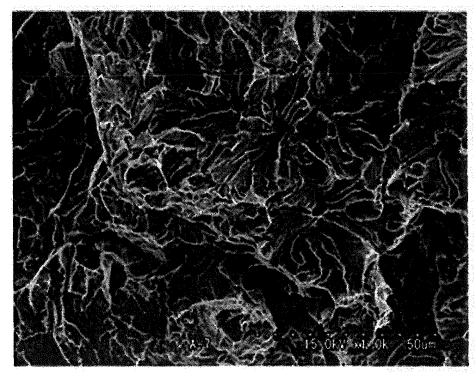
# COMPARATIVE EXAMPLE





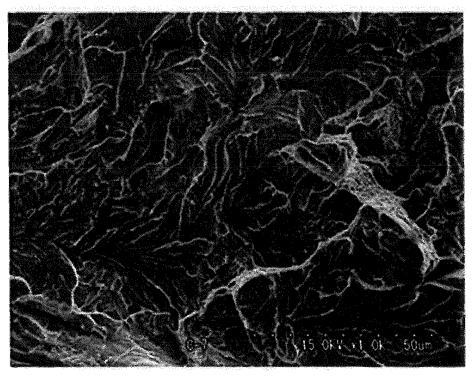


# FIG. 9A



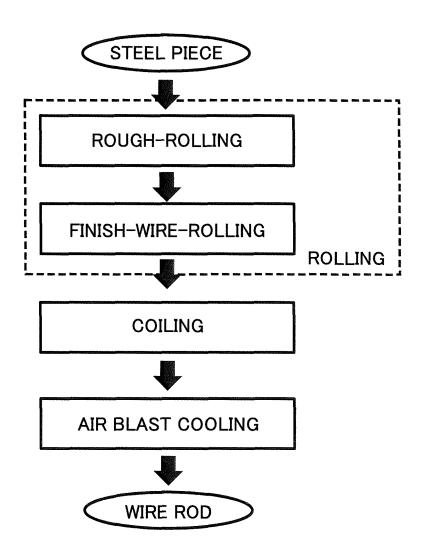
EXAMPLE (×1000)

# FIG. 9B



COMPARATIVE EXAMPLE (×1000)

FIG. 10



#### INTERNATIONAL SEARCH REPORT International application No. PCT/JP2014/061460 A. CLASSIFICATION OF SUBJECT MATTER 5 C22C38/00(2006.01)i, B21B3/00(2006.01)i, C21D8/06(2006.01)i, C22C38/32 (2006.01)i According to International Patent Classification (IPC) or to both national classification and IPC FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) 10 C22C38/00-38/60, B21B3/00, C21D8/06 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 1971-2014 Toroku Jitsuyo Shinan Koho Kokai Jitsuyo Shinan Koho 1994-2014 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) 20 DOCUMENTS CONSIDERED TO BE RELEVANT Category\* Citation of document, with indication, where appropriate, of the relevant passages Relevant to claim No. Χ JP 2008-7856 A (Nippon Steel Corp.), 1,2 17 January 2008 (17.01.2008), entire text 25 (Family: none) JP 2010-229469 A (Nippon Steel Corp.), 1 - 4Х 14 October 2010 (14.10.2010), steel A of the present invention (Family: none) 30 JP 2000-192148 A (Kobe Steel, Ltd.), 1 - 5Α 11 July 2000 (11.07.2000), paragraph [0058] (Family: none) 35 Further documents are listed in the continuation of Box C. See patent family annex. 40 later document published after the international filing date or priority date and not in conflict with the application but cited to understand Special categories of cited documents: "T "A" document defining the general state of the art which is not considered to 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 45 cited to establish the publication date of another citation or other special reason (as specified) document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art document referring to an oral disclosure, use, exhibition or other means document published prior to the international filing date but later than the priority date claimed document member of the same patent family Date of mailing of the international search report Date of the actual completion of the international search 50 25 July, 2014 (25.07.14) 05 August, 2014 (05.08.14) Name and mailing address of the ISA/ Authorized officer Japanese Patent Office 55 Telephone No.

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