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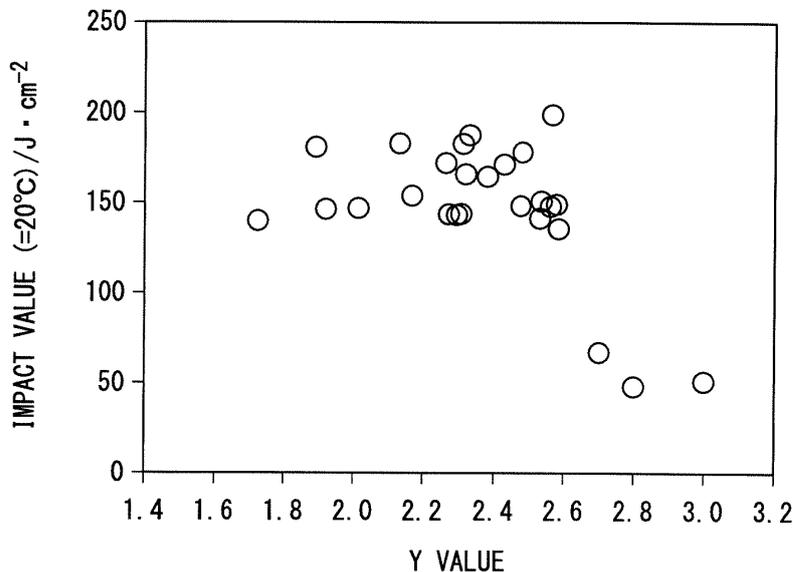
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(54) **STEEL**

(57) According to an aspect of the present invention, there is provided a steel containing, by unit mass%, C: 0.08% to 0.12%, Si: 0.05% to 0.50%, Mn: 1.50% to 3.00%, P: 0.040% or less, S: 0.020% or less, V: 0.010% or less, Ti: 0.010% or less, Nb: 0.005% or less, Cr: 1.00% to 2.50%, Cu: 0.01% to 0.50%, Ni: 0.75% to 1.60%, Mo:

0.10% to 0.50%, Al: 0.025% to 0.050%, N: 0.0100% to 0.0200%, Ca: 0% to 0.0100%, Zr: 0% to 0.0100%, Mg: 0% to 0.0100%, and a remainder including Fe and impurities, in which a ratio of an Al content to a N content is 2.6 or less, a ratio of a Mn content to a Ni content is 1.5 or more and 3.0 or less.

**FIG. 1**



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**Description**

[Technical Field of the Invention]

5 **[0001]** The present invention relates to steel having a high strength and an excellent low-temperature toughness after quenching and tempering.

[Related Art]

10 **[0002]** Recently, in response to changes in energy situation, active efforts have been made across the globe in order to develop new energy sources. In such circumstances, offshore oil fields have drawn attentions as sources developed onshore have been depleted, and development using oil-drilling rigs has been conducted across a broad range of regions, mainly, continental shelves. In particular, recently, the number of marine structures represented by offshore oil-drilling rigs that are operated in the depths of the sea has been rising, and, in order to prevent damage to drilling rigs by large-scale hurricanes, there has been a demand for increasing the strength of chains for mooring drilling rigs. Broken chains lead directly to serious accidents such as the collapse of rigs. In order to ensure safety which is a vital object, an increase in both the strength and toughness of chains has been pursued. Specifically, there has been a demand for chains having a tensile strength of 1,200 MPa or more and a Charpy impact value at -20°C of 75 J/cm<sup>2</sup> or more.

15 **[0003]** Such chains are manufactured by cutting a hot rolled steel bar having a diameter of  $\phi$  50 mm or more to a predetermined length, forming the steel bar to an annular shape, and welding butted end surfaces through flash butt welding. After flash butt welding, there are cases where a stud is press-fitted into the center of the annular chain. After that, the chain is quenched and tempered, thereby imparting a high strength and a high toughness to the chain.

20 **[0004]** Patent Documents 1 to 6 and the like can be exemplified as invention examples of steel for a high strength and high toughness chain. However, all of the documents aim to provide a chain having a tensile strength of 800 MPa to 1,000 MPa and do not study a case where the strength of steel is set to 1,200 MPa or more. In recent years, although an additional increase in strength has been demanded for chains, it is known that an increase in the strength of steel generally degrades the toughness of steel and thus decreases the impact value of steel. When the strength of the steel having the chemical composition proposed by the above described documents is set to 1,200 MPa or more, it is not possible to obtain an intended impact value.

25 **[0005]**

[Prior Art Document]

[Patent Document]

30 **[0005]**

[Patent Document 1] Japanese Unexamined Patent Application, First Publication No. S58-22361

[Patent Document 2] Japanese Unexamined Patent Application, First Publication No. S58-96856

35 **[0005]**

[Patent Document 3] Japanese Unexamined Patent Application, First Publication No. S59-159972

[Patent Document 4] Japanese Unexamined Patent Application, First Publication No. S59-159969

40 **[0005]**

[Patent Document 5] Japanese Unexamined Patent Application, First Publication No. S62-202052

[Patent Document 6] Japanese Unexamined Patent Application, First Publication No. S63-203752

[Disclosure of the Invention]

45 **[0005]**

[Problems to be Solved by the Invention]

50 **[0006]** An object of the present invention is to provide a steel having a high strength and an excellent low-temperature toughness (particularly, fracture toughness at a low temperature) after quenching and tempering. Specifically, the object of the invention is to provide a steel in which the Charpy impact value at -20°C reaches 75 J/cm<sup>2</sup> or more, when quenching and tempering are carried out so that the tensile strength reaches 1,200 MPa or more.

[Means for Solving the Problem]

**[0007]** The gist of the present invention is as described below.

**[0008]**

(1) According to an aspect of the present invention, there is provided a steel containing, by unit mass%, C: 0.08% to 0.12%, Si: 0.05% to 0.50%, Mn: 1.50% to 3.00%, P: 0.040% or less, S: 0.020% or less, V: 0.010% or less, Ti: 0.010% or less, Nb: 0.005% or less, Cr: 1.00% to 2.50%, Cu: 0.01% to 0.50%, Ni: 0.75% to 1.60%, Mo: 0.10% to 0.50%, Al: 0.025% to 0.050%, N: 0.0100% to 0.0200%, Ca: 0% to 0.0100%, Zr: 0% to 0.0100%, Mg: 0% to 0.0100%, and a remainder including Fe and impurities, in which a Y value defined by Equation (a) is 2.6 or less, and a Z value defined by Equation (b) is 1.5 or more and 3.0 or less.

$$Y=(Al)/(N) \quad \cdots \quad (a)$$

$$Z=(Mn)/(Ni) \quad \cdots \quad (b)$$

symbols (Al), (N), (Mn), and (Ni) in the equations represent amounts of elements relating to the respective symbols in the steel, by unit mass%.

(2) The steel according to (1) may further contain, by unit mass%, one or more selected from the group consisting of Ca: 0.0005% to 0.0100%, Zr: 0.0005% to 0.0100%, and Mg: 0.0005% to 0.0100%.

[Effects of the Invention]

**[0009]** According to the present invention, it is possible to provide steel having a tensile strength of 1,200 MPa or more and a Charpy impact value at -20°C of 75 J/cm<sup>2</sup> or more after quenching and tempering.

[Brief Description of the Drawings]

**[0010]**

Fig. 1 is a graph showing a relationship between a Y value of steel and an impact value at -20°C of steel after quenching and tempering.

Fig. 2 is a graph showing a relationship between a Z value of the steel and an impact value at -20°C of steel after quenching and tempering.

[Embodiments of the Invention]

**[0011]** The present inventors have continued a variety of researches in order to realize steel having a high strength and an excellent low-temperature toughness, as a result, the present inventors obtained the following findings.

**[0012]**

(A) A decrease in the C content for decreasing the amount of cementite which may act as an origin of fracture is effective to improve the low-temperature toughness of steel. However, in order to set a tensile strength of the steel after quenching and tempering to 1,200 MPa or more, it is not possible to set the C content to less than 0.08%.

(B) The addition of Ni to steel improves the low-temperature toughness of the steel. However, it is not possible to sufficiently improve the low-temperature toughness of steel only with this means.

(C) The appropriate addition of Al and N in addition to Ni further improves the low-temperature toughness of the steel. This is because fine AlN formed of Al and N miniaturizes crystal grains and accelerates the effect of Ni for improving the low-temperature toughness. In order to obtain this effect, it is necessary to set the Al content to 0.025% or more and set the N content to 0.0100% or more.

**[0013]** Here, it is necessary that the ratio Y ( $Y=[Al]/[N]$ ) of the Al content to the N content is set to 2.6 or less. When the value of Y exceeds 2.6, the number of alumina based non-metallic inclusions in the steel is increased, and, conversely, the low-temperature toughness is degraded.

(D) Furthermore, in order to sufficiently improve the low-temperature toughness of steel, it is necessary that the

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ratio  $Z$  ( $Z=[\text{Mn}]/[\text{Ni}]$ ) of the Mn content to the Ni content is set to 1.5 or more and 3.0 or less. When the value of  $Z$  is less than 1.5, the amount of residual austenite is increased, and, when the value of  $Z$  exceeds 3.0, the Mn content forming a solid solution in the steel is increased. In both cases, the low-temperature toughness of the steel is not sufficient. That is, as described above, Ni has an effect for improving the low-temperature toughness of steel; however, when the Ni content is excessive,  $Z$  reaches less than 1.5, and the low-temperature toughness is impaired. (E) In addition, in order to sufficiently improve the low-temperature toughness of steel, it is necessary to limit the V content, the Nb content and the Ti content. VN, NbC, and Ti(C, N) which are generated from V, Nb, and Ti degrade the low-temperature toughness of the steel.

(F) Furthermore, in order to sufficiently improve the low-temperature toughness of steel, it is necessary to add Mo to the steel. This is because Mo miniaturizes cementite which causes the degradation of the low-temperature toughness and makes the cementite harmless.

**[0014]** On the basis of the above described findings, the present inventors found a structural component having a high strength and a high low-temperature toughness, particularly, steel which can be used for manufacturing chains. Hereinafter, a specific aspect of steel according to the present embodiment will be described. In addition, although the steel according to the present embodiment is steel having an effect in which the tensile strength reaches 1,200 MPa or more and the Charpy impact value at - 20°C reaches 75 J/cm<sup>2</sup> or more after quenching and tempering, the strength and the impact value before quenching and tempering are not particularly limited. Hereinafter, unless particularly otherwise described, description of mechanical properties such as strength and toughness relates to the steel according to the present embodiment after quenching and tempering.

**[0015]** Hereinafter, the reasons for limiting the amounts of individual alloying elements of the steel according to the present embodiment will be described. The unit "%" of the amounts of the alloying elements indicates mass%.

C: 0.08% to 0.12%

**[0016]** C is an important element that determines the strength of the steel. In order to obtain a tensile strength of 1,200 MPa or more after quenching and tempering, the lower limit of the C content is set to 0.08%. On the other hand, when the C content is excessive, the strength of the steel is excessively increased, and thus the toughness of the steel is degraded. In addition, when the C content is excessive, the amount of cementite which acts as an origin of fracture is increased, and the toughness of the steel is significantly degraded. Therefore, the upper limit of the C content is set to 0.12%. The upper limit of the C content is preferably 0.11%. The lower limit of the C content is preferably 0.09%.

Si: 0.05% to 0.50%

**[0017]** Si has an action of ensuring the strength of the steel and also an action as a deoxidizing agent. When the Si content is less than 0.05%, the deoxidizing action cannot be sufficiently obtained, the number of non-metallic inclusions in the steel is increased, and the toughness of the steel is degraded. On the other hand, when the Si content is more than 0.50%, Si causes the degradation in the toughness of the steel. Therefore, the Si content is set to 0.05% to 0.50%. The upper limit of the Si content is preferably 0.40%, 0.30%, or 0.20%. The lower limit of the Si content is preferably 0.06%, 0.07%, or 0.08%.

Mn: 1.50% to 3.00%

**[0018]** Mn is an essential element for ensuring required hardenability. In order to ensure sufficient hardenability for setting a tensile strength of the steel after quenching and tempering to 1,200 MPa or more, the lower limit of the Mn content is set to 1.50%. On the other hand, when the Mn content is excessive, the toughness of the steel is degraded, and thus the upper limit of the Mn content is set to 3.00%. The upper limit of the Mn content is preferably 2.90%, 2.80%, or 2.70%. The lower limit of the Mn content is preferably 1.70%, 1.90%, or 2.00%.

P: 0.040% or less

**[0019]** P is an impurity that is incorporated into the steel during the manufacturing process of the steel. When the P content exceeds 0.040%, the toughness of the steel is degraded more than a permissible limit, and thus the P content is limited to 0.040% or less. The upper limit of the P content is preferably 0.030%, 0.025%, or 0.020%. The steel according to the present embodiment does not need P, and thus the lower limit of the P content is 0%; however, when the capability of a refining facility and the like are taken into account, the lower limit of the P content may be set to 0.001 %, 0.002%, or 0.003%.

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S: 0.020% or less

5 **[0020]** S is, similar to P, an impurity that is incorporated into the steel during the manufacturing process of the steel. When the S content exceeds 0.020%, S forms a large amount of MnS in the steel, and the toughness of the steel is degraded. Therefore, the S content is limited to 0.020% or less. The upper limit of the S content is preferably 0.015%, 0.012%, or 0.010%. The steel according to the present embodiment does not need S, and thus the lower limit of the S content is 0%; however, when the capability of a refining facility and the like are taken into account, the lower limit of the S content may be set to 0.001%, 0.002%, or 0.003%.

10 Cr: 1.00% to 2.50%

15 **[0021]** Cr has an action for enhancing the hardenability of the steel. In order to set a tensile strength of the steel after quenching and tempering to 1,200 MPa or more due to ensuring sufficient hardenability, the lower limit of the Cr content is set to 1.00%. On the other hand, when the Cr content is excessive, the toughness of the steel is degraded. Therefore, the upper limit of the Cr content is set to 2.50%. The upper limit of the Cr content is preferably 2.40%, 2.30%, or 2.20%. The lower limit of the Cr content is preferably 1.30%, 1.40%, or 1.50%.

Cu: 0.01% to 0.50%

20 **[0022]** Cu is an effective element for improving the hardenability and corrosion resistance of the steel. In order to ensure sufficient hardenability and corrosion resistance for setting a tensile strength of the steel after quenching and tempering to 1,200 MPa or more, the lower limit of the Cu content is set to 0.01%. On the other hand, when the Cu content is excessive, the toughness of the steel is degraded. Therefore, the upper limit of the Cu content is set to 0.50%. The upper limit of the Cu content is preferably 0.40%, 0.30%, or 0.20%. The lower limit of the Cu content is preferably 0.02%, 0.03%, or 0.05%.

Ni: 0.75% to 1.60%

30 **[0023]** Ni is an extremely effective element for improving the toughness of the steel and an essential element for increasing the toughness of the steel according to the present embodiment after quenching and tempering. When the Ni content is less than 0.75%, it is difficult to sufficiently exhibit the effects. On the other hand, when the Ni content is excessive, the amount of residual austenite is increased, and thus the low-temperature toughness is, conversely, degraded. Therefore, the upper limit of the Ni content is set to 1.60%. The upper limit of the Ni content is preferably 1.50%, 1.35%, or 1.20%. The lower limit of the Ni content is preferably 0.80%, 0.85%, or 0.90%.

35 Mo: 0.10% to 0.50%

40 **[0024]** Mo has an effect for improving the low-temperature toughness of the steel. Mo miniaturizes cementite which acts as an origin of fracture and makes cementite harmless. In addition, Mo miniaturizes the block size of a martensite, decreases the ductile-brittle transition temperature of the steel, and thus prevents brittle fracture from easily occurring at a low temperature. When the Mo content is less than 0.10%, it is difficult to sufficiently exhibit the effects. On the other hand, when the Mo content exceeds 0.50%, the effect for improving toughness is saturated. Therefore, the Mo content is set to 0.10% to 0.50%. The upper limit of the Mo content is preferably 0.47%, 0.45%, or 0.42%. The lower limit of the Mo content is preferably 0.15%, 0.20%, or 0.25%.

45 Al: 0.025% to 0.050%

50 **[0025]** In addition to a deoxidizing action, Al has an action for adjusting the crystal grain size of a metallographic structure and miniaturizing the metallographic structure when Al is precipitated as AlN. When the Al content is less than 0.025%, it is not possible to obtain a sufficient miniaturizing effect, and thus the toughness of the steel is degraded. On the other hand, when the Al content in the steel exceeds 0.050%, the amount of AlN precipitated is saturated, the number of alumina based non-metallic inclusions in the steel is increased, and the toughness of the steel is degraded. Therefore, the Al content is set to 0.025% to 0.050%. The upper limit of the Al content is preferably 0.045%, 0.042%, or 0.040%. The lower limit of the Al content is preferably 0.027%, 0.029%, or 0.030%.

55 N: 0.0100% to 0.0200%

**[0026]** N has an action for precipitating AlN, which is effective for adjusting the crystal grain size of the metallographic

structure, by bonding to Al. When the N content is less than 0.0100%, this action is not sufficiently exhibited. On the other hand, when the N content in the steel exceeds 0.0200%, the number of solute N is increased, and the toughness of the steel is degraded. Therefore, the N content is set to 0.0100% to 0.0200%. The upper limit of the N content is preferably 0.0180%, 0.0170%, or 0.0160%. The lower limit of the N content is preferably 0.0110%, 0.0120%, or 0.0130%.

**[0027]** V: 0.010% or less

Ti: 0.010% or less

Nb: 0.005% or less

**[0028]** In the steel according to the present embodiment, the V content, the Ti content and the Nb content are preferably small. This is because VN, NbC, and Ti(C, N) which are generated from V, Nb, and Ti degrade the low-temperature toughness of the steel. The present inventors found that, in order to prevent the degradation in the low-temperature toughness of the steel, it is necessary that to the V content is limited to 0.010% or less, the Ti content is limited 0.010% or less, and the Nb content is limited to 0.005% or less. The upper limit of the V content is preferably 0.009%, 0.007%, or 0.005%. The upper limit of the Ti content is preferably 0.009%, 0.007%, or 0.005%. The upper limit of the Nb content is preferably 0.004%, 0.003%, or 0.002%.

**[0029]** In the steel according to the present embodiment, since the V content, the Ti content and the Nb content are preferably small, the lower limits of the V content, the Ti content and the Nb content are 0%. However, when these elements are incorporated into the steel as impurities, there are cases where it is not preferable to completely remove these elements from the steel in consideration of cost-effectiveness. Therefore, in consideration of the capability of the refining facility, the economic efficiency, and the like, the lower limit of the V content may be set to 0.003%, 0.002%, or 0.001%, the lower limit of the Ti content may be set to 0.003%, 0.002%, or 0.001%, and the lower limit of the Nb content may be set to 0.0010%, 0.0009%, or 0.0008%.

**[0030]** One or more selected from the group consisting of Ca: 0% to 0.0100%, Zr: 0% to 0.0100%, and Mg: 0% to 0.0100%

**[0031]** The steel according to the present embodiment does not need Ca, Zr, and Mg. Therefore, the lower limits of the the Ca content, the Zr content, and the Mg content is 0%. However, all of Ca, Zr, and Mg have an effect for forming an oxide, acting as a crystallization nucleus of MnS, and uniformly and finely dispersing MnS so as to improve the impact value of the steel. Therefore, as an optional element, the steel may contain 0.0005% or more, 0.0010% or more, or 0.0015% or more of Ca, may contain 0.0005% or more, 0.0010% or more, or 0.0015% or more of Zr, and may contain 0.0005% or more, 0.0010% or more, or 0.0015% or more of Mg. On the other hand, when each of the Ca content, the Zr content, and the Mg content exceeds 0.0100%, an excess amount of a hard inclusion such as an oxide and a sulfide is generated, and the toughness of the steel is degraded. Therefore, the upper limits of each of the Ca content, the Zr content, and the Mg content is set to 0.0100% or less. The upper limit of the Ca content is preferably 0.0090%, 0.0070%, or 0.0050%, the upper limit of the Zr content is preferably 0.0090%, 0.0070%, or 0.0050%, and the upper limit of the Mg content is preferably 0.0090%, 0.0070%, or 0.0050%.

Remainder: Fe and impurities

**[0032]** The remainder of the chemical composition of the steel according to the present embodiment consists of Fe and impurities. The impurities refer to elements which are incorporated by a raw material such as an ore or a scrap, or a variety of causes in the manufacturing process during the industrial manufacturing of the steel, and the impurities are permitted to an extent in which the steel according to the present embodiment is not adversely influenced.

Ratio (Y value) of Al content to N content: 2.6 or less

**[0033]** In the steel according to the present embodiment, the ratio (Y value) of the Al content to the N content is defined by the following Equation a.

$$Y=(Al)/(N) \quad \cdots \quad \text{Equation a}$$

**[0034]** In the equation a, symbols in parentheses represent the amounts of elements relating to the symbols, by unit mass%.

**[0035]** AlN has an effect for miniaturizing crystal grains and improving the low-temperature toughness of the steel. However, when the ratio (Y value) of the Al content to the N content in the steel exceeds 2.6, the number of alumina based non-metallic inclusions in the steel is increased, and the steel becomes brittle, and thus, conversely, the low-temperature toughness is degraded. Therefore, the Y value is set to 2.6 or less. The upper limit of the Y value is preferably 2.55, 2.50, or 2.45. On the other hand, the lower limit of the Y value is not particularly limited; however, when the lower limit of the Al content and the upper limit of the N content which are described above are taken into account, the Y value

does not become less than 1.25.

**[0036]** The present inventors obtained the above described finding from an experiment that will be described below. The present inventors carried out quenching and tempering on a variety of steels having properties other than the Y value which are all in the specification ranges of the steel according to the present embodiment and different Y values under the following conditions and then carried out a Charpy impact test at -20°C.

- Quenching treatment: The steel was heated to 900°C, held for 30 minutes, and then cooled by water
- Tempering treatment: The steel was heated to 135°C, held for 30 minutes, and then cooled in the air

**[0037]** Therefore, the present inventors obtained a graph showing the relationship between the Y value and the impact value at -20°C (Fig. 1). As shown in Fig. 1, steels having a Y value of more than 2.6 did not have sufficient low-temperature toughness after quenching and tempering.

Ratio (Z value) of Mn content to Ni content: 1.5 or more and 3.0 or less

**[0038]** In the steel according to the present embodiment, the ratio (Z value) of the Mn content to the Ni content is defined by the following Equation b.

$$Z=(\text{Mn})/(\text{Ni}) \quad \cdots \quad \text{Equation b}$$

**[0039]** In the equation b, symbols in parentheses represent the amounts of elements relating to the symbols, by unit mass%.

**[0040]** As described above, Ni improves the low-temperature toughness of the steel. However, when the Ni content is excessive, and the ratio (Z value) of the Mn content to the Ni content in the steel is less than 1.5, the number of residual austenite is increased, and the low-temperature toughness of the steel is impaired. In addition, when the Z value exceeds 3.0, the ratio of the amount of solute Mn to the Ni content becomes excessive, the effect of Ni for improving low-temperature toughness is negated, the steel becomes brittle, and the low-temperature toughness is degraded. Therefore, the Z value is set to 1.5 or more and 3.0 or less. The upper limit of the Z value is preferably 2.9, 2.8, or 2.7. The lower limit of the Z value is preferably 1.6, 1.7, or 1.8.

**[0041]** The present inventors obtained the above described finding from an experiment that will be described below. The present inventors carried out quenching and tempering on a variety of steels having properties other than the Z value which are all in the specification ranges of the steel according to the present embodiment and different Z values under the following conditions and then carried out a Charpy impact test at -20°C.

- Quenching treatment: The steel was heated to 900°C, held for 30 minutes, and then cooled by water
- Tempering treatment: The steel was heated to 135°C, held for 30 minutes, and then cooled in the air

**[0042]** Therefore, the present inventors obtained a graph showing the relationship between the Z value and the impact value at -20°C (Fig. 2). As shown in Fig. 2, steels having a Z value of less than 1.5 or more than 3.0 did not have sufficient low-temperature toughness after quenching and tempering.

**[0043]** Meanwhile, the number density of AlN, the grain diameters, the dispersion state, and the like in the steel change depending on the conditions of a heat treatment (for example, quenching and tempering) that is carried out on the steel. In addition, when the Al content and the N content are controlled as described above, regardless of the state of AlN before quenching and tempering, AlN effectively functions during quenching and tempering under conditions which is selected so as to set a tensile strength of the steel to 1,200 MPa or more, and the toughness of the steel is improved. That is, the object of the steel according to the present embodiment is to set a Charpy impact value at -20°C of the steel to 75 J/cm<sup>2</sup> or more after a heat treatment is carried out on the steel so that the tensile strength reaches 1,200 MPa, but the control of the state of AlN is not necessary to achieve the object of the steel according to the present embodiment. Therefore, in the steel according to the present embodiment, the state of AlN is not particularly specified. Meanwhile, from the result of the experiment, the present inventors assume that, when the steel is heated to 850°C to 900°C, AlN is preferably precipitated regardless of the state of the steel before heating, and, when the steel in this state is cooled, the structure is preferably miniaturized due to AlN.

**[0044]** Even when the steel according to the present embodiment is quenched and tempered so that the tensile strength reaches 1,200 MPa or more, the Charpy impact value at -20°C can be maintained at 75 J/cm<sup>2</sup> or more. Therefore, the steel according to the present embodiment is particularly preferably used as steel for quenching.

**[0045]** For example, when a quenching treatment in which steel is heated to 900°C, held for 30 minutes, and then cooled by water is carried out on the steel according to the present embodiment, and furthermore, a tempering treatment

in which the steel is heated to 135°C and held for 30 minutes is carried out on the steel, steel having a tensile strength of 1,200 MPa or more and a Charpy impact value at -20°C of 75 J/cm<sup>2</sup> or more is obtained. In the steel according to the present embodiment on which the heat treatment under the above described quenching and tempering conditions is carried out, the average grain size of cementite is 0.05 μm or less, the average size of martensite blocks is 5.5 μm or less, and the amount of residual austenite is 5% or less. The steel according to the present embodiment contains 0.08% or more of C and thus has a tensile strength of 1,200 MPa or more when the heat treatment under the above described quenching and tempering conditions is carried out thereon. Generally, when the tensile strength of the steel is 1,200 MPa or more, the low-temperature toughness (particularly, low-temperature toughness) is impaired. However, the steel according to the present embodiment contains 0.025% to 0.050% of Al, 0.0100% to 0.0200% of N, and 0.10% to 0.50% of Mo, and thus, even when the heat treatment under the above-described quenching and tempering conditions is carried out thereon, martensite blocks and cementite are sufficiently miniaturized, and the steel has the high low-temperature toughness. In addition, the steel according to the present embodiment contains 0.75% to 1.60% or Ni and thus has the high low-temperature toughness even when the heat treatment under the above-described quenching and tempering conditions is carried out thereon. There is concern that an excessive amounts of Al and Ni impairs the low-temperature toughness; however, in the steel according to the present embodiment, the ratio of the Al content to the N content and the ratio of the Ni content and the Mn content are controlled, and thus the low-temperature toughness is not impaired. Furthermore, in the steel according to the present embodiment, the V content is controlled to 0.010% or less, the Ti content is controlled to 0.010% or less, and the Nb content is controlled to 0.005% or less, and thus, even when the heat treatment under the above described quenching and tempering conditions is carried out on the steel, the precipitation of inclusions is suppressed, and the steel has the high low-temperature toughness.

**[0046]** Meanwhile, quenching and tempering treatment according to the above described conditions is simply an example of the use of the steel according to the present embodiment. According to the purposes, a heat treatment under random conditions can be carried out on the steel according to the present embodiment. In addition, the properties of the steel according to the present embodiment on which the heat treatment is carried out on the basis of an example of the above described quenching and tempering conditions do not limit the technical scope of the steel according to the present embodiment. The object of the steel according to the present embodiment is to obtain a Charpy impact value at -20°C of 75 J/cm<sup>2</sup> or more after a heat treatment is carried out so that the tensile strength reaches 1,200 MPa or more. In order to achieve this object, it is necessary to control the chemical composition, the ratio of the Al content to the N content, and the ratio of the Ni content to the Mn content as described above. However, other constitutions, for example, controlling martensite, cementite, residual austenite, and the like before heat treatment are not needed in order to achieve the object of the steel according to the present embodiment.

**[0047]** The steel according to the present embodiment has a high tensile strength and an excellent low-temperature toughness after quenching and tempering and is thus capable of exhibiting particularly excellent effects, when the steel according to the present embodiment is used as a material for chains for mooring offshore oil-drilling rigs.

[Examples]

**[0048]** Hereinafter, the present invention will be described in detail using examples. Meanwhile, these examples are intended to describe the technical meaning and effects of the present invention and do not limit the scope of the present invention.

**[0049]** Steel having chemical composition shown in Table 1 was melted and hot-forged using a 180 kg vacuum melting furnace, thereby obtaining a round steel bar having a diameter of 86 mm. The round steel bar was cut, and a quenching treatment by heating to 900°C, holding for 30 minutes, and furthermore, cooling by water was carried out on thereon, and then a tempering treatment by heating to 135°C and holding for 30 minutes was carried out on the round steel bar. These quenching conditions and tempering conditions are the same as heat treatment conditions which are recommended for the production of chains using the present invention steel. Three JIS No. 14A tensile test pieces and four JIS No. 4 V-notch Charpy impact test pieces were produced from a 1/4D portion (a region at a depth of approximately 1/4 of a diameter D of the round steel bar from the surface of the round steel bar) of a C cross section of this round steel bar. A tensile test was carried out at normal temperature and a rate of 20 mm/min according to JIS Z 2241. A Charpy impact test was carried out at -20°C according to JIS Z 2242.

**[0050]** Furthermore, a 10 mm x 10 mm sample was cut out from the 1/4D portion of the C cross section of the quenched and tempered round steel bar, the cross section of the sample was corroded with a nital etching solution, five structural photographs of the cross section of the sample were captured using a scanning electron microscope at a magnification of 5,000 times, and the average grain size of the cementite included in the photographs was obtained by means of an image analysis using Luzex (registered trademark) and considered as the average grain size of cementite in the round steel bar. In addition, a crystal orientation analysis was carried out using an electron backscatter diffraction pattern pattern, and the area-weighted average equivalent circle diameter of crystal grains surrounded by high-angle grain boundaries which had an orientation difference angle of 15 degrees, which was obtained from the above described

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analysis, was considered as the average grain size of martensite blocks of the round steel bar. Furthermore, the amount of the residual austenite in the round steel bar was measured using an X-ray diffraction method.

[0051] The results of the above described experiments are shown in Table 1-1, Table 1-2, and Table 2. Table 1-1 and Table 1-2 show the chemical compositions of example steels and comparative example steels, and Table 2 shows the tensile strengths, the impact values, the average grain sizes of cementite, the average sizes of martensite blocks, and the amounts of residual austenite in the example steels and the comparative example steels after quenching and tempering under the above described conditions were carried out. In Table 1-2, values outside the specification ranges of the present invention are underlined.

[Table 1-1]

Steel type	Classification	Chemical composition of Elements (mass%)															Y value	Z value			
		C	Si	Mn	P	S	V	Ti	Nb	Cr	Cu	Ni	Mo	Al	N	Ca			Zr	Mg	
1	Example	0.08	0.12	2.53	0.010	0.008	0.008	0.007	0.003	2.01	0.12	0.97	0.35	0.031	0.0133	-	-	-	2.3	2.6	
2		0.12	0.14	2.48	0.012	0.012	0.008	0.009	0.003	1.96	0.09	0.95	0.31	0.029	0.0125	-	-	-	2.3	2.6	
3		0.10	0.06	2.45	0.016	0.015	0.007	0.008	0.002	1.85	0.10	1.12	0.28	0.033	0.0143	0.0020	-	-	-	2.3	2.2
4		0.11	0.48	2.58	0.015	0.010	0.006	0.008	0.004	2.12	0.11	1.08	0.38	0.028	0.0122	-	-	0.0050	2.3	2.4	
5		0.09	0.15	1.50	0.013	0.018	0.009	0.009	0.003	2.05	0.13	0.87	0.37	0.038	0.0147	-	-	-	2.6	1.7	
6		0.10	0.16	2.99	0.012	0.009	0.007	0.007	0.003	1.98	0.10	1.23	0.29	0.036	0.0159	-	0.0070	-	2.3	2.4	
7		0.11	0.12	2.41	0.011	0.007	0.006	0.006	0.004	1.02	0.10	1.21	0.30	0.038	0.0148	-	-	-	2.6	2.0	
8		0.11	0.14	2.45	0.010	0.010	0.008	0.008	0.003	2.48	0.11	1.07	0.27	0.035	0.0154	-	-	-	2.3	2.3	
9		0.10	0.12	2.51	0.011	0.013	0.007	0.008	0.004	1.94	0.02	0.99	0.32	0.034	0.0137	-	-	-	2.5	2.5	
10		0.10	0.13	2.57	0.012	0.009	0.006	0.006	0.003	2.02	0.48	1.06	0.34	0.030	0.0149	-	-	-	2.0	2.4	
11		0.10	0.16	2.02	0.015	0.015	0.009	0.005	0.004	2.00	0.09	0.75	0.21	0.035	0.0138	0.0010	-	-	2.5	2.7	
12		0.09	0.13	2.74	0.009	0.015	0.007	0.008	0.002	1.97	0.10	1.58	0.33	0.031	0.0143	-	0.0080	-	2.2	1.7	
13		0.09	0.12	2.53	0.017	0.011	0.007	0.009	0.003	1.84	0.11	1.00	0.10	0.039	0.0154	-	-	-	2.5	2.5	
14		0.11	0.12	2.58	0.023	0.009	0.008	0.008	0.003	1.95	0.12	1.17	0.49	0.031	0.0164	-	-	-	1.9	2.2	
15		0.10	0.15	2.41	0.017	0.008	0.009	0.009	0.004	2.12	0.09	0.94	0.28	0.025	0.0145	-	-	-	1.7	2.6	
16		0.10	0.16	2.54	0.015	0.011	0.006	0.005	0.003	2.14	0.09	0.99	0.31	0.049	0.0190	-	-	-	2.6	2.6	
17		0.09	0.15	2.50	0.010	0.019	0.007	0.006	0.002	1.87	0.09	1.07	0.30	0.026	0.0105	-	-	-	2.5	2.3	
18		0.10	0.12	2.37	0.009	0.012	0.008	0.009	0.003	1.85	0.12	1.02	0.34	0.038	0.0198	-	-	-	1.9	2.3	
19		0.09	0.15	2.81	0.010	0.010	0.008	0.008	0.002	1.97	0.11	1.23	0.24	0.031	0.0121	-	-	-	2.6	2.3	
20		0.09	0.14	2.42	0.016	0.009	0.009	0.008	0.004	1.84	0.11	0.92	0.26	0.030	0.0126	-	-	-	2.4	2.6	
21		0.11	0.12	2.19	0.019	0.012	0.006	0.004	0.003	2.01	0.10	1.42	0.37	0.031	0.0134	-	-	-	2.3	1.5	
22		0.11	0.12	2.42	0.021	0.018	0.008	0.006	0.003	2.11	0.12	0.82	0.32	0.029	0.0136	-	-	-	2.1	3.0	
23		0.10	0.18	2.71	0.017	0.015	0.007	0.008	0.002	1.89	0.09	1.01	0.28	0.034	0.0140	-	-	-	2.4	2.7	

[Table 1-2]

Steel type	Classification	Chemical composition of Elements (mass%)															Y value	Z value		
		C	Si	Mn	P	S	V	Ti	Nb	Cr	Cu	Ni	Mo	Al	N	Ca			Zr	Mg
24	Comparative Example	0.07	0.14	2.47	0.014	0.012	0.008	0.008	0.003	1.87	0.10	1.21	0.32	0.032	0.0132	-	-	-	2.4	2.0
25		0.13	0.13	2.56	0.016	0.009	0.007	0.007	0.004	1.94	0.11	0.97	0.30	0.031	0.0128	-	-	-	2.4	2.6
26		0.10	0.52	2.51	0.021	0.018	0.007	0.009	0.003	2.14	0.11	1.01	0.24	0.029	0.0145	-	-	-	2.0	2.5
27		0.11	0.14	3.05	0.022	0.011	0.006	0.007	0.004	2.08	0.09	1.23	0.28	0.028	0.0139	-	-	-	2.0	2.5
28		0.10	0.13	2.57	0.018	0.012	0.012	0.008	0.003	1.97	0.09	1.11	0.26	0.038	0.0148	-	-	-	2.6	2.3
29		0.09	0.11	2.61	0.021	0.008	0.008	0.011	0.002	2.08	0.11	0.94	0.32	0.034	0.0134	-	-	-	2.5	2.8
30		0.10	0.11	2.48	0.020	0.009	0.007	0.007	0.007	2.12	0.13	0.91	0.30	0.029	0.0157	-	-	-	1.8	2.7
31		0.10	0.14	2.63	0.017	0.011	0.011	0.012	0.003	1.94	0.10	1.27	0.27	0.031	0.0144	-	-	-	2.2	2.1
32		0.09	0.12	2.55	0.023	0.009	0.007	0.011	0.006	1.90	0.09	1.14	0.33	0.028	0.0154	-	-	-	1.8	2.2
33		0.09	0.11	2.41	0.022	0.013	0.011	0.015	0.008	2.09	0.09	0.96	0.29	0.033	0.0132	-	-	-	2.5	2.5
34		0.11	0.10	2.50	0.019	0.018	0.009	0.007	0.003	2.52	0.13	0.98	0.24	0.034	0.0151	-	-	-	2.3	2.6
35		0.09	0.14	1.88	0.017	0.009	0.008	0.007	0.004	1.86	0.13	0.72	0.36	0.033	0.0138	-	-	-	2.4	2.6
36		0.10	0.12	2.73	0.023	0.008	0.007	0.008	0.004	2.10	0.12	1.65	0.31	0.029	0.0143	-	-	-	2.0	1.7
37		0.10	0.10	2.38	0.020	0.010	0.008	0.005	0.003	2.07	0.09	1.21	0.08	0.028	0.0133	-	-	-	2.1	2.0
38		0.09	0.13	2.53	0.009	0.012	0.008	0.009	0.002	1.94	0.08	0.89	0.30	0.022	0.0130	-	-	-	1.7	2.8
39		0.11	0.17	2.64	0.014	0.009	0.009	0.008	0.003	1.84	0.10	1.14	0.31	0.031	0.0210	-	-	-	1.5	2.3
40		0.10	0.15	2.51	0.017	0.014	0.009	0.007	0.003	2.01	0.10	1.08	0.38	0.030	0.0141	0.0110	-	-	2.1	2.3
41		0.11	0.13	2.56	0.016	0.015	0.006	0.009	0.004	2.00	0.11	1.17	0.26	0.029	0.0138	-	0.0120	-	2.1	2.2
42		0.11	0.14	2.49	0.023	0.010	0.007	0.004	0.003	1.97	0.09	1.35	0.22	0.035	0.0154	-	-	0.0120	2.3	1.8
43		0.09	0.13	2.68	0.014	0.008	0.009	0.008	0.004	2.21	0.15	1.14	0.36	0.031	0.0113	-	-	-	2.7	2.4
44		0.09	0.12	2.37	0.015	0.008	0.008	0.007	0.003	2.04	0.11	1.06	0.32	0.042	0.0142	-	-	-	3.0	2.2
45		0.10	0.12	2.49	0.018	0.010	0.009	0.007	0.003	1.94	0.09	1.11	0.29	0.037	0.0132	-	-	-	2.8	2.2
46		0.10	0.10	2.24	0.010	0.010	0.006	0.009	0.004	1.77	0.09	1.60	0.35	0.032	0.0137	-	-	-	2.3	1.4
47		0.09	0.13	1.64	0.012	0.012	0.007	0.008	0.004	1.91	0.12	1.58	0.27	0.035	0.0151	-	-	-	2.3	1.0
48		0.10	0.11	2.52	0.009	0.018	0.009	0.007	0.003	2.01	0.08	0.81	0.30	0.032	0.0124	-	-	-	2.6	3.1
49		0.10	0.12	2.94	0.009	0.011	0.008	0.009	0.004	2.05	0.10	0.82	0.28	0.029	0.0141	-	-	-	2.1	3.6

[Table 2]

Steel type	Classification	Tensile strength (MPa)	Impact value (J/cm <sup>2</sup> )	Average grain size of cementite (μm)	Average size of martensite blocks (μm)	Amount of residual austenite (%)
1		1211	188	0.03	3.5	3

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(continued)

Steel type	Classification	Tensile strength (MPa)	Impact value (J/cm <sup>2</sup> )	Average grain size of cementite (μm)	Average size of martensite blocks (μm)	Amount of residual austenite (%)
2	Example	1383	166	0.03	4.7	4
3		1296	144	0.03	4.3	2
4		1343	143	0.04	4.1	3
5		1278	136	0.04	3.7	4
6		1309	172	0.03	4.7	3
7		1339	199	0.04	4.4	3
8		1358	144	0.04	3.7	2
9		1332	178	0.03	3.9	3
10		1321	147	0.04	4.1	3
11		1297	151	0.04	3.8	2
12		1275	154	0.03	3.8	3
13		1268	141	0.04	3.3	2
14		1334	181	0.03	4.2	3
15		1303	140	0.04	3.8	2
16		1302	149	0.03	5.2	3
17		1273	148	0.04	4.9	2
18		1312	146	0.04	3.7	2
19		1267	148	0.03	5.4	4
20		1254	165	0.04	4.2	2
21		1353	183	0.04	4.7	2
22		1330	183	0.03	5.5	2
23		1308	171	0.04	4.3	3
24		Comparative Example	1184	157	0.03	4.7
25	1414		61	0.04	4.5	4
26	1309		62	0.02	3.3	2
27	1345		49	0.03	4.1	2
28	1324		34	0.03	3.2	3
29	1297		42	0.04	3.1	4
30	1314		38	0.03	3.4	2
31	1332		51	0.03	3.2	3
32	1299		34	0.04	3.4	3
33	1311		33	0.03	3.1	2
34	1341		68	0.04	3.2	3
35	1262		60	0.03	4.5	2
36	1294		47	0.04	4.6	12
37	1294		52	0.08	8.1	<u>3</u>

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(continued)

Steel type	Classification	Tensile strength (MPa)	Impact value (J/cm <sup>2</sup> )	Average grain size of cementite (μm)	Average size of martensite blocks (μm)	Amount of residual austenite (%)
38		1262	44	0.04	10.6	2
39		1345	63	0.04	5.2	2
40		1293	66	0.03	3.2	2
41		1360	60	0.03	4.3	2
42		1335	58	0.03	4.1	2
43		1262	67	0.04	3.7	3
44		1289	51	0.03	4.3	4
45		1310	48	0.04	3.9	3
46		1299	49	0.04	3.9	15
47		1307	27	0.03	4.2	20
48		1300	58	0.03	5.3	2
49		1284	44	0.04	4.3	3

**[0052]** In the examples of steels Nos. 1 to 23 in which the chemical composition was in the specification range of the present invention, after quenching and tempering under the above described conditions were carried out, the tensile strength was 1,200 MPa or more, and the Charpy impact value at -20°C was 75 J/cm<sup>2</sup> or more. In the steels Nos. 1 to 23, after quenching and tempering under the above described conditions were carried out, cementite and martensite blocks were miniaturized, and the amount of residual austenite was decreased.

**[0053]** In contrast, in Comparative Example No. 24, the C content was insufficient, and thus a necessary tensile strength could not be obtained after quenching and tempering. In Comparative Example No. 25, the C content was excessive, and thus the tensile strength became excessively high after quenching and tempering, and the low-temperature toughness was insufficient.

**[0054]** In Comparative Example No. 26, the Si content was excessive, in Comparative Example No. 27, the Mn content was excessive, and, in Comparative Example No. 34, the Cr content was excessive. These excessive Si, Mn, and Cr degraded the toughness of the steel, and thus the low-temperature toughness was insufficient in Comparative Examples Nos. 26, 27, and 34 after quenching and tempering.

**[0055]** In Comparative Examples Nos. 28 to 33, one or more of the V content, the Ti content, and the Nb content were excessive, and thus the precipitation strengthening by VN, NbC, or Ti(C, N) degraded the toughness of the steel, and the low-temperature toughness was insufficient in Comparative Examples Nos. 28 to 33 after quenching and tempering.

**[0056]** In Comparative Example No. 35, the Ni content was insufficient, and the effect of Ni for improving low-temperature toughness was small, and thus the low-temperature toughness was insufficient. On the other hand, in Comparative Example No. 36, the Ni content was large, and the amount of residual austenite increased after quenching and tempering, and thus the low-temperature toughness was insufficient after quenching and tempering.

**[0057]** In Comparative Example No. 37, the Mo content was insufficient, cementite which acted as an origin of fracture became coarse after quenching and tempering, and the martensite (the block size) also became coarse, and thus the low-temperature toughness was poor.

**[0058]** In Comparative Example No. 38, the Al content was insufficient, and thus an effect for miniaturizing grains could not be obtained sufficiently, the martensite (the block size) became coarse after quenching and tempering, and the low-temperature toughness was insufficient.

**[0059]** In Comparative Example No. 39, the N content was excessive, and thus the low-temperature toughness was insufficient after quenching and tempering due to an increase in the amount of solute of N.

**[0060]** In Comparative Examples Nos. 40 to 42, the Ca content, the Zr content, or the Mg content was excessive, and thus these elements degraded the toughness of the steel, and the low-temperature toughness was insufficient after quenching and tempering.

**[0061]** In Comparative Examples Nos. 43 to 45, 48, and 49, the amounts of the respective alloying elements were in the specification ranges, but the Y value or the Z value exceeded the specification range, and thus, conversely, the steel became brittle, and the low-temperature toughness was insufficient after quenching and tempering.

[0062] In Comparative Examples Nos. 46 and 47, the amounts of the respective alloying elements were in the specification ranges, but the Y value was below the specification range, and thus, the amount of residual austenite increased after quenching and tempering, and the low-temperature toughness was insufficient.

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**Claims**

1. A steel comprising, by unit mass%,  
 C: 0.08% to 0.12%;  
 Si: 0.05% to 0.50%;  
 Mn: 1.50% to 3.00%;  
 P: 0.040% or less;  
 S: 0.020% or less;  
 V: 0.010% or less;  
 Ti: 0.010% or less;  
 Nb: 0.005% or less;  
 Cr: 1.00% to 2.50%;  
 Cu: 0.01% to 0.50%;  
 Ni: 0.75% to 1.60%;  
 Mo: 0.10% to 0.50%;  
 Al: 0.025% to 0.050%;  
 N: 0.0100% to 0.0200%;  
 Ca: 0% to 0.0100%;  
 Zr: 0% to 0.0100%;  
 Mg: 0% to 0.0100%; and  
 a remainder including Fe and impurities,  
 wherein a Y value defined by Equation (a) is 2.6 or less, and  
 a Z value defined by Equation (b) is 1.5 or more and 3.0 or less,

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$$Y=(Al)/(N) \quad \cdots \quad (a)$$

$$Z=(Mn)/(Ni) \quad \cdots \quad (b)$$

35

symbols (Al), (N), (Mn), and (Ni) in the equations represent amounts of elements relating to the respective symbols in the steel, by unit mass%.

2. The steel according to claim 1 comprising, by unit mass%, one or more selected from the group consisting of  
 Ca: 0.0005% to 0.0100%;  
 Zr: 0.0005% to 0.0100%; and  
 Mg: 0.0005% to 0.0100%.

40

45

50

55

FIG. 1

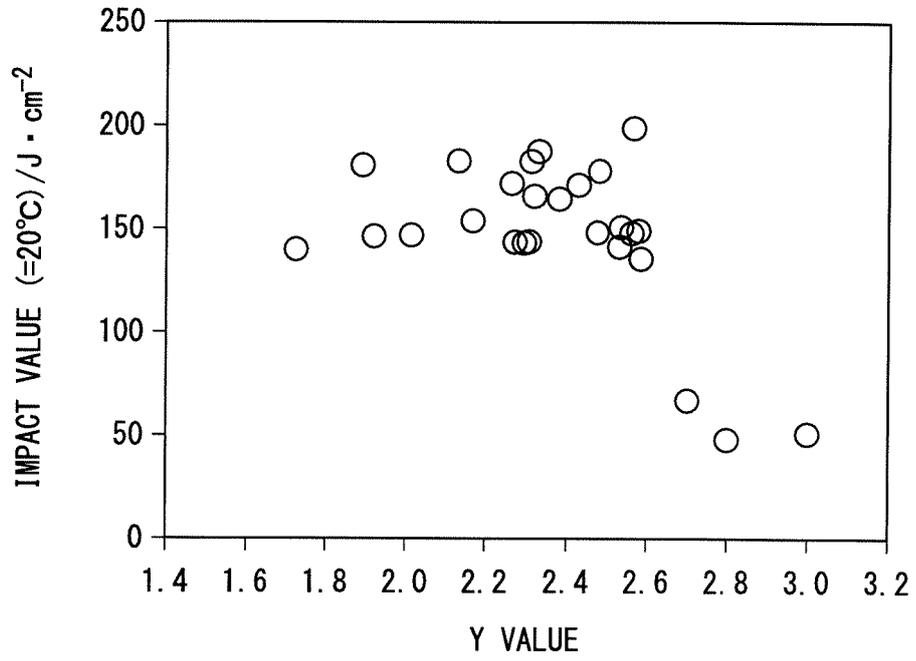
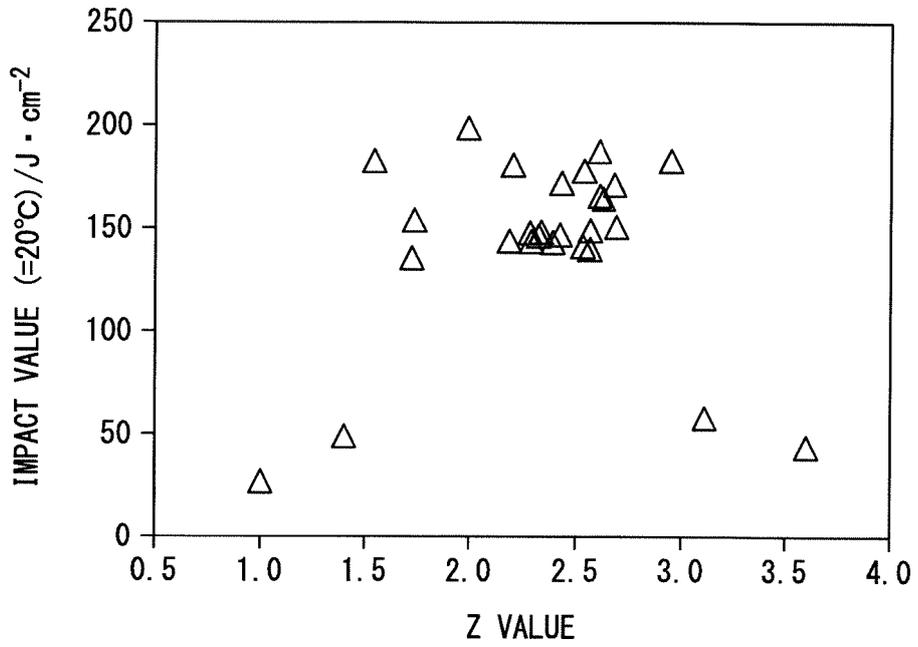


FIG. 2



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2016/054853

5	A. CLASSIFICATION OF SUBJECT MATTER C22C38/00(2006.01) i, C22C38/58(2006.01) i	
	According to International Patent Classification (IPC) or to both national classification and IPC	
10	B. FIELDS SEARCHED	
	Minimum documentation searched (classification system followed by classification symbols) C22C38/00-38/60	
15	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 1996-2016 Kokai Jitsuyo Shinan Koho 1971-2016 Toroku Jitsuyo Shinan Koho 1994-2016	
	Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)	
20	C. DOCUMENTS CONSIDERED TO BE RELEVANT	
	Category*	Citation of document, with indication, where appropriate, of the relevant passages
25	A	WO 2007/009517 A1 (RUD KETTEN RIEGER & DIETZ GMBH U. CO. KG), 25 January 2007 (25.01.2007), & EP 1802894 B1 & DE 102005034140 A1
30	A	EP 2159296 A1 (SIDENOR INVESTIGACION Y DESARROLLO, S.A.), 03 March 2010 (03.03.2010), & WO 2008/125700 A1 & BR PI0721566-5 A2
35	A	JP 2012-149277 A (Daido Steel Co., Ltd.), 09 August 2012 (09.08.2012), (Family: none)
40	<input checked="" type="checkbox"/> Further documents are listed in the continuation of Box C. <input type="checkbox"/> See patent family annex.	
45	* Special categories of cited documents:	"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
	"A" document defining the general state of the art which is not considered to be of particular relevance	"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
	"E" earlier application or patent but published on or after the international filing date	"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
	"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&" document member of the same patent family
	"O" document referring to an oral disclosure, use, exhibition or other means	
	"P" document published prior to the international filing date but later than the priority date claimed	
50	Date of the actual completion of the international search 16 May 2016 (16.05.16)	Date of mailing of the international search report 24 May 2016 (24.05.16)
55	Name and mailing address of the ISA/ Japan Patent Office 3-4-3, Kasumigaseki, Chiyoda-ku, Tokyo 100-8915, Japan	Authorized officer  Telephone No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2010-111936 A (Sumitomo Metal Industries, Ltd.), 20 May 2010 (20.05.2010), (Family: none)	1-2
A	JP 2009-114484 A (Sanyo Special Steel Co., Ltd.), 28 May 2009 (28.05.2009), (Family: none)	1-2

**REFERENCES CITED IN THE DESCRIPTION**

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- JP S5822361 B [0005]
- JP S5896856 B [0005]
- JP S59159972 B [0005]
- JP S59159969 B [0005]
- JP S62202052 B [0005]
- JP S63203752 B [0005]