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(54) **STEEL FOR WARM WORKING, METHOD OF WARM WORKING OF THE STEEL, AND STEEL MATERIAL AND STEEL PART OBTAINED BY THE SAME**

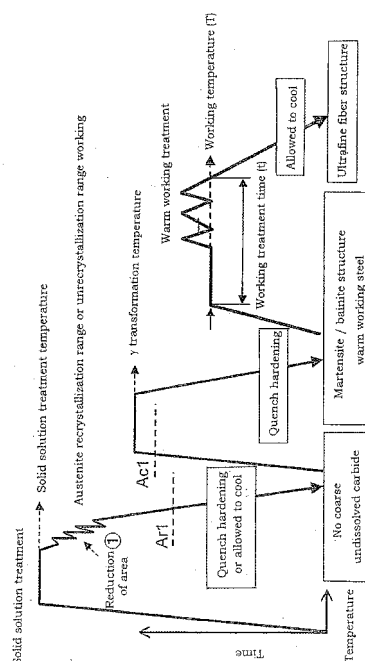
(57) There are provided a steel for warm working, to be subjected to warm working as various structures, components of cars, and the like, a warm working method thereof, and a steel material and a steel component obtainable from the warm working method. [Solving Means] A steel is to have a particle dispersion type fiber structure formed in the matrix by warm working. The steel is **characterized in that** the total amount of the dispersed second-phase particles at room temperature is 7×10^{-3} or more in terms of volume fraction, and the Vickers hardness (HV) is equal to or larger than the hardness H of the following equation (2):

$$H = (5.2 - 1.2 \times 10^{-4} \lambda) \times 10^2 \dots (2)$$

when the steel is subjected to any of annealing, tempering, and aging treatments in the as-unworked state under conditions such that a parameter λ expressed by the following equation (1):

$\lambda = T(\log t + 20)$ (T; temperature (K), t; time (hr)) ... (1)
is 1.4×10^4 or more in a prescribed temperature range of 350°C or more and Ac1 point or less. This steel is taken as the steel for warm working.

Fig. 1



Description

Technical Field

[0001] The present invention relates to a steel to be worked into various structures, components of cars, and the like for use. More particularly, it relates to a steel for warm working to be subjected to warm working, and a warm working method thereof, and a steel material and a steel component obtainable from the warm working method.

Background Art

[0002] In recent years, there has been a demand for a tougher and higher performance high strength steels than ever with an increase in size of structures, and a reduction in weight of car components or the like. As the means for improving the toughness of the steel, conventionally, there are generally known: (1) reduction of impurity elements such as P and S causing embrittlement, (2) refinement and reduction of inclusions, (3) addition of alloy elements, (4) reduction of carbon, (5) crystal grain refinement, (6) refinement of dispersed second-phase particles such as carbide particles, and the like.

[0003] Out of these, crystal grain refinement receives attention because of the following: it has both the effects of reduction of concentration of stress to the grain boundary and dilution at the grain boundary of impurity elements, and it can raise the brittleness fracture stress simultaneously with an increase in yield stress. For example, in recent years, an attempt has been made to reduce the ferrite grain size as ultrafine as 1 μm or less in low carbon steel allowing for conservation of natural resources or recyclability, and thereby to achieve strengthening and the longer life of the steel.

[0004] However, the studies on the crystal grain refinement of a low carbon ferrite steel up to this point concentrate on the strength level of 1000 MPa or less (e.g., Non-Patent Document 1-2; Patent Document 1-2). This is due to the following. In order to obtain a high strength of 1000 MPa or more only by refinement of ferrite grains, the crystal grains are required to be reduced in size to as ultrafine as 0.5 μm or less. Thus, the reduction in grain size to as ultrafine as 0.5 μm or less is very difficult with a thermo-mechanical treatment of a steel intended for mass production. Further, on a laboratory scale, ultrafine grains of 0.5 μm or less can be obtained with a super heavy deformation method such as MM (Non-Patent Document 3) or ARB (Non-Patent Document 4) of powder metallurgy. However, such an ultrafine grain steel shows almost no uniform elongation, and the elongation is mostly caused by ununiform deformation due to necking, resulting in a large reduction in ductility. The same early plasticity instability as this is also observed in a pure iron wire dislocation strengthened by wire drawing (Non-Patent Document 5).

In general, strengthening of a steel unfavorably largely reduces various characteristics such as ductility, toughness, delayed fracture resistance characteristics, fatigue characteristics, formability. Particularly, when a very versatile low alloy martensitic steel is strengthened to 1.2 GPa or more, it is remarkably reduced in toughness, delayed fracture resistance characteristics, and the like. For this reason, the high strength steel is largely prevented from being put into practical use. Under such circumstances, there is a strong demand for simultaneously achieving higher strength and higher toughness, and the improvement of the delayed fracture resistance characteristics of a low alloy steel. However, according to conventional findings, as the means for improving the fracture characteristics of the low alloy martensitic steel, the following are conceivable: (a) high temperature tempering avoiding the tempering embrittlement temperature range in the vicinity of 500°C, (b) prior-austenite grain refinement, (c) ausforming, and (d) formation of fibrous structure, or combinations thereof. However, the application of these means faces the following problems.

(a) High temperature tempering

High temperature tempering is carried out at about 550°C or more, and A 1 point or less. According to this, there are advantages as follows: (1) the internal stress introduced upon quenching can be largely reduced accompanied by recovery of dislocation; (2) the coherent precipitate (e.g., film-like cementite) reducing the fracture toughness can be made incoherent (be spheroidized), and other advantages. For this reason, for a steel for a mechanical structure particularly requiring toughness, tempering is generally carried out in the vicinity of 650°C. However, within such a temperature range, the dispersed second-phase particles also grow with ease during tempering, and hence the reduction in strength of the steel is inevitable. Further, in the related art, there is adopted a method in which large quantity of carbon is added to increase the amount of carbide precipitated, thereby to increase the strength. However, the toughness is reduced. Therefore, strengthening only by high temperature tempering has its limitation. The ones of which strengthening can be achieved even by high temperature tempering are limited to the steels in which a large amount of special alloy elements have been added such as maraging steels (Non-Patent Documents 6-10).

(b) Crystal grain refinement

For strengthening of the steel, it is indispensable to refine prior-austenite grains so as to ensure enough toughness. As the method of austenite grain refinement, there are (1) a method by recrystallization of processed austenite, and

(2) a method using phase transformation. Out of these, the thermo-mechanical treatment for performing an austenitizing treatment after processing a martensite structure within the cold or warm range, classified into the latter, was thought to be capable of refining austenite grains most effectively (Non-Patent Documents 11 and 12). For example, it is known (Patent Document 3) that refinement of austenite grains of several micrometers or less improves the toughness of the tempered martensitic steel (Non-Patent Document 13), and improves the delayed fracture characteristics (Patent Document 4). With refinement of austenite, as the crystal grains become finer, the grain growth rate also increases. For this reason, it is a particularly important point how the grain growth is controlled in austenite. Under such circumstances, in the related art, the following are generally applied: dispersion of pinning grains effective for suppressing the growth of austenite, reduction of the austenitization temperature, austenitization for a rapid short time using high-frequency heating, and the like. However, it is very difficult to suppress the growth of ultrafine austenite grains. In actuality, grain refinement reaches a limit at about several micrometers. Whereas, excessive refinement of crystal grains promotes the diffusion type phase transformation at the grain boundary, which unfavorably makes hardening difficult, and also causes other problems. Thus, the process window for austenite grain refinement is relatively narrow.

(c) Ausforming

Ausforming is a treatment in which an austenitized steel is quenched to a metastable austenite range, and processed at the temperature, followed by quench hardening, thereby to cause martensite or bainite transformation, and then, tempering is carried out. It has a feature of being capable of strengthening the steel without much impairing the toughness. With the ausforming, it is considered as follows. The effects such as (1) refinement of packets or blocks regarded as effective crystal grains, (2) succession of dislocation from worked austenite to martensite, and (3) pinning of dislocation by carbon atoms or carbides occur in an overlapping manner, thereby to strengthen the steel. In recent years, improved ausforming in which working is carried out within the high-temperature metastable austenite range has been applied to a medium carbon low alloy steel. Thus, improvements of the fatigue and delayed fracture characteristics have been reported. Further, the main factors of the improvements of characteristics by improved ausforming are considered to be refinement of the matrix structure, suppression of formation of the coarse grain boundary cementite due to introduction of the grain boundary unevenness (Non-Patent Document 14) or formation of the texture (Non-Patent Document 15). However, ausforming is working of the austenite structure. Therefore, it requires that the alloy components and the thermo-mechanical treatment conditions should be strictly adjusted so as to prevent the metastable austenite phase from undergoing proeutectoid ferrite transformation or pearlite transformation during working. Further, there is also another problem that quenching crack is caused during cooling after working. Accordingly, the applicable members are also limited to those in simple shapes such as a plate and a rod.

(d) Fibrous structure formation

For enhancing the toughness of a steel, it is also effective to effect the formation of a fiber structure in the inside by cold or warm working. This has already been proposed for the steel subjected to an ausforming treatment (Non-Patent Documents 16 and 17), the heavy cold drawing high-strength low carbon wire rod (Patent Document 5), piano wire, pure iron wire (Non-Patent Document 5), and the like.

[0005] For working of steel materials, cold working is the main process of member formation today because it can mass-produce members in complicated shapes such as bolts with high dimensional accuracy. However, for such steel materials as those having a tensile strength of more than 1.2 GPa, cold forging thereof is very difficult because of the strength. For this reason, the members in which a fiber structure is formed by the cold molding process as described above are limited to wire rods and the like.

[0006] On the other hand, many attempts have also been made until now on warm working in a two phase range of a ferrite phase and a carbide at Ac 1 point or less. For example, there are known a method and a forming method in which a material for a high strength member and a high strength steel material is prepared; the material is warm worked so as to form a member in a desired geometrical shape in such a state as to substantially hold or enhance the strength characteristics of the material; as a result, a fiber structure is formed, thereby to make a high strength steel structure member with a tensile strength of at least 1 GPa (Patent Document 6).

[0007] Further, there is also known a manufacturing method of a formed product characterized by the following: a material having an ultrafine structure is warm worked or cold worked, and a steel material including drawn ferrite grains with a minor axis of 3 μm or less is used as a material; it is not subjected to a refining treatment, and only forming is carried out, and a refining treatment is not carried out (Patent Document 3).

[0008] Whereas, for a steel having a duplex phase structure such as a tempered martensite structure, warm working is applied for the purpose of obtaining a worked structure before a quench hardening treatment for refining a reverse-transformed austenite (Non-Patent Documents 11 and 12). The strength of the steel is achieved by a refining treatment following warm working. For this reason, an attempt has not been made to use the material in the as-warm worked state of the tempered martensite structure.

[0009] Further, for warm straightening working of a high carbon steel having a carbon content of 0.7 wt% or more, an

over 1.8 GPa class wire rod can be obtained. However, the elongation of the wire rod is as low as around 6 % (Non-Patent Document 18).

Non-Patent Document 1: TETSU TO HAGANE, 85 (1999), P. 620

Non-Patent Document 2: ISIJ International, 44 (2004), P. 1063

5 Non-Patent Document 3: SOSEI TO KAKOU (Journal of the Japan Society for technology of plasticity), 41 (2000), P. 13

Non-Patent Document 4: TETSU TO HAGANE, 88 (2002), P. 359

Non-Patent Document 5: ASM, 62 (1969), P. 623

Non-Patent Document 6: Trans. ASM, 61 (1968), P. 798

Non-Patent Document 7: Metal. Trans., 1 (1970), P. 2011

10 Non-Patent Document 8: Mat. Sci. Tech., 19 (2003), P. 117

Non-Patent Document 9: Mat. Sci. Tech., 7 (1991), P. 1082

Non-Patent Document 10: Mat. Sci. Eng., A398 (2005), P.367

Non-Patent Document 11: TEKKOU NO KESSYOURYU CYOUBISAIKA BUKAI Report (The Iron and Steel Institute of Japan), (1991), P. 64

15 Non-Patent Document 12: Proc. First International Conference on Advanced Structural Steels, (2002), P. 65

Non-Patent Document 13: Ultrafine-Grain Metals, Proc. the 16th sagamore Army Materials Conference, (1969), P. 138

Non-Patent Document 14: CAMP-ISIJ, 12 (1999), P. 565

Non-Patent Document 15: CAMP-ISIJ, 12 (1999), P. 1045-1048

Non-Patent Document 16: ASM, 55 (1962), P654

20 Non-Patent Document 17: Met Trans., 1 (1970), P3037

Non-Patent Document 18: J. Japan Inst. Metals, 32 (1968), P. 289

Patent Document 1: JP-A-2004-285437

Patent Document 2: JP-A-2005-194547

Patent Document 3: JP-A-2004-60046

25 Patent Document 4: JP-A-11-80903

Patent Document 5: JP-B-6-53915

Patent Document 6: U.S. Pat. No. 5236520

Disclosure of the Invention

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Problems that the Invention is to Solve

[0010] As described above, prior-austenite grain refinement and ausforming are important toughness-enhancing technology of a steel, and studies and inventions thereon add up to massive amounts. However, in these processes, quench
35 hardening and tempering are basic, so that strengthening receives restrictions by the problems of hardenability and quenching crack, and the problem of temper brittleness. Further, with an increase in strength, the amount of the dispersed second-phase particles of carbides or the like necessary for strengthening also increases, which makes softening by spheroidizing or the like difficult. Whereas, when particularly carbides become coarse by annealing, unfavorably, cracks occur in the inside of the material in the process of forming the material into a component by cold forging or the like, or
40 other problems occur. For these reasons, as far as the conventional strengthening process by quench hardening and tempering, it is considered impossible to largely improve the characteristics of such an over 1.5 GPa class high strength steel as to result in a tensile strength of 1.2 GPa or more, and further, as to make softening difficult, and to put the steel into practical use.

[0011] Further, the studies and inventions regarding warm working up to this point mainly aim at forming into a member and manufacturing of the prior structure. For this reason, in most cases, a relatively soft matrix structure such as a ferrite or pearlite structure with a low deformation resistance, or a martensite structure subjected to tempering at high temper-
45 atures is used as a starting material. Thus, under such conditions as to result in reduction of the deformation resistance, warm working is carried out. Further, the fine duplex structure is not formed in consideration of the dispersion state of the dispersed second-phase particles and the thermal stability. Thus, there has not yet been implemented a high strength
50 member with a tensile strength of 1.2 GPa or more after warm working, and excellent in ductility, toughness, delayed fracture characteristics, and the like. Particularly for the duplex phase structure steel such as a tempered martensitic steel having a tensile strength of 1.2 GPa or more at room temperature, there is a possibility that warm working cannot be carried out because of its strength. For this reason, application of warm working thereto has been regarded almost impossible conventionally.

[0012] Under such circumstances, it is an object of the present invention to provide a steel for warm working which resolves the problems as described above, and which can form a particle dispersion type fibrous structure for obtaining a high strength steel having a tensile strength of 1.2 GPa or more, being excellent in ductility and delayed fracture resistance characteristics, and has been tremendously improved in toughness by warm working, and a warm working

method using the same. Further, it is another object to provide steel materials such as a steel plate and a rod steel, and steel components such as a bolt and cut machined products having the foregoing characteristics obtained therefrom.

Means for Solving the Problems

[0013] The present inventors conducted a close study in order to resolve the foregoing problems. As a result, they made the following inventions.

[0014] First a steel for warm working, being to have a particle dispersion type fiber structure formed in the matrix by warm working, the steel characterized by including an alloy element or/and dispersed second-phase particles such that the total amount of the dispersed second-phase particles at room temperature is 7×10^{-3} or more in terms of volume fraction, and the steel characterized by having a Vickers hardness (HV) of equal to or larger than the hardness H of the following equation (2):

$$H = (5.2 - 1.2 \times 10^{-4}\lambda) \times 10^2 \dots (2)$$

when the steel is subjected to any heat treatment of annealing, tempering, and aging treatments in the as-unworked state under conditions such that a parameter λ expressed by the following equation (1):

$$\lambda = T(\log t + 20) \text{ (T; temperature (K), t; time (hr))} \dots (1)$$

is 1.4×10^4 or more in a prescribed temperature range of 350°C or more and Ac1 point or less.

[0015] Second: the steel for warm working, characterized in that 80 % by volume or more of the matrix structure is any single structure of martensite and bainite, or a mixed structure thereof.

[0016] Third: the steel for warm working, characterized by including, in chemical composition, C: 0.70 wt% or less, Si: 0.05 wt% or more, Mn: 0.05 wt% or more, Cr: 0.01 wt% or more, Al: 0.5 wt% or less, O: 0.3 wt% or less, and N: 0.3 wt% or less, and the balance being substantially Fe and inevitable impurities, in the claim.

[0017] Fourth: the steel for warm working, characterized by further including, one or two or more selected from a group consisting of Mo: 5.0 wt% or less, W: 5.0 wt% or less, V: 5.0 wt% or less, Ti: 3.0 wt% or less, Nb: 1.0 wt% or less, and Ta: 1.0 wt% or less.

[0018] Fifth: the steel for warm working, characterized by further including one or two of Ni: 0.05 wt% or more and Cu: 2.0 wt% or less.

[0019] Sixth: a warm working method characterized by performing warm working for imparting a stain of 0.7 or more in a temperature range of 350°C or more and Ac1 point -20°C or less on any of the foregoing steels for warm working.

[0020] Seventh: the warm working method, characterized in that after performing warm working, an aging treatment is performed in a temperature range of 350°C or more and Ac1 point or less.

[0021] Eighth: a steel material which is a steel having a particle dispersion type fiber structure obtained by warm working any of the foregoing steels for warm working, characterized in that the average grain diameter of the minor axes of a fibrous ferrite crystal forming the matrix structure is 3 μm or less, the second-phase particles are finely dispersed in the matrix structure at a volume fraction of 7×10^{-3} or more, and the Vickers hardness at room temperature is HV 3.7×10^2 or more.

[0022] Ninth: the steel material, characterized by having a matrix structure including a fibrous crystal of which the average grain diameter of the minor axes is 1 μm or less.

[0023] Tenth: the steel material being any of the foregoing steel materials, characterized by having a matrix structure including a fibrous crystal of which the average grain diameter of the minor axes is 0.5 μm or less.

[0024] Eleventh: the steel material being any of the foregoing steel materials, characterized in that the average particle diameter of the major axes of the dispersed second-phase particles is 0.1 μm or less.

[0025] Twelfth: a steel plate obtained by warm working any of the foregoing steels for warm working into a plate form, characterized by including a fiber structure formed in at least the surface layer part thereof.

[0026] Thirteenth: a wire rod steel obtained by warm working any of the foregoing steels for warm working into a bar form or a wire form, characterized by including a fiber structure formed in at least the surface layer part thereof.

[0027] Fourteenth: a bolt obtained by warm working any of the foregoing steels for warm working, characterized by including a fiber structure formed in at least the surface layer part of the screw part.

[0028] Fifteenth: a steel component characterized by being the one obtained by working the steel material according to any of the foregoing items into a component by cutting. Advantage of the Invention

[0029] As for the steel for warm working of the first invention, the softening resistance when the steel is heated, namely,

the thermal stability and the total amount of the matrix structure and the dispersed second-phase particles are controlled. As a result, a particle dispersion type fibrous structure can be formed when the steel is subjected to warm working, and the Vickers hardness after warm working can be set at 3.7×10^2 or more. As a result, there is provided a steel for warm working capable of being tremendously improved in toughness while keeping the tensile strength of 1.2 GPa or more at ordinary temperatures.

[0030] In accordance with the second invention, the structure of the steel for warm working as the prior working structure is transformed into an ultrafine duplex structure including dispersed second-phase particles such as carbide particles finely dispersed therein by using martensite transformation or bainite transformation. As a result, it becomes possible to effect the formation of a fiber structure even in the inside with efficiency when the steel is subjected to warm working. In addition to this, it becomes possible to largely improve the delayed fracture resistance characteristics.

[0031] In accordance with the third invention, the alloy composition excellent in cost efficiency and recyclability can achieve strengthening of the steel obtained when the steel is subjected to warm working.

[0032] In accordance with the fourth invention, it is possible to disperse dispersed second-phase particles which are finer and excellent in hydrogen trapping property. Further, it is possible to strengthen the steel material obtained when the steel is subjected to warm working, and to largely enhance the toughness in a low temperature range, and the delayed fracture resistance characteristics.

[0033] In accordance with the fifth invention, it is possible to improve the toughness further to a lower temperature range.

[0034] In accordance with the sixth invention, while working the steel for warm working into a desired shape, a fiber structure can be formed to obtain a high toughness. Incidentally, as the equipment, warm working equipment which has been conventionally put into practical use can be utilized. Therefore, the invention has a very high practical utility.

[0035] In accordance with the seventh invention, by performing an aging treatment with the fiber structure finely held, it is possible to manufacture a steel showing less variations in characteristics than the sixth invention.

[0036] In accordance with the eighth invention, there is implemented a steel material which not only has high toughness, but also has also been improved in secondary workability by formation of the fine fiber structure.

[0037] In accordance with the ninth invention, a dense fiber structure with an average spacing of the minor axes of 1 μm or less is developed, and in accordance with the tenth invention, a dense fiber structure with an average spacing of the minor axes of 0.5 μm or less is developed. Thus, there are implemented steel materials which have been much more enhanced in strength, toughness, and workability than before warm working.

[0038] In accordance with the eleventh invention, by controlling the average particle diameter of the major axes of the dispersed second-phase particles to 0.1 μm or less, it is possible to implement much more strengthening and enhancement of the toughness with dispersion of a small amount of the dispersed second-phase particles.

[0039] In accordance with the twelfth and thirteenth inventions, the steel material not only has a high toughness and tensile strength, but also has a secondary workability. For this reason, there are implemented a steel plate and a steel rod wire which have been tremendously enhanced in practical utility, usable for manufacturing various components and products.

[0040] In accordance with the fourteenth invention, there is implemented a bolt excellent in impact strength and delayed fracture resistance, in which a fiber structure is formed in the root of the thread of the screw part to which a stress particularly concentrates.

[0041] In accordance with the fifteenth invention, even a high strength component in a complicated shape is provided as the one excellent in impact strength and delayed fracture resistance.

[0042] As described above, there is provided a high strength steel multiphased by fine dispersion of a small amount of dispersed second-phase particles. Particularly, even an ultrahigh strength steel which is hard to soften and is hard to form is applied with prescribed deformation in a temperature range in which the deformation resistance is reduced and no cracks occur in the material, to be formed into a prescribed shape (thin plate, thick plate, wire rod, or component). As a result, conventional spheroidizing and quench hardening and tempering treatments after component forming are omitted. At the same time, an ultrafine duplex phase structure is developed into a fibrous form. Thus, there is provided a high strength steel largely improved in the ductility, particularly the toughness, and the delayed fracture resistance characteristics in the relation of trade-off balance with high strength, and a member thereof.

[0043] The foregoing effects are due to the following mechanisms:

(a) CUltra grain refinement of crystal and formation of fibrous matrix structure by warm working

The following finding has been reached. A material satisfying given specific conditions can form a particle dispersion type fiber structure far more excellent in toughness and delayed fracture resistance characteristics even than conventional ausformed steels in the member. Namely, the pinning effect due to fine dispersion or precipitation of the second-phase particles is effectively used. Thus, in a temperature range in which recovery of the dislocation introduced by deformation appropriately occurs, but primary recrystallization or remarkable grain growth does not occur, the material is deformed, and applied with prescribed strain, thereby to refine crystal grains. As a result, it is possible to form an ultrafine grain duplex phase structure which is low in internal stress and has no starting point for occurrence

of cracks. Particularly, in such ultrafine grains, a fiber structure having a further narrower crystal grain boundary spacing is developed. As a result, it is possible to suppress not only the occurrence of cracks but also the propagation of cracks, and thereby to largely enhance the fracture toughness.

(b) Refinement of coarse second-phase particles

Even such coarse dispersed second-phase particles as to cause occurrence of cracks with cold working can be deformed relatively easily without occurrence of cracks with warm working. Thus, by utilizing decomposition and reprecipitation of the dispersed second-phase particles formed particularly during working, coarse film-like precipitates considered as the cause of grain boundary cracking can be not only spheroidized but also finely dispersed to be utilized for strengthening.

(c) Dispersion of ultrafine alloy carbides, intermetallic compounds, and the like

Alloy elements high in carbide forming ability such as Mo, V, W, Ta, Ti, and Nb form nano-size alloy carbides such as Mo₂C, V₄C₃, W₂C, TaC, NbC, and TiC in a temperature range in the vicinity of 500°C to 600°C independently from already existing cementite. For this reason, addition of these alloy elements is effective for strengthening of the steel. The maximum value of precipitation strengthening due to these nano-size alloy carbides is obtained in the transition range of the strengthening mechanism of from Cutting to Orowan mechanism. However, at such an aging stage, much coherent strain occurs around the precipitates, so that the toughness of the steel is reduced. For this reason, in general, the steel is tempered to the sufficiently overaged state of these carbides even somewhat sacrificing the strength of the steel. On the other hand, when the dynamic precipitation of these alloy carbides due to warm working is utilized, it is also possible to effect incoherent precipitation of the carbides without causing much growth of the carbides even in the precipitation transition temperature range. Namely, it is also possible to make the maximum use of precipitation strengthening of the alloy carbides due to the Orowan mechanism. Further, the same effects can also be expected for precipitation of intermetallic compounds including the alloy elements, and Ni, Al, or the like, nitrides, oxides, Cu particles, and the like.

Brief Description of Drawings

[0044]

[FIG. 1] FIG. 1 is a view showing one example of a thermo-mechanical treatment pattern.

[FIG. 2] FIG. 2 is a view showing one example of the thermo-mechanical treatment pattern.

[FIG. 3] FIG. 3 is a view showing one example of the thermo-mechanical treatment pattern.

[FIG. 4] FIG. 4 is a view showing the relationship of the temper hardness and $T(\log t + 20) = \lambda$, where T denotes the temper temperature (K), and t denotes the temper time (hr).

[FIG. 5] FIG. 5 is a view showing a 500°C warm worked structure (ultrafine fiber structure).

[FIG. 6] FIG. 6 is a view showing the relationship between the tensile strength and the impact value (U notch).

[FIG. 7] FIG. 7 is a view showing the relationship between the tensile strength and the absorption energy (V notch).

[FIG. 8] FIG. 8 is a view showing the relationship between the absorption energy and the test temperature.

[FIG. 9] FIG. 9 is a photographic view showing one example of the fracture form of a B steel subjected to a Charpy impact test (U notch).

[FIG. 10] FIG. 10 is a view showing the relationship between the hardness of the warm worked material and the aging temperature.

[FIG. 11] FIG. 11 is a view showing an ultrafine fiber structure formed in the center part of a plate material.

[FIG. 12] FIG. 12 is a view showing an ultrafine fiber structure formed in the surface layer part of a rod material.

Best Mode for Carrying Out the Invention

[0045] The present invention has the features as described above. However, below, the requirements of the invention and the like will be described in details.

[0046] A steel for warm working of the present invention is a steel which is to have a particle dispersion type fiber structure formed in the matrix by warm working, the steel characterized by including an alloy element or/and dispersed second-phase particles such that the total amount of the dispersed second-phase particles at room temperature is 7×10^{-3} or more in terms of volume fraction, and the steel characterized by having a Vickers hardness (HV) of equal to or larger than the hardness H of the following equation (2):

$$H = (5.2 - 1.2 \times 10^{-4}\lambda) \times 10^2 \dots (2)$$

when the steel is subjected to any heat treatment of annealing, tempering, and aging treatments in the as-unworked state under conditions such that a parameter λ expressed by the following equation (1):

$$\lambda = T(\log t + 20) \quad (T: \text{temperature (K)}, t: \text{time (hr)}) \dots (1)$$

is 1.4×10^4 or more, and preferably 1.5×10^4 or more in a prescribed temperature range of 350°C or more and Ac1 point or less. Thus, the steel for warm working of the invention changes in the dispersion state of the dispersed second-phase particles and the matrix structure during warm working to be performed thereon. Therefore, it is configured such that the lower limit of the equation (2) is set with respect to the hardness (structure) of the non-worked material obtained from the heat treatment simulating the heat history of warm working. Namely, as described below, the structure state is expressed by the hardness.

(a) Structure of steel for warm working

In order to simultaneously implement strengthening and enhancement of the toughness of a duplex phase structure steel by warm working, it is important that strengthening by dispersion of the dispersed second-phase particles in as small amount as possible and as fine as possible, and refinement of the matrix structure and the formation of the fiber structure can be simultaneously carried out. Then, in order to implement the formation of the ultrafine duplex phase structure, fine dispersion or fine dispersive power of the dispersed second-phase particles in the steel for warm working which is a material is important.

[0047] In the present invention, for the fine dispersion or fine dispersive power of the second-phase particles, the following three patterns can be considered:

- (i) In the steel for warm working, the second-phase particles have already been dispersed;
- (ii) In the steel for warm working, the second-phase particles are not dispersed, but during warm working, one type or two or more types of second-phase particles precipitate, and after a working treatment, a particle dispersion type fiber structure is formed; and
- (iii) In the steel for warm working, the second-phase particles have already been dispersed, but during warm working, other particles than these precipitate.

[0048] Then, dispersion (precipitation) strengthening by the dispersed second-phase particles depends upon the dispersion conditions such as the volume fraction of the secondary phase duplex particles, and the size, hardness, and shape of the particles. When dispersion strengthening is caused by the Orowan mechanism, from the following equation (A) (TEKKOU NO SEKISYUTSUSEIGYO METARAJII SAIZENNSENN, (the Iron and Steel Institute of Japan) (2001) P. 69), the amount of dispersion strengthening increases with a decrease in particle diameter (d) and with an increase in volume fraction (f). Namely, the dispersion conditions (and the dispersive power) of the dispersed second-phase particles have close relation with the hardness.

[0049]

$$\Delta\sigma = (3.2 Gb)/[(0.9 f^{1/2} - 0.8)d] \dots (A)$$

where G denotes the shear modulus of the steel, 80 GPa, and b denotes the Burgers vector, 0.25 nm.

However, when the particles is excessively reduced in diameter than a critical particle diameter, the dislocation ceases to be pinned by the particles. Thus, the particles come to be sheared by dislocation, so that the Orowan mechanism ceases to hold. In the so-called Cutting mechanism, in which particles are sheared by dislocation, the amount of dispersion strengthening increases with an increase in particle diameter. Namely, the minimum particle diameter with which the Orowan mechanism holds can provide the maximum amount of dispersion strengthening. The minimum particle diameter capable of achieving the maximum dispersion strengthening depends upon the hardness of the particles, and decreases in inverse proportion to the hardness of the particles (TEKKOU NO SEKISYUTSUSEIGYO METARAJII SAIZENNSENN, (the Iron and Steel Institute of Japan) (2001) P. 69). Therefore, when comparison is made in terms of the same volume fraction, the minimum particle diameter with which the Orowan mechanism holds decreases with an increase in hardness of the particles. Accordingly, the maximum amount of particle dispersion strengthening also increases.

[0050] For example, it is known that TiC is capable of carrying out effective dispersion particle strengthening because of its higher hardness and smaller density among alloy carbides. Now, assuming that TiC can provide a minimum particle

diameter to which the Orowan mechanism is applicable of 7 nm, a particle dispersion strengthening amount of about 0.9 GPa (TS (GPa) is nearly equal to 0.0032 HV, HV 2.8×10^2) is expectable in dispersion at a volume fraction of 7×10^{-3} . Incidentally, with a density of TiC of 4.94 Mg/m³, an atomic weight of Ti of 47.9, and an atomic weight of C of 12, Ti and C necessary for precipitating TiC at a volume fraction of 7×10^{-3} are in an amount of 0.35 wt% and 0.087 wt%, respectively. In addition, the strength of the matrix of the practical ferrite steel is about 0.3 GPa (about 0.9×10^2 in HV). Therefore, the room temperature strength of the steel including the TiC dispersed in the ferrite matrix is expected to be 1.2 GPa or more (HV 3.7×10^2 or more). Accordingly, considering the ideal dispersion conditions for TiC, with the dispersed particles to which the Orowan mechanism is applicable, a size of 7 nm or more can sufficiently satisfy an HV of 3.7×10^2 only by dispersion strengthening at a volume fraction as small as 7×10^{-3} . The same effects as with this are also expectable for the dispersed second-phase particles including a carbonitride, an intermetallic compound, an oxide, Cu particles, and the like. Then, as such dispersed second-phase particles, for example, specifically, there can be considered carbides such as Mo₂C, V₄C₃, W₂C, TaC, NbC, and TiC, oxides such as Fe₃O₄, Fe₂O₃, Al₂O₃, Cr₂O₃, SiO₂, and Ti₂O₃, nitrides such as AlN, CrN, and TiN, intermetallic compounds such as Ni₃Ti, NiAl, TiB, Fe₂Mo, Ni₃Nb, and Ni₃Mo, metal particles such as Cu particles, and the like.

[0051] Incidentally, it is known that metal carbide particles of Mo, Ti, or the like generally have a size of around 10 nm, and can effectively effect strengthening even by dispersion in an amount as small as less than 10×10^{-3} in volume fraction. However, the size of the dispersed second-phase particles and the distribution in the matrix structure also varies according to segregation of alloy elements or the like, or other factors. Therefore, in the invention, considering such that a fine crystal structure can be obtained with stability by warm working even when there are variations in distribution of the dispersed second-phase particles, the volume fraction at room temperature of the dispersed second-phase particles is specified at 7×10^{-3} or more. Incidentally, for a low alloy martensitic steel or bainite steel, in view of the fact that the average grain diameter of a general cementite (Fe₃C) prior to warm working is several tens nanometers or more, the volume fraction of the dispersed second-phase particles is preferably set at 20×10^{-3} or more.

[0052] Whereas, the upper limit of the volume fraction of the dispersed second-phase particles has no particular restriction in effecting strengthening. However, in view of the toughness, it is preferably set at 12×10^{-2} or less. Further, particle dispersion strengthening by the Orowan mechanism is expected to become remarkable in the region of several tens nanometers or less from the equation (A). Thus, with the dispersion conditions of the dispersed second-phase particles having an average particle diameter of more than 0.5 μm, it is difficult to obtain a strength of 1.2 GPa or more. Therefore, the average particle diameter of the dispersed second-phase particles is desirably 0.5 μm or less, and more preferably 0.1 μm or less as the steel for warm working.

[0053] However, the foregoing conditions are predicated upon the fact that the dispersed second-phase particles do not grow even in the temperature range equal to or higher than that of the third or more stage of tempering of 350°C. In other words, in order for the steel to have a strength of 1.2 GPa or more even after warm working, it becomes a necessary condition that, during heating and working, and after working, in addition to the matrix structure, particularly, the dispersed second-phase particles do not undergo Ostwald ripening, resulting in a reduction of the strength. Therefore, when the thermal stability of the structure is evaluated using λ expressed by the following equation (1) commonly known as a temper parameter as an index, conceivably, it is a necessary and sufficient condition for the prior working structure, i.e., the steel for warm working of the invention to show such a softening resistance that the Vickers hardness (HV) at room temperature when the steel is subjected to any heat treatment of annealing, tempering, and aging in the as-unworked state under the condition $\lambda \geq 1.4 \times 10^4$ in a prescribed temperature range of 350°C or more and Ac 1 point or less is equal to or higher than the hardness H given by the following equation (2).

[0054]

$$\lambda = T(\log t + 20) \dots (1)$$

where T denotes the temperature (K), and t denotes the time (h).

[0055]

$$H = (5.2 - 1.2 \times 10^{-4}\lambda) \times 10^2 \dots (2)$$

Incidentally, the wording "in a prescribed temperature range" denotes that the foregoing conditions may be satisfied at any temperature of from 350°C to the Ac₁ point, and means that the foregoing conditions are not required to be satisfied over the whole temperature range. In other words, also in the case where when an aging or tempering treatment is carried out, the material undergoes remarkable aging hardening or secondary hardening to have a hardness of H or

higher only in a given temperature range within the foregoing range, it can serve as the steel for warm working of the invention.

[0056] Herein, for example, for the TiC, the particle growth suppressing effect will be considered. The stable crystal grain diameter D resulting from the normal particle growth of the ferrite structure including TiC dispersed therein ($d = 7 \times 10^{-3} \mu\text{m}$, volume fraction $f = 7 \times 10^{-3}$, $B = 4/9$ to $4/3$) is estimated from the commonly well known Zener's relational expression ($D = B \times d/f$). Then, it is found to be about 0.4 to 1.3 μm . In other words, such stable crystal grains are established for the normal grain growth of recrystallized grains. Therefore, the following can be sufficiently expected: with warm working in a lower temperature range than the recrystallization temperature, a fibrous structure with an average grain size of 3 μm or less is obtained by the two effects of refinement of the matrix structure by impartment of a predetermined strain and grain boundary pinning by TiC.

[0057] In order to obtain an ultrafine duplex phase structure having a tensile strength of 1.2 GPa or more by warm working based on precipitation strengthening due to the ideal dispersion conditions of a TiC carbide in this manner, the necessary and sufficient condition of the prior working structure is as follows: the lower limit value of the volume fraction of the dispersed second-phase particles is set at 7×10^{-3} , and the steel after any heat treatment of annealing, tempering, and aging under the condition $T(\log t + 20) \geq 1.4 \times 10^4$ has a hardness of $\text{HV} \geq (5.2 - 1.2 \times 10^{-4}\lambda) \times 10^2$. Namely, the invention has the following features as a steel for warm working: fine dispersion or precipitation of the dispersed second-phase particles in the matrix structure as particle dispersion strengthening particles, and the structure control to enhance the thermal stability of the dispersed second-phase particles.

[0058] As for the structure of the steel for warm working of the present invention as described up to this point, during the treatment of warm working, the dispersion conditions of the dispersed second-phase particles and the matrix structure variously change. Therefore, although not limited by the room-temperature structure form, all the steels with a strength of 1.2 GPa or more except for the steels having a pearlite structure as the main structure can be considered as the steel for warm working. As such ones, for example, specifically, for martensitic steels (tempered martensite structures), there are JIS-G4053 low alloy steels, JIS-G-4801 spring steels, secondary hardened steels with a hardness equal to or higher than this, maraging steels, TRIP steels, and ausformed steels.

[0059] Then, the second steel for warm working of the invention is configured such that 80 percent by volume or more of the matrix structure is any single structure of martensite and bainite or a mixed structure thereof. This is due to the following fact. It is elucidated from a recent study that the width of the block regarded as the effective crystal grain of martensite is 1 μm or less in a medium carbon low alloy steel (Scripta Mater., 49 (2003), P. 1157). Thus, by subjecting the tempered martensite structure including a carbide or the like finely dispersed therein to warm working, it is possible to form a fiber structure with efficiency. In addition, the bainite structure also has a needle-like or plate-like structure form including a carbide finely dispersed therein. Thus, also when this is taken as the prior working structure, it is possible to obtain a fibrous structure similarly. In the steel for warm working of the invention, it is a preferred form that a single structure of any of such martensite and bainite or a mixed structure thereof accounts for 90 percent by volume or more of the matrix structure.

[0060] Particularly, in order to keep the strength of 1.2 GPa or more after warm working with stability, it is desirable that a martensite or bainite structure having a temper softening resistance equal to or higher than that of a tempered martensitic steel of JIS-SCM430 steel is included in a volume of 80 % or more. Incidentally, 20 % by volume or less structure other than martensite or bainite and a mixed structure thereof may be accounted for by any structure such as a ferrite, pearlite, or austenite structure. This is for the following reason. Such a ferrite, pearlite, or austenite structure, or the like decomposes or disappears, or changes into a microstructure during a warm thermo-mechanical treatment. Therefore, when it is present in an amount of 20 % by volume or less, it is judged as no problem.

(b) Chemical composition

The third to fifth steels for warm working of the invention are alloy designed based on the foregoing findings. The gist resides in a steel for warm working characterized by containing, as the chemical composition, C: 0.70 wt% or less, Si: 0.05 wt% or more, Mn: 0.05 wt% or more, Cr: 0.01 wt% or more, Al: 0.5 wt% or less, O: 0.3 wt% or less, and N: 0.3 wt% or less, and the balance substantially being Fe and inevitable impurities: Whereas, the following and the like can be considered. The steel for warm working further contains one or two or more selected from a group consisting of Mo: 5.0 wt% or less, W: 5.0 wt% or less, V: 5.0 wt% or less, Ti: 3.0 wt% or less, Nb: 1.0 wt% or less, and Ta: 1.0 wt% or less, or contains one or two or more of Ni: 0.05 wt% or more and Cu: 2.0 wt% or less. Below, the reasons why the component structure of the steel in the invention is restricted will be described.

[0061] C: C forms a carbide particle, and is the most effective component for strengthening. However, when the content exceeds 0.70 wt%, the toughness degradation is caused. For this reason, the content is set at 0.70 wt% or less. In order that strengthening is sufficiently expectable, the content is preferably 0.08 wt% or more, and more preferably 0.15 wt% or more.

[0062] Si: Si is an effective element for enhancing the strength of the steel by deoxidation and solid solution in ferrite, and finely dispersing cementite. Therefore, the content is set at 0.05 wt% or more inclusive of the one added as a deoxidizer, and to remain in the steel. The upper limit is not particularly restricted for strengthening. However, in view

of the workability of the steel material, the content is preferably set at 2.5 wt% or less.

[0063] Mn: Mn is an effective element for reducing the austenitization temperature, and refining austenite. In addition, it is an effective element for the hardenability, and being dissolved in a solid solution form in cementite and suppressing coarsening of cementite. When the content is less than 0.05 wt%, desired effects cannot be obtained. Therefore, the content is set at 0.05 wt% or more. More preferably, the content is 0.2 wt% or more. The upper limit is not particularly restricted for strengthening. However, in view of the toughness of the resulting steel material, the content is preferably set at 3.0 wt% or less.

[0064] Cr: Cr is an effective element for improving the hardenability, and it is an element having a strong action of being dissolved in a solid solution form in cementite and delaying the growth of cementite. Further, it is also one of the important elements in the present invention for forming a high Cr carbide which is thermally more stable than cementite, or improving the corrosion resistance by being added in a relatively larger amount. Therefore, Cr is required to be contained at least in an amount of 0.01 wt% or more. It is contained in an amount of preferably 0.1 wt% or more, and more preferably 0.8 wt% or more.

[0065] Al: Al is an effective element for deoxidization and forming an intermetallic compound with an element such as Ni and enhancing the strength of the steel. However, excessive addition reduces the toughness. Therefore, the content is set at 0.5 wt% or less. Incidentally, when the intermetallic compound of Al and other elements, nitride or oxide of Al, or the like is not used as the dispersion strengthening particles, the content is preferably set at 0.02 wt% or less, and further restrictively 0.01 wt% or less.

[0066] O: O (oxygen) effectively acts not as an inclusion but as grain growth preventing or dispersion strengthening particles when it can be finely and uniformly dispersed as an oxide. However, when oxygen is contained excessively, the toughness is reduced. Therefore, the content is set at 0.3 wt% or less. When the oxide is not used as the dispersion strengthening particles, the content is preferably set at 0.01 wt% or less.

[0067] N: N (nitrogen) effectively acts as grain growth preventing or dispersion strengthening particles when it can be finely and uniformly dispersed as a nitride. However, when nitrogen is contained excessively, the toughness is reduced. Therefore, the content is set at 0.3 wt% or less. When the nitride is not used as the dispersion strengthening particles, the content is preferably set at 0.01 wt% or less.

[0068] Mo: Mo is an effective element for strengthening the steel in the invention. It not only improves the hardenability of the steel, but also is dissolved in a small amount in a solid solution form also in cementite to make cementite thermally stable. Particularly, completely separately from cementite, it newly causes separate nucleation of an alloy carbide on dislocation in the matrix phase, thereby to effect secondary hardening, resulting in strengthening of the steel. Further, the formed alloy carbide is effective for grain refinement, and is also effective for replacement of hydrogen. Therefore, Mo is contained in an amount of preferably 0.1 wt% or more, and more preferably 0.5 wt% or more. However, it is an expensive element. In addition, excessive addition forms a coarse undissolved carbide or intermetallic compound to degrade the toughness. Therefore, the upper limit of the content is set at 5 wt%. From the viewpoint of cost efficiency, the content is preferably set at 2 wt% or less.

[0069] Incidentally, also for W, V, Ti, Nb, and Ta, the same effects as with Mo are exerted. The respective upper limits of the content are set. Further, the composite addition of these elements is effective in finely dispersing dispersion strengthening particles.

[0070] Ni: Ni is an element effective for improving the hardenability, and effective for reducing the austenitization temperature, and refining austenite, improving the toughness, and improving the corrosion resistance. Further, it is also an effective element for forming an intermetallic compound with Ti or Al, and precipitation strengthening the steel when it is contained in a proper amount. When the content is less than 0.01 wt%, desired effects cannot be obtained. Therefore, the content is set at 0.01 wt% or more. Ni is more preferably contained in an amount of 0.2 wt% or more. The upper limit is not particularly restricted. However, Ni is an expensive element, and hence it is preferably contained in an amount of 9 wt% or less.

[0071] Cu: Cu is a detrimental element causing hot brittleness. But on the other hand, when it is added in a proper amount, it causes precipitation of fine Cu particles at 500°C to 600°C, thereby to strengthen the steel. When it is added in a large amount, it causes hot brittleness. Therefore, the content is set at 2 wt% or less which is roughly the maximum amount of solid solution into ferrite.

[0072] Incidentally, when strengthening due to precipitation of a fine intermetallic compound is intended, it is also effective that Co is contained in an amount of 15 wt% or less.

[0073] P (phosphorus) and S (sulfur) are not particularly specified. However, P or S reduces the grain boundary strength, and hence it is an element which is desired to be removed as much as possible. Each content is preferably set at 0.03 wt% or less.

[0074] Incidentally, for other elements than the foregoing ones, various elements are allowed to be contained in such an amount as not to reduce the effects of the invention.

[0075] (c) Preparation of steel for warm working

Incidentally, as the methods for manufacturing the steel for warm working as described above, for example, various

ones can be considered according to the methods for manufacturing martensite structures or bainite structures of JIS standard, and the like. These are not limited to dissolution and forging methods. For example, other manufacturing methods such as powder metallurgy can also be used. Specifically, for example, the following procedure or the like is also possible. By using a technique such as a ball milling method, most undissolved compounds such as oxides in the steel are steel powder dispersed with a size of nanometer size, and then, (ISIJ International, 39 (1999), p176), such a mechanical milled powder is consolidated and formed in a proper temperature range to obtain an objective bulk body.

[0076] (d) Warm working

The warm working method of the invention is characterized by subjecting any steel for warm working described above to warm working for applying 0.7 or more strain in the temperature range of 350°C or more and Ac1 point -20°C or less. It can also be considered that after performing warm working, an aging treatment is performed in the temperature range of 350°C or more and Ac1 point or less. According to such warm working, the following advantages can be obtained:

(1) Recovery of dislocation moderately occurs, and crystal grain refinement can be achieved, and the internal stress can be reduced;

(2) Diffusion of alloy elements becomes relatively easy, and decomposition and re-precipitation of the dispersed second-phase particles of carbides or the like remarkably occur, which enables refinement of the structure; and

(3) The deformation resistance (high temperature hardness) of the steel is remarkably reduced, so that the steel can be formed without occurrence of cracks and the like.

[0077] As for such a working temperature, more specifically, for example, in the case of a medium carbon low alloy steel for use as a steel for general mechanical structures, including a martensite structure as the matrix, it can be set at 350°C or more roughly corresponding to the third stage of tempering in which cementite precipitates. Particularly, in order to effectively use an alloy carbide, an intermetallic compound, Cu, or the like as the dispersed second-phase particles, it is desirable that working is carried out in the temperature range of 500°C to 650°C which is the precipitation temperature of the second-phase particles.

[0078] On the other hand, in the portion which has undergone austenite transformation during working, phase transformation such as pearlite transformation or martensite transformation is effected during the cooling process. As a result, there is a high possibility that such an inhomogeneous structure as to cause the occurrence of cracks is formed. Further, also in view of an increase in temperature due to working heat generation, the upper limit temperature of working is set at Ac1 point -20°C. However, as the combination of the working temperature and time of the material, when the hardness is arranged by a tempering parameter λ , the combination such that the Vickers hardness at room temperature when the material is subjected to any of annealing, tempering, and aging treatments in the as-unworked state does not become 3.7×10^2 or less in HV is preferable in order to obtain a strength of 1.2 GPa or more after warm working. Particularly, for working in a high temperature range, the time required for working is required to be shortened in view of the softening resistance and the heating time of the material.

[0079] The degree to which the structure is developed depends upon the prior working structure, the working temperature, and the strain amount. In other words, the necessary strain amount varies according to the prior working structure or the working temperature. Therefore, although the strain amount cannot be strictly specified, it is preferable that a strain of 0.7 or more, and more preferably 1 or more is imposed when a fibrous structure is desired to be formed in the inside of the material. As for the steel for warm working having a martensite or bainite structure in which prior-austenite grains have been elongated in fine fibers by previously applying working in the unrecrystallization temperature of austenite, it is possible to homogeneously form a fine fiber structure by application with a strain amount of less than 1. However, in most cases, it is desirable that the strain amount is preferably 1 or more, and more preferably 1.5 or more.

[0080] At this step, the strain to be imparted may be introduced not only in a single working pass, but in a plurality of divided passes. Further, the direction of working is not constantly limited to the same direction. Still further, the inter-pass time is also not particularly restricted. Furthermore, the process also includes imposing a prescribed strain not over the entire region of the material to be worked, but on a specific region (e.g., the surface layer requiring strengthening, or R part of a component). However, the actual strain amount can be understood only after considering the material characteristics of the material to be worked, the friction conditions (e.g., the type or the presence or absence of a lubricant) of the roll (mold for forging) and the material to be worked, the deformation of the roll (mold for forging), rolling (forging) rate, the rolling (forging) temperature, and the like. Particularly, when component forming is carried out by forging, it is necessary that ununiform strain has been introduced. Accordingly, it is desirable to estimate the amount of strain with high precision numerical analysis technology. However, in general, when the cumulative rolling reduction is 45 % or more for plate rolling intended for the plane strain state, or when the cumulative reduction of area is 45 % or more for wire rod rolling, it can be considered that a strain of 0.7 or more has been introduced into the entire region of the material to be worked. Incidentally, when the cumulative rolling reduction or the cumulative reduction of area is 58 % or more, it can be considered that a strain of 1 or more has been introduced into the entire region of the material to be worked. However, for example, even when the rolling reduction (reduction of area) is less than 45 %, a strain of 0.7 or more may

be introduced into the entire region or into a specific region of the material to be worked under the influence of friction or the like. Therefore, in that case, it is necessary to quantitatively study the amount of introduced strain by numerical analysis.

[0081] (e) Steel material

The steel material of the invention is a steel obtained by warm working a steel for warm working as described above. It is characterized in the following respects: it has a matrix structure including a fibrous crystal having an average grains size of the minor axis of $3\text{ }\mu\text{m}$ or less; the second-phase particles are finely dispersed in the matrix structure at a volume fraction of 7×10^{-3} or more at room temperature; and the Vickers hardness at room temperature is 3.7×10^2 or more in HV. Incidentally, it can be understood that the matrix structure in the steel material of the invention includes a fibrous ferrite crystal with an expansion degree (aspect ratio) of more than 2, and typically with an aspect ratio of 5 or more, in which the second-phase particles are finely dispersed.

[0082] It is known that the effect of the crystal grain refinement exerted on the mechanical characteristics of the steel becomes remarkable in the crystal grain region of several micrometers or less. In the invention, the upper limit of the average spacing (i.e., minor axis average grain diameter) of the matrix structure including the fibrous crystal is set at $3\text{ }\mu\text{m}$. Incidentally, herein, the word "crystal grains" denotes the crystal grains surrounded by the grain boundaries with a crystal orientation difference of 15° or more. On the other hand, when the average particle diameter of the major axis of the dispersed second-phase particles is larger than $0.3\text{ }\mu\text{m}$, particle dispersion strengthening can be hardly expected. Further, for the steel of 1.2 GPa or more, there is a high possibility that the toughness is remarkably degraded. Accordingly, the average particle diameter of the major axes is desirably $0.3\text{ }\mu\text{m}$ or less.

[0083] Particularly, the effects of crystal grain refinement becomes especially remarkable in the region in which the average crystal grain diameter is $1\text{ }\mu\text{m}$ or less; and particle dispersion strengthening due to the Orowan mechanism, in the region in which the average particles diameter is $0.1\text{ }\mu\text{m}$ or less. Accordingly, in order to effectively use strengthening by crystal fiber formation and particle dispersion strengthening in a superposed manner, it is effective that the minor axis average grain diameter of the fibrous crystal is set at $1\text{ }\mu\text{m}$ or less, and further $0.5\text{ }\mu\text{m}$ or less. Then, it is more preferable that the average particle diameter of the major axes of the dispersed second-phase particles is also set at $0.1\text{ }\mu\text{m}$ or less, and further $0.05\text{ }\mu\text{m}$ or less according to the refinement of the matrix structure.

[0084] To such a steel material for warm working, other than the foregoing strengthening mechanisms, strengthening mechanisms such as solid solution strengthening and dislocation strengthening can also be applied. The effects of superposition of these strengthening mechanisms lead to provide such a high performance material as unpredictable with simple addition of the strengthening mechanisms.

[0085] Such fine fiber structures can be formed by warm forming of rod wire materials, screw members of bolts, and the like, including plate materials. Particularly even when the cumulative strain amount is small, a fiber structure can be formed in the surface layer part which has locally undergone intense deformation or the like. This can largely improve the characteristics of various components and the desirable parts.

[0086] Below, examples will be shown by reference to the accompanying drawings, and embodiments of the present invention will be described in more details. Of course, this invention is not limited to the following examples, and it is needless to say that various forms are possible for the details.

Examples

[0087] Table 1 shows the steel components (A to K, M, N, and O) within the scope of the invention and the steel component (L) outside the scope. Incidentally, in examples, carbides are used as the dispersed second-phase particles. Table 2 shows the volume fractions of alloy carbides dispersible as the dispersed second-phase particles and cementites for the steels of the compositions of Table 1. The steels of the examples cover martensitic steels of from SCM435 to 2 GPa class secondary hardened steels except for Co-added maraging steels.

[0088]

[Table 1]

Chemical composition (wt%)													
Steel type	C	Si	Cr	Mn	Ni	Mo	Cu	Nb	P	S	T-Al	T-N	O
A	0.20	1.95	1.01	0.21	-	1.02	-	-	0.001	0.0010	0.010	0.0022	0.0007
B	0.39	1.98	1.04	0.21	-	1.05	-	-	<0.001	<0.001	0.041	0.0020	<0.005
C	0.59	1.99	0.98	0.20	-	1.01	-	-	<0.002	0.0007	0.004	0.0016	0.0005
D	0.21	0.09	2.01	0.21	2.02	1.01	-	-	0.010	0.0020	0.011	<0.01	<0.004
E	0.22	0.09	2.00	0.20	2.00	1.00	-	0.034	0.009	0.0020	0.007	<0.01	<0.004
F	0.40	0.08	2.00	0.20	2.01	1.03	-	-	0.010	0.0020	0.009	<0.01	<0.004
G	0.57	1.96	1.02	0.16	-	0.002	-	-	<0.001	<0.001	0.041	0.0018	<0.0005
H	0.35	0.20	1.10	0.70	0.25	0.20	0.053	-	0.006	0.0020	0.009	0.0070	0.0040
I	0.40	0.20	1.03	0.77	0.07	0.17	0.040	-	0.023	0.0080	-	0.0050	0.0010
J	0.38	0.97	2.00	0.46	3.01	0.95	0.010	-	0.018	0.0040	0.013	0.0010	0.0040
K	0.38	0.24	2.00	0.45	1.50	0.95	<0.01	-	0.017	0.0040	0.012	0.0010	0.0040
L	0.22	0.01	<0.001	<0.005	0.01	<0.002	<0.001	-	<0.002	0.0020	0.003	0.0014	0.0018
M	0.62	1.97	0.01	0.20	2.00	0.98	-	-	<0.002	0.0007	0.003	0.0036	0.0006
N	0.40	0.10	2.00	0.20	1.00	0.70	-	-	0.015	0.0030	0.020	-	-
O	0.20	0.25	0.15	0.50	3.00	3.00		-	0.015	0.0030	0.020	-	-

[0089]

[Table 2]

AMOUNT OF ALLOY CARBIDE AND CEMENTITE DISPERSED (calculated value)				
Steel Type	$f\text{Mo}_2\text{C} \times 10^3$	$f\text{NbC} \times 10^3$	$f\text{Fe}_3\text{C} \times 10^3$	Total volume fraction $\times 10^3$
A	9.6	-	21.0	31
B	9.9	-	49.5	59
C	9.5	-	79.5	89
D	9.5	-	22.5	32
E	9.4	0.41	24.0	34
F	9.7	-	51.0	61
G	-	-	85.5	86
H	1.9	-	51.0	53
I	1.6	-	58.5	60
J	8.9	-	48.0	57
K	8.9	-	48.0	57
L	-	-	33.0	33
M	9.2	-	84.0	93
N	6.6	-	51.0	58
O	28.2	-	3.0	31
Total volume fraction (f) of secondary phase particles in each steel $> 7 \times 10^{-3}$				

[0090] Carbides of various stoichiometric compositions are present in actual steels according to the components of the steel and the heat treatment conditions. For this reason, it is difficult and not practical to strictly measure the volume fraction of the dispersed second-phase particles by chemical analysis or structure observation. Under such circumstances, the present inventors determined the volume fraction of each carbide from the known theoretical density determined by the structural analysis or the like of the carbide (KAGAKU DAIJITENN, TOKYO KAGAKU DOJIN Co. Ltd., (1989), P. 1361 to 1363). The approximate expressions and the like are as shown in Table 3.

[0091]

[Table 3]

Approximate expression for determining the volume fraction (f) of MxCy type carbide $f\text{MxCy} = \rho_{\text{Fe}} / \rho_{\text{MxCy}} / \{ \text{XM}^* / (\text{XM}^* + 12\text{Y}) \} (\text{wt}\%\text{M}) / 100$

M^* : atomic weight

For example,

$$f\text{Fe}_3\text{C} = \rho_{\text{Fe}} / \rho_{\text{Fe}_3\text{C}} / \{ 12 / (3 * 55.85 + 12) \} (\text{wt}\%\text{C}) / 100 = 0.15 (\text{wt}\%\text{C})$$

$$f\text{Mo}_2\text{C} = 0.0094 (\text{wt}\%\text{Mo})$$

$$f\text{NbC} = 0.012 (\text{wt}\%\text{Nb})$$

$$f\text{TiC} = 0.020 (\text{wt}\%\text{Ti})$$

where

Density of ferrite iron: $\rho_{\text{Fe}} = 7.86 \text{ Mg/m}^3$

Density of Fe_3C : $\rho_{\text{Fe}_3\text{C}} = 7.72 \text{ Mg/m}^3$

Density of Mo_2C : $\rho_{\text{Mo}_2\text{C}} = 8.90 \text{ Mg/m}^3$

Density of NbC : $\rho_{\text{NbC}} = 7.78 \text{ Mg/m}^3$

Density of TiC : $\rho_{\text{TiC}} = 4.94 \text{ Mg/m}^3$

The density of each carbide is cited from the following document: (KAGAKU DAIJITENN, TOKYO KAGAKU DOJIN Co. Ltd., (1989))

[0092] For calculation, it is assumed that the alloy elements respectively combine with carbons in order of decreasing carbide forming ability ($\text{Nb} > \text{Mo} > \text{Cr} > \text{Fe}$, and the like) to form carbides. As for Nb or Mo, it is well known that it is an element which tends to form its specific carbide in the steel and is less likely to be dissolved in cementite. Thus, precipitation of NbC or Mo₂C is assumed. However, for a G steel or a L steel, Mo in an amount of 0.002 wt% can be sufficiently dissolved in a solid solution form in cementite, and hence it is excluded from the estimation of the volume fraction of the Mo carbide. As for Cr, when Cr is added in a large amount, it forms a carbide such as M₂₃C₆ or M₇C₃ with a high Cr concentration. However, when Cr is added in the amount of this example, there is a low possibility that Cr is dissolved in a solid solution form in cementite to form the alloy carbides. Therefore, the volume fraction of the alloy carbides of Cr is excluded from the estimation.

[0093] The most important thing herein is the following: The amount of carbide serving as the dispersion strengthening particles to be dispersed depends upon the carbon content in a medium carbon low alloy steel. Particularly, when there is no possibility that a alloy carbide with a sufficiently large density with respect to cementite is formed, or when the amount of elements for forming alloy carbides to be added is small, the amount of the second-phase particles to be dispersed is roughly determined by the amount of cementite. Namely, as shown in Table 2, in the steels having a C content of 0.2 wt% or more used in examples of Table 1, the total amount of the volume fractions of the second phase sufficiently exceeds 7×10^{-3} .

[0094] In FIGS. 1, 2, and 3, steps of the thermo-mechanical treatment applied in examples are shown. This process basically includes (1) a solution treatment and working for reducing coarse undissolved carbides; (2) a quench hardening treatment and tempering for obtaining a tempered martensite or bainite structure as a structure of the steel for warm working of the invention; and (3) warm working also serving as shape forming into a component. Incidentally, in the thermo-mechanical treatment pattern 1 of FIG. 1, refinement of reverse transformed austenite grains due to austenitizing at low temperatures following the solution treatment is taken into consideration. In the pattern 2 of FIG. 2, quench hardening from recrystallized austenite resulting from hot working following the solution treatment or the unrecrystallized austenite (elongated austenite) structure resulting from warm working is taken into consideration. FIG. 3 shows a quench hardening process from the worked austenite (elongated austenite) structure by an ausforming treatment in a metastable austenite range. With these thermo-mechanical treatment processes, it is possible to obtain a microstructure by warm working with a smaller cumulative strain amount for finer crystal grains. Particularly, as the prior working structure for developing a fiber structure with efficiency, it is most effective to employ the martensite resulting from fine unrecrystallized austenite (elongated austenite) as the prior structure.

[0095] First, a square bar of about 40 mm square $\times$ 120 mm in length cut from a hot rolled steel sheet or a forged material was subjected to the steps up to the quench hardening treatment in the thermo-mechanical treatment patterns 1, 2, and 3, thereby to obtain a martensite single structure close to nearly 100 % by volume. This corresponds to one example of the steel for warm working of the invention. Then, the square bar was heated to a prescribed temperature for 0.5 hour, and tempered. Then, it was subjected to warm rolling working to a prescribed reduction of area by the use of a groove roll, and applied with a strain, and air cooled.

[0096] For the structure of the resulting steel material, the cross section in parallel with the rolling direction (RD) was polished and observed by the use of an optical microscope, a transmission electron microscope (TEM), and a FE-SEM with EBSD analyzer. The polished surface was corroded with picric acid alcohol, and the prior-austenite grain boundary was revealed. Thus, the prior-austenite grain diameter was determined according to the comparison method or the cutting method specified in JIS G 0552. The average particle diameter of the dispersed second-phase particles was determined in the following manner. By the use of TEM or SEM, 3 or more visual fields were observed at a magnification of 10000 times to 100000 times to measure the length of each major axis of a total of 250 or more particles. Incidentally, when some particles combine with each other and agglomerate, these are regarded as one particle. The maximum particle diameter is allowed to correspond to the length of the major axis of the largest carbide of the carbides measured. As for the average grain diameters of the minor axes and the major axes of the elongated grains in the fiber structure, according to EBSD analysis, the average section lengths of the minor axes and the major axes of the elongated crystal grains having a crystal orientation difference of 15° or more were measured with a cutting method (see FIG. 5).

[0097] The hardness of the resulting steel material was measured under a load of 20 kg and for a holding time of 15 s by means of a Vickers hardness tester according to the testing method specified in JIS Z 2244.

[0098] The tensile test was performed at ordinary temperatures by means of an Instron type tensile test machine according to the testing method specified in JIS Z 2241, for 1) a JIS No. 14 proportional test piece with a parallel part diameter of 3.5 mm, a length of 24.5 mm, and a mark-to-mark distance of 17.5 mm, or with a size of 6 mm, a length of 42 mm, and a mark-to-mark distance of 30 mm, or for 2) a JIS No. 4 sub-size test piece with a parallel part diameter of 10 mm, a length of 45 mm, and a mark-to-mark distance of 35 mm. The cross head speeds were 0.5 mm/min and 10 mm/min for 1) JIS No. 14A and 2) JIS No. 4, respectively. The elongation was measured until rupture by mounting an extensometer on each test piece.

[0099] The impact test was performed according to the testing method specified in JIS Z 2242 for a U notch or V notch test piece of 55 mm in length and 10 mm in height and width manufactured by cutting machining from a steel material

of 1.8 cm² or more in cross section.

[0100] The hydrogen embrittlement characteristics were evaluated at room temperature at a cross head speed of 0.005 mm/min using a slow strain rate tensile test machine for each notch test piece of 10 mm in diameter, 6 mm in notch bottom diameter, and 4.9 in stress concentration coefficient. For the hydrogen embrittlement test, the test was carried out after setting the following conditions. The average hydrogen amount in the test piece was changed by 72-hour cathode charge with varying charged solution and current density, to perform Cd plating. This prevents hydrogen in the test piece from dissipating. The analysis of hydrogen was carried out by a thermal desorption analysis using a quadrupole mass spectrometer for a sample from which Cd-plating had been removed. Thus, the hydrogen to be released up to 300°C was defined as diffusive hydrogen, and determined.

[0101] Table 4 summarizes the manufacturing conditions and the structure form of each steel for warm working, and the quench hardening and tempering conditions of the unworked material and the hardness thereof, and the results of evaluation of the suitability as the steel for warm working of the invention.

[0102] FIG. 4 shows the relationship between $T(\log t + 20) = \lambda$ and the hardness of the tempered martensitic steel in the as-unworked state.

[0103]

[Table 4]

Manufacturing conditions and structure form of steel for warm working, and temper hardness of unworked material											
Steel type	Manufacturing conditions and structure form of steel for warm working								Temper hardness of unworked material		
	1)	Solution treatment temperature (°C) × 10 ⁻²	Reduction hardening of area (1): e1 (%)	Quench (1) or γ transformation temperature (°C) × 10 ⁻²	Reduction of area (2) 2 (%)	Quench hardening temperature (2) (°C) × 10 ⁻²	Average prior γ grain diameter (μm) × 10 ⁻³	Quench hardening hardness (HV) × 10 ⁻²	$T(\log t + 20) = \lambda \times 10^{-4}$	Tempered hardness (HV) × 10 ⁻⁴	
A	2	12.0	40	9.0			0.06	5.0	1.55	4.4	Forworking 1
B	1	12.0	40	9.2			0.03	6.7	1.55	5.5	Forworking 2
	2	12.0	40	9.0			0.06	6.8	1.55 1.75	6.2 5.0	Forworking 3
C	2	12.0	40	9.0			0.06	8.7	1.55	6.2	Forworking 4
									1.75	5.5	
D	1	12.0	40	8.0			0.01	4.8	1.55	3.7	Forworking 5
E	1	12.0	40	8.0			0.009	4.6	1.55	4.1	Forworking 6
F	1	12.0	40	8.0			0.007	6.7	1.55	4.4	Forworking 7
G	1	12.0	40	12.0			0.5	8.0	1.55	5.0	Forworking 8
									1.75	4.1	
H	1	12.0	40	9.2			0.04	6.0	1.55	3.8	Forworking 9
I	1			11.0			0.1	6.5	1.56	4.0	Forworking 10
J	2	12.0	40	9.0			0.06	6.7	1.55	5.3	Forworking 11

(continued)

Manufacturing conditions and structure form of steel for warm working, and temper hardness of unworked material											
Steel type	Manufacturing conditions and structure form of steel for warm working								Temper hardness of unworked material		
	1)	Solution treatment temperature (°C) × 10 ⁻²	Reduction hardening of area (1): e1 (%)	Quench (1) or γ transformation temperature (°C) × 10 ⁻²	Reduction of area (2) 2 (%)	Quench hardening temperature (2) (°C) × 10 ⁻²	Average prior γ grain diameter (μm) × 10 ⁻³	Quench hardening hardness (HV) × 10 ⁻²	T(logt + 20) = λ × 10 ⁻⁴	Tempered hardness (HV) × 10 ⁻⁴	
K	2	12.0	40	9.0			0.06	6.7	1.55	5.0	For working 12
L	1			10.5			0.07	4.8	1.36	2.7	Comp. Example 1
M	1	12.0	0	12.0			0.5	8.5	1.55	5.4	For working 13
									1.75	4.4	
O	2	12.0	40	9.0			0.06	4.8	1.55	4.2	For working 14
	3	12.0	40	10.2	0	5.8	0.06	4.6	1.55	4.2	For working 15
					33	5.8	0.05*	5.5	1.55	4.7	For working 16
					55	5.7	0.04*	5.6	1.55	4.9	For working 17
					70	5.8	0.03*	5.7	1.55	5.0	For working 18

1) Thermo-mechanical treatment pattern * For ausformed (elongated grain) structure, the grain diameter of the minor axis is measured.

[0104] As for the L steel of the comparative material, the volume fraction of cementite is 33×10^{-3} . However, the alloy elements specified in the invention are not properly contained. Therefore, cementite is not thermally stable, and grows with ease by heating. Accordingly, with a tempering treatment at $\lambda = 1.4 \times 10^4$ or more, the hardness of the L steel is less than $H = (5.2 - 1.2 \times 10^{-4}\lambda)$ indicated with a broken line in the diagram. Thus, with warm working at 350°C or more,

[0105] FIG. 5 shows an example of analysis of the structure of the material obtained by subjecting an I steel to γ transformation at 11.0×10^2 °C, followed by water cooling, and subjecting it to a tempering treatment at 5.0×10^2 °C for 1.5 hours, followed by warm groove rolling. Incidentally, the cumulative strain amount imparted at this step is 2.4, and the hardness is HV 3.7×10^2 . As indicated from the EBSD analysis diagram (a) and the TEM photograph (b) of the Bcc phase, there is obtained an ultrafine fiber structure in which spheroidal carbide is dispersed in a fibrously elongated ferrite phase matrix. By the EBSD analysis, the average grain diameter of the minor axes of crystal grains having a crystal orientation difference of 15° or more was measured with a cutting method. As a result (c), the average grain diameter of the minor axes of the elongated crystal grains was found to be 0.3 μm . However, in this steel, the fiber structure has been developed in a complicated form, so that it was not possible to measure the average grain diameter of the major axes. On the other hand, the 287 carbide particle diameters (major axis lengths) were measured by TEM. As a result, the average particle diameter of the carbide was found to be 0.06 μm , and the maximum diameter thereof was found to be 0.2 μm (d).

[0106] The inverse pole figure with respect to the rolling direction (RD) indicates that there is formed a fiber structure in which $\langle 011 \rangle // \text{RD}$ texture has developed. Incidentally, also for other developed steels, the same textures were formed. The cleavage plane of the Bcc iron is $\{100\}$. Therefore, the formation of such a $\langle 011 \rangle$ fiber structure is considered to be very effective for fracture due to tensile deformation in the direction of fiber axis, flexural deformation receiving flexural moment along the direction of fiber, or the like.

[0107] Table 5 shows the relationship between the warm working conditions and the structure and hardness of the resulting warm worked material. Incidentally, T and t in the table denote the working temperature and the working treatment time shown in FIGS. 1 to 3, respectively.

[0108]

[Table 5]

Warm working conditions and structure form of worked material													
Steel type		Warm working conditions					Structure form of warm worked material						
		1)	Working temperature (°C) × 10 ⁻²	T(log+20) Reduction= λ × 10 ⁻⁴	area e (%)	Cumulative equivalent strain amount: ε *1	Average carbide particle diameter (μm) *2	Maximum carbide particle diameter (μm) *2	Minor axis average grain diameter of elongated grains L1 (μm)	Major axis average grain diameter of elongated grains L2 (μm)	Elongation rate (L2/L1)	Worked material hardness (HV) × 10 ⁻²	
For working 1	A	2	5.0	1.55	76	1.7	<0.1	0.07	0.4	Immeasurable		5.2	Example 1
	For working 2	1	5.0	1.55	76	1.7	<0.1		0.3	Immeasurable		4.9	Example 2
For working 3		B		5.0	1.55	76	1.7	<0.1	0.1	0.3	Immeasurable		5.6
			5.0	1.55	12	0.2	<0.1		XX	Immeasurable		5.3	Comp. Example 2
			5.0	1.55	27	0.4	<0.1			Immeasurable		5.4	Example 4
			5.0	1.55	51	0.8	<0.1			Immeasurable		5.2	Example 5
			6.0	1.75	76	1.7	<0.1	0.3	0.3	Immeasurable		4.6	Example 6
			7.0	1.96	76	1.7	0.2	0.85	0.5			3.3	Comp. Example 3

(continued)

Warm working conditions and structure form of worked material													
Steel type		Warm working conditions				Structure form of warm worked material							
		1)	Working temperature (°C) × 10 ⁻²	T(logt+20) Reduction= λ × 10 ⁻⁴	area e (%)	Cumulative equivalent strain amount: ε *1	Average carbide particle diameter (μm) *2	Maximum carbide particle diameter (μm) *2	Minor axis average grain diameter of elongated grains L1 (μm)	Major axis average grain diameter of elongated grains L2 (μm)	Elongation rate (L2/L1)	Worked material hardness (HV) × 10 ⁻²	
C	For working 4	2	5.0	1.55	76	1.7	<0.1	0.15	0.3	Immeasurable		Example 7	
			6.0	1.75	76	1.7	<0.1		0.4	Immeasurable		Example 8	
			7.0	1.96	76	1.7	0.2	1.2	0.9	5.4	6	3.6	Comp. Example 4
D	For working 5	1	5.0	1.55	76	1.7	<0.1	0.4	0.3	Immeasurable		Example 9	
E	For working 6	1	5.0	1.55	76	1.7	<0.1	0.3	0.3	Immeasurable		Example 10	
F	For working 7	1	5.0	1.55	76	1.7	<0.1	0.3	0.3	Immeasurable		Example 11	
G	For working 8	1	5.0	1.55	76	1.7	<0.1	0.4	0.4	Immeasurable		Example 12	
			6.0	1.75	76	1.7	0.2	0.6	0.5	Immeasurable		3.8	Example 13
			7.0	1.95	76	1.7	0.3	0.8	0.7	1.6	2	3.2	Comp. Example 5

(continued)

Warm working conditions and structure form of worked material													
Steel type		Warm working conditions					Structure form of warm worked material						
		1)	Working temperature (°C) × 10 ⁻²	T(logt+20) Reduction= λ × 10 ⁻⁴	area e (%)	Cumulative equivalent strain amount: ε *1	Average carbide particle diameter (μm) *2	Maximum carbide particle diameter (μm) *2	Minor axis average grain diameter of elongated grains L1 (μm)	Major axis average grain diameter of elongated grains L2 (μm)	Elongation rate (L2/L1)	Worked material hardness (HV) × 10 ⁻²	
For working 9	H	1	5.0	1.55	76	1.7	<0.1	0.25	0.5	Immeasurable		3.8	Example 14
			5.0	1.55	57	1.0	<0.1	0.3	1.4	Immeasurable		3.8	Example 15
			5.0	1.56	87	2.4	0.06	0.2	0.3	Immeasurable		3.7	Example 16
For working 10	I	1	6.0	1.76	87	2.4	0.08	0.25	0.4	Immeasurable		3.1	Comp. Example 6
			7.0	1.96	87	2.4	0.11	0.48	0.7	2.8	4	2.4	Comp. Example 7
For working 11	J	2	5.0	1.55	76	1.7	<0.1	0.2	0.3	Immeasurable		5.3	Example 17
For working 12	K	2	5.0	1.55	76	1.7	<0.1	0.25	0.3	Immeasurable		4.9	Example 18
For working 13	M	1	5.0	1.56	76	1.7	<0.1		0.3	Immeasurable		5.7	Example 19
			6.0	1.76	76	1.7	<0.1		0.7	Immeasurable		4.3	Example 20

(continued)

Warm working conditions and structure form of worked material													
Steel type		Warm working conditions					Structure form of warm worked material						
		1)	Working temperature (°C) × 10 ⁻²	T(logt+20) Reduction= $\lambda \times 10^{-4}$	area e (%)	Cumulative equivalent strain amount: ε^{*1}	Average carbide particle diameter (μm) *2	Maximum carbide particle diameter (μm) *2	Minor axis average grain diameter of elongated grains L1 (μm)	Major axis average grain diameter of elongated grains L2 (μm)	Elongation rate (L2/L1)		Worked material hardness (HV) × 10 ⁻²
For working 14	O	2	5.0	1.55	76	1.7	<0.1	<0.1	0.9	Immeasurable		5.6	Example 21
		3	5.0	1.55	79	1.8	<0.1	<0.1	0.8	Immeasurable		5.7	Example 22
			5.0	1.55	68	1.3	<0.1	<0.1	1.0	Immeasurable		5.9	Example 23
1) Thermo-mechanical treatment pattern *1 $\varepsilon = 2/\sqrt[3]{\ln(1/(1-e/100))}$ *2 TEM observation or SEM observation													

[0109] The hardness of the worked material largely depends on the temper softening resistance. When the comparison is made in the same $\lambda = T(\log t + 20)$, a steel having a larger temper softening resistance provides a worked material with a higher hardness. Particularly, with a worked material of $HV\ 4.0 \times 10^2$ or more, the matrix structure has been refined to as ultrafine as $0.5\ \mu\text{m}$ or less in average width. In a worked material of $HV\ 4.0 \times 10^2$ or more, very fine particles are densely dispersed. For this reason, it was not possible to strictly determine the average carbide particle diameter. However, when comparison was made with the one including relatively large particles such as the I steel of FIGS. 5, it was possible to judge the diameter as less than $0.1\ \mu\text{m}$.

[0110] However, even in the steel for warm working high in temper softening resistance, for example, with working in a high temperature range of 700°C , carbide particles and the like grow with ease during working. Therefore, it becomes difficult to obtain a warm worked material of $HV\ 3.7 \times 10^2$ or more (Comparative Examples 3, 4, 5, and 7). Therefore, in working within such a high temperature range, it is desirable that short-time heating and working are combined and carried out so as to prevent carbides and the like from growing by the use of, for example, high frequency heating. Further, with working within a high temperature range in the vicinity of 700°C , grain growth becomes more likely to occur, and hence the proportion of the crystal grains with a small aspect and a relatively large grain diameter increases. As a result, the expansion degree is reduced. For example, in Comparative Examples 4, 5, and 7, the expansion degrees were measured to be 6, 2, and 4, respectively. As for Examples, it was not possible to measure the expansion degree. However, in comparison in the structure with Comparative Example 7, it was possible to judge the expansion degree as 6 or more.

[0111] Tables 6 and 7 summarize Examples and Comparative Examples for the mechanical properties. Incidentally, in the tables, UE and VE denote the absorption energies of the U notch and V notch test pieces, respectively.

[0112]

[Table 6]

Tensile deformation characteristics at room temperature of warm worked steel and impact absorption energy (J) at each test temperature													
Steel type		Proof stress	Tensile strength TS (GPa)	Uniform elongation (%)	Total elongation (%)	Reduction of area (%)	TS × total elongation balance	Room temperature toughness UE20 (J)	Low temperature toughness UE-20 (J)	Low temperature toughness UE-60 (J)	Room temperature toughness VE20 (J)	Low temperature toughness VE-20 (J)	Low temperature toughness VE-60 (J)
Ex. 1	A	1.66	1.66	3.8	19.2	56	32				244	249	136
	Ex. 2	1.73	1.73	6.7	16.4	45	28	160	228	174		148	
Ex. 3	B	1.86	1.86	6.5	16.9	51	31	214		229	226	293	248
Comp. Ex. 2		1.70	1.78	2.7	12.3	45	22				18	16	
Ex. 4		1.65	1.74	5.7	13.6	47	24					21	
Ex. 5		1.74	1.79	6.5	15.0	49	27				45	26	
Ex. 6		1.36	1.46	9.2	18.0	52	26	167		254			
		Ex. 7	2.04	2.08	6.0	11.3	33	24	132	84	39		
Ex. 8	C	1.44	1.53	7.7	12.3	38	19	183	150	87			
Ex. 9	D	1.53	1.53	5.1	16.8	58	26	181	197	197		154	
Ex. 10	E	1.53	1.53	4.5	14.1	60	22	181		2.3			
Ex. 11	F	1.68	1.68	3.9	15.2	51	26	119	136	136		201	
Ex. 12	G	1.40	1.49	7.8	13.9	49	21	132	132	89			
Ex. 13		1.09	1.22	9.6	18.0	50	22	101	138	121			
Ex. 14	H	1.27	1.27	6.9	17.9	52	23	156	143	150		125	
Ex. 15		1.22	1.27	6.0	15.2	53	19	98	104	90			
Ex. 17	J	1.78	1.80	6.2	18.5	45	33				306	300	185
Ex. 18	K	1.75	1.75		15.6	44	27				196	269	158
Ex. 19	M	1.90	1.92	5.2	9.6	30	18	115	89	45		125	
Ex. 20		1.30	1.37	8.1	13.9	45	19	94	79				
Ex. 21	O	2.04	2.04		10.3	54	21					38	
Ex. 22		2.01	2.01		10.0	52	20					27	
Ex. 23		2.03	2.03		9.2	51	19					28	

[0113]

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[Table 7]

Tensile deformation characteristics at room temperature of unworked steel (QT material) and impact absorption energy (J) at each test temperature												
Steel type	Proof stress (GPa)	Tensile strength TS (GPa)	Uniform elongation (%)	Total elongation (%)	Reduction of area (%)	TS × total elongation balance	Room temperature toughness UE20 (J)	Low temperature toughness UE-20 (J)	Low temperature toughness UE-60 (J)	Room temperature toughness VE-20 (J)	γ transformation temperature (°C) × 10 ⁻²	Tempering temperature (°) × 10 ⁻²
Comp. Ex. 8	1.04	1.37	6.9	15.3	54	21	-	-	-	15	9.9	5.0
Comp. Ex. 9	1.42	1.65	5.9	15.2	54	25	-	-	-	24	9.5	6.0
Comp. Ex. 10	1.49	1.77	4.5	10.2	31	18	-	-	-	12	9.5	5.0
Comp. Ex. 11	1.50	1.74	4.5	12.0	48	21	32	35	-	-	9.2	5.0
Comp. Ex. 12	1.62	2.06	4.7	9.1	31	19	21	21	-	-	9.2	4.5
Comp. Ex. 13	1.66	2.00	4.7	9.1	32	18	21	17	-	-	9.2	5.0
Comp. Ex. 14	1.58	1.80	6.0	12.7	44	23	33	24	21	-	9.2	5.7
Comp. Ex. 15	1.14	1.30	8.5	15.9	46	21	43	-	-	-	9.2	6.5
Comp. Ex. 16	1.59	1.79	4.6	10.3	36	18	26	-	-	-	9.2	4.5
Comp. Ex. 17	1.13	1.21	5.2	18.1	60	22	-	-	-	69	8.5	5.0
Comp. Ex. 18	0.94	1.02	7.3	21.0	63	21	-	-	-	106	8.5	6.0
Comp. Ex. 19	1.10	1.21	4.4	13.0	55	16	77	68	38	-	9.2	5.0

[0114] The steels of the compositions herein shown have been subjected to proper alloy design and heat treatments so that the second-phase particles are finely dispersed as the steels for warm working. Even unworked steels of Comparative Examples show a tensile strength $\times$ total elongation balance of 16 or more. However, when comparison is made for the same composition, the developed steel subjected to warm working provides a larger tensile strength $\times$ total elongation balance than Comparative Examples. Further, even addition of carbon in an amount of about 0.2 wt% provides an over 1.5 GPa class almost the same as the quench hardening hardness when alloy elements such as Mo are properly added. Further, the ductility is excellent. These receive attention (A, D, and E steels). Further, O steel provides a 2 GPa class ultrahigh strength steel.

[0115] On the other hand, the impact absorption energy indicates that each developed steel has a far more excellent toughness than conventional high strength steels to a low temperature range.

FIG. 6 summarizes the relationship between the tensile strength and the impact value (U notch test piece) at room temperature. Incidentally, in the diagram, there is also shown data of the steel for mechanical structure specified in JIS (SHINNNIHON CYUUTANZOU KYOUKAI: GENNBAYOU KIKAIKOUZOUYOU HAGANEZAIROYOU DATA SHEETS (1995)). With conventional steels, the impact value is largely reduced in the strength range of 1.2 GPa or more, and 70 J/cm² or less at a strength of 1.5 GPa or more. In contrast, the steels of the invention show a very high impact value of 150 J/cm² or more particularly even at a strength of 1.5 GPa or more.

[0116] FIG. 7 summarizes the relationship between the tensile strength and the absorption energy at room temperature (V notch test piece). Incidentally, in the diagram, there is also shown data of the steel for mechanical structure specified in JIS (Institute of Metal Material Technology Fatigue Data sheet Reference 5). The invention is also superior in toughness in a high strength region to conventional ausformed steels, fine grain steels, maraging steels, and the like.

[0117] Fig. 8 shows the relationship between the test temperature and the absorption energy. For example, from Example 1 and Comparative Example 8, and Examples 3 and 5 and Comparative Examples 10, it can be confirmed that materials with high absorption energy are obtained by a working treatment. Particularly, the following receives attention. For some developed steels, the absorption energy in the vicinity of room temperature is not only higher than that of the comparative steels, but also shows such a specific temperature dependency as to show the maximum value in a low temperature range and decrease. For example, for the A steel of Example 1, or the B steel of Example 3, a peak is observed in the vicinity of -40°C; for the F steel of Example 11, in the vicinity of -100°C. There are also some partially fractured ones in the peak temperature range. Then, such developed steels are, as shown in FIG. 9, characterized in that the fractured surface shows such a fibrous form as upon breaking bamboo. The phenomenon similar to this has been observed when an ausformed 0.2 wt% C-3 wt% Ni-3 % Mo steel (tensile strength; 1.6 GPa) was tested in the vicinity of 200°C. However, the absorption energy in the vicinity of ordinary temperatures has been reduced down to about 33 J (Non-Patent Document 16). Further, also for the steel obtained by the improved ausforming treatment of a 0.5 wt% C-0.9 wt% Mn-0.8 wt% Cr steel (5150 steel), when an impact test is performed, fibrous fracture occurs, and the improvement of toughness is observed. However, the maximum absorption energy at ordinary temperatures is about 90 J at a strength level of 1.5 GPa (Non-patent Document 17). Therefore, the following are the findings unprecedented and worthy of special mention. At a tensile strength of 1.2 GPa or more, as is the case with the developed steels of this invention, the absorption energy in the vicinity of normal temperatures is far higher than that of existing ausformed steels, and in addition, the absorption energy shows the maximum value in a low temperature range of -40°C or less.

[0118] The excellent mechanical characteristics, particularly the high impact characteristics of the developed steels as described up to this point are largely due to the ultrafinefiber structure with <011>//RD texture which has been densely developed by warm working of the particle dispersion type duplex structure.

[0119] FIG. 10 shows the relationship between the hardness of the warm working material and the aging temperature. As for the warm working material to which a secondary hardening element such as Mo has been added, it is also possible to keep the hardness up to a high temperature, or to more enhance the strength than in the as-warm worked state by an aging treatment.

[0120] FIG. 11 shows an example of observation of the ultrafine fiber structure formed in the central part of the plate material with warm rolling at 650°C of N steel by SEM.

[0121] FIG. 12 shows an example of observation of the ultrafine fiber structure formed in the surface layer part of the locally intense strained rod material by SEM.

[0122] Table 8 shows the results of the hydrogen embrittlement resistance characteristic test.

[0123]

[Table 8]

Results of hydrogen embrittlement resistance characteristics evaluation							
Steel type		Tensile strength (GPa) *1	0.7 TS (GPa)	Diffusive hydrogen content (ppm)	Notch strength (GPa)*2	Notch strength h (GPa) *3	Hydrogen embrittlement resistance characteristics
Ex. 1	A	1.66	1.16	0.36	2.41	1.76	AA
Ex. 3	B	1.86	1.30	0.36	2.59	1.78	AA
Ex. 7	C	2.08	1.46	0.32	2.17	1.63	AA
Comp. Ex. 14	C	1.80	1.26	0.34	2.22	1.79	AA
Comp. Ex. 12	C	2.06	1.44	0.25	1.91	0.73	CC
Comp. Ex. 16	G	1.79	1.25	0.31	2.00	0.77	CC
Comp. Ex. 20	I	1.40	0.98	0.31	2.05	0.61	CC
*1; Tensile strength (TS) of smooth tensile test with no hydrogen charging *2; Notch tensile strength of notch test piece not charged with hydrogen (Kt = 4.9) *3; Notch tensile strength of notch test piece charged with hydrogen (Kt = 4.9) Hydrogen embrittlement resistance characteristics; the case where the notch tensile strength is 0.7 time or more the TS of the smooth test piece at a hydrogen content of about 0.3 mass ppm is indicated with AA.							

[0124] Herein, a notch tensile test of a steel charged with hydrogen in an amount of about 0.3 mass ppm was carried out by a slow strain rate tensile test. The hydrogen embrittlement resistance characteristics were evaluated according to whether the notch tensile strength at this step is 0.7 time or more the tensile strength of a smooth tensile test piece not charged with hydrogen.

[0125] The developed steels satisfy these conditions even when the tensile strength is at a high strength level of 1.6 GPa or more, and it can be judged as being excellent in hydrogen embrittlement resistance characteristics. Incidentally, Comparative Example 14 is a steel for a high strength mechanical structure excellent in delayed fracture invented in Japanese Patent Application No. 2001-264399.

Industrial Applicability

[0126] In accordance with the present invention, as described in details up to this point, there is provided a high strength steel multiphased by fine dispersion of a small amount of dispersed second-phase particles. Particularly, even an ultrahigh strength steel which is hard to soften and is hard to form is applied with prescribed deformation in a temperature range in which the deformation resistance is reduced and no cracks occur in the material, to be formed into a prescribed shape (thin plate, thick plate, wire rod, or component). As a result, conventional spheroidizing and quench hardening and tempering treatments after component forming are omitted. At the same time, an ultrafine duplex phase structure is developed into a fibrous form. Thus, there is provided a high strength steel largely improved in the ductility, particularly the toughness, and the hydrogen embrittlement resistance characteristics in the relation of trade-off balance with high strength, and a member thereof.

[0127] These are useful as a steel to be worked into various structures, car components and the like for use, or these are useful as members.

Claims

1. A steel for warm working, being to have a particle dispersion type fiber structure formed therein by warm working, the steel **characterized by** including an alloy element or/and dispersed second-phase particles such that the total amount of the dispersed second-phase particles at room temperature is 7×10^{-3} or more in terms of volume fraction,

and the steel **characterized by** having a Vickers hardness (HV) of equal to or larger than the hardness H of the following equation (2):

$$H = (5.2 - 1.2 \times 10^{-4}\lambda) \times 10^2 \dots (2)$$

when the steel is subjected to any heat treatment of annealing, tempering, and aging treatments in the as-unworked state under conditions such that a parameter λ expressed by the following equation (1):

$$\lambda = T(\log t + 20) \text{ (T; temperature (K), t; time (hr))} \dots (1)$$

is 1.4×10^4 or more in a prescribed temperature range of 350°C or more and Ac1 point or less.

2. The steel for warm working according to claim 1, **characterized in that** 80 % by volume or more of the matrix structure is any single structure of martensite and bainite, or a mixed structure thereof.
3. The steel for warm working according to claim 1 or 2, **characterized by** including, in chemical composition, C: 0.70 wt% or less, Si: 0.05 wt% or more, Mn: 0.05 wt% or more, Cr: 0.01 wt% or more, Al: 0.5 wt% or less, O: 0.3 wt% or less, and N: 0.3 wt% or less, and the balance being substantially Fe and inevitable impurities.
4. The steel for warm working according to claim 3, **characterized by** further including, one or two or more selected from a group consisting of Mo: 5.0 wt% or less, W: 5.0 wt% or less, V: 5.0 wt% or less, Ti: 3.0 wt% or less, Nb: 1.0 wt% or less, and Ta: 1.0 wt% or less.
5. The steel for warm working according to claim 3 or 4, **characterized by** further including one or two of Ni: 0.05 wt% or more and Cu: 2.0 wt% or less.
6. A warm working method **characterized by** performing warm working for imparting a strain of 0.7 or more in a temperature range of 350°C or more and Ac1 point -20°C or less on the steel for warm working according to any of claims 1 to 5.
7. The warm working method according to claim 6, **characterized in that** after performing warm working, an aging treatment is performed in a temperature range of 350°C or more and Ac1 point or less.
8. A steel material which is a steel having a particle dispersion type fiber structure manufactured from the steel for warm working according to any of claims 1 to 5, **characterized in that** the average grain diameter of the minor axes of a fibrous ferrite crystal forming the matrix structure is 3 μm or less, the second-phase particles are finely dispersed in the matrix structure at a volume fraction of 7×10^{-3} or more, and the Vickers hardness at room temperature is HV 3.7×10^2 or more.
9. The steel material according to claim 8, **characterized by** having a matrix structure including a fibrous ferrite crystal of which the average grain diameter of the minor axes is 1 μm or less.
10. The steel material according to claim 8 or 9, **characterized by** having a matrix structure including a fibrous ferrite crystal of which the average grain diameter of the minor axes is 0.5 μm or less.
11. The steel material which is the steel according to any of claims 8 to 10, **characterized in that** the average particle diameter of the major axes of the dispersed second-phase particles is 0.1 μm or less.
12. A steel plate which is the steel material according to any of claims 8 to 11, **characterized by** being in the shape of a plate, and including a particle dispersion type fiber structure formed in at least the surface layer part thereof.
13. A wire rod steel, which is the steel material according to any of claims 8 to 11, **characterized by** being in the shape of a rod or a wire, and including a particle dispersion type fiber structure formed in at least the surface layer part thereof.
14. A bolt comprising the steel material according to any of claims 8 to 11, **characterized by** including a particle

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dispersion type fiber structure formed in at least the surface layer part of the screw part.

15. A steel component **characterized by** being a cut machined product of the steel material according to any of claims 8 to 11.

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Fig. 1

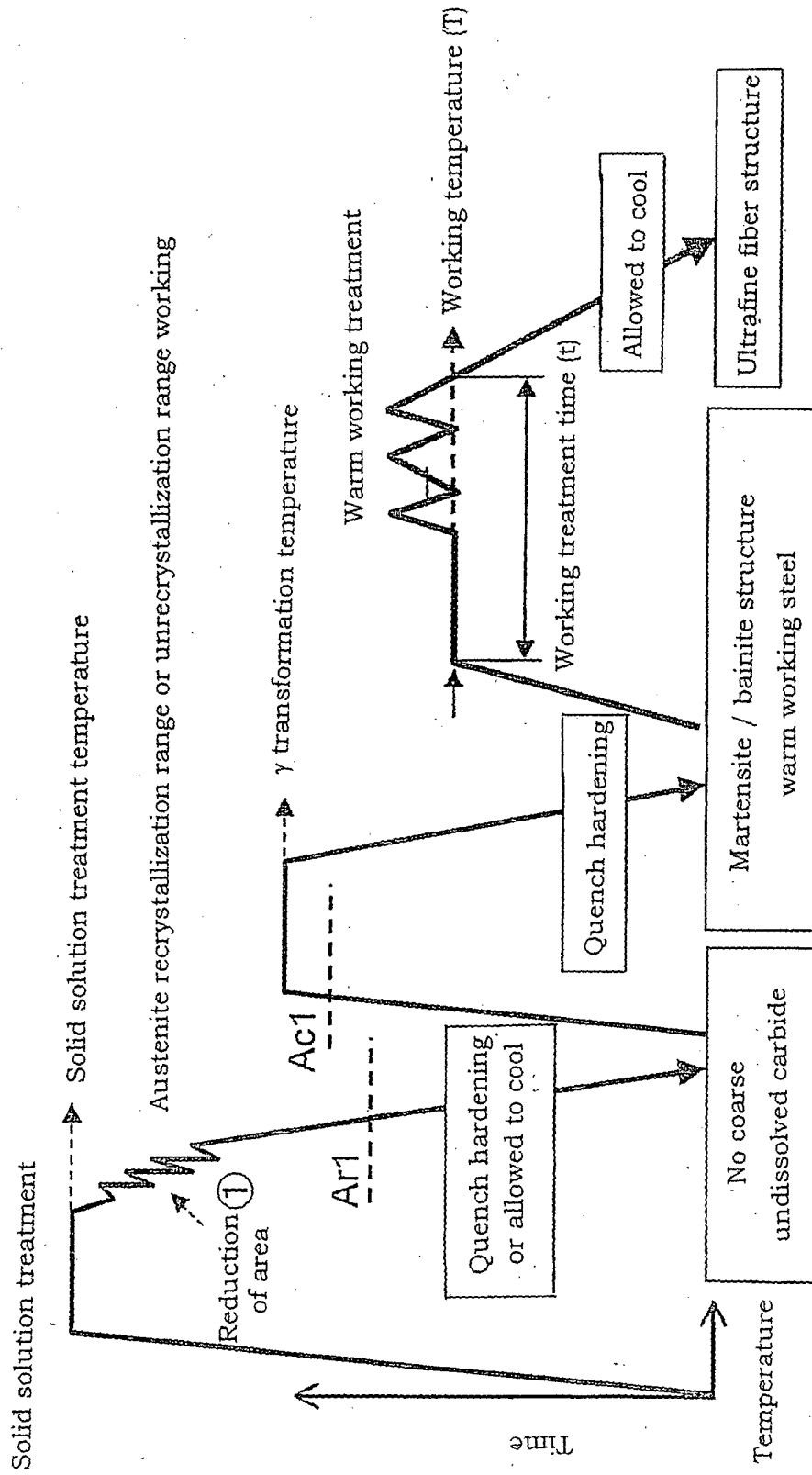


Fig. 2

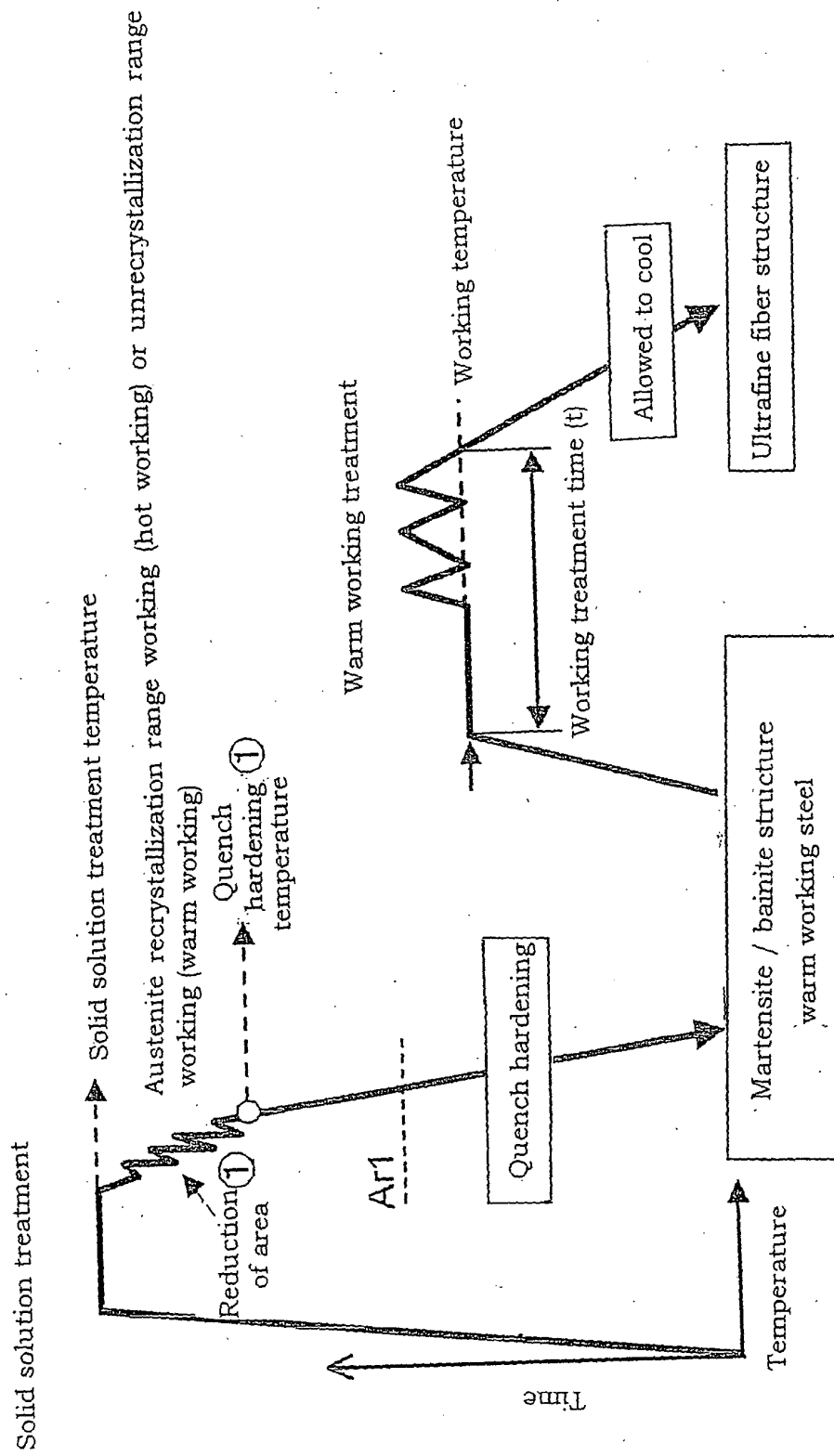


Fig. 3

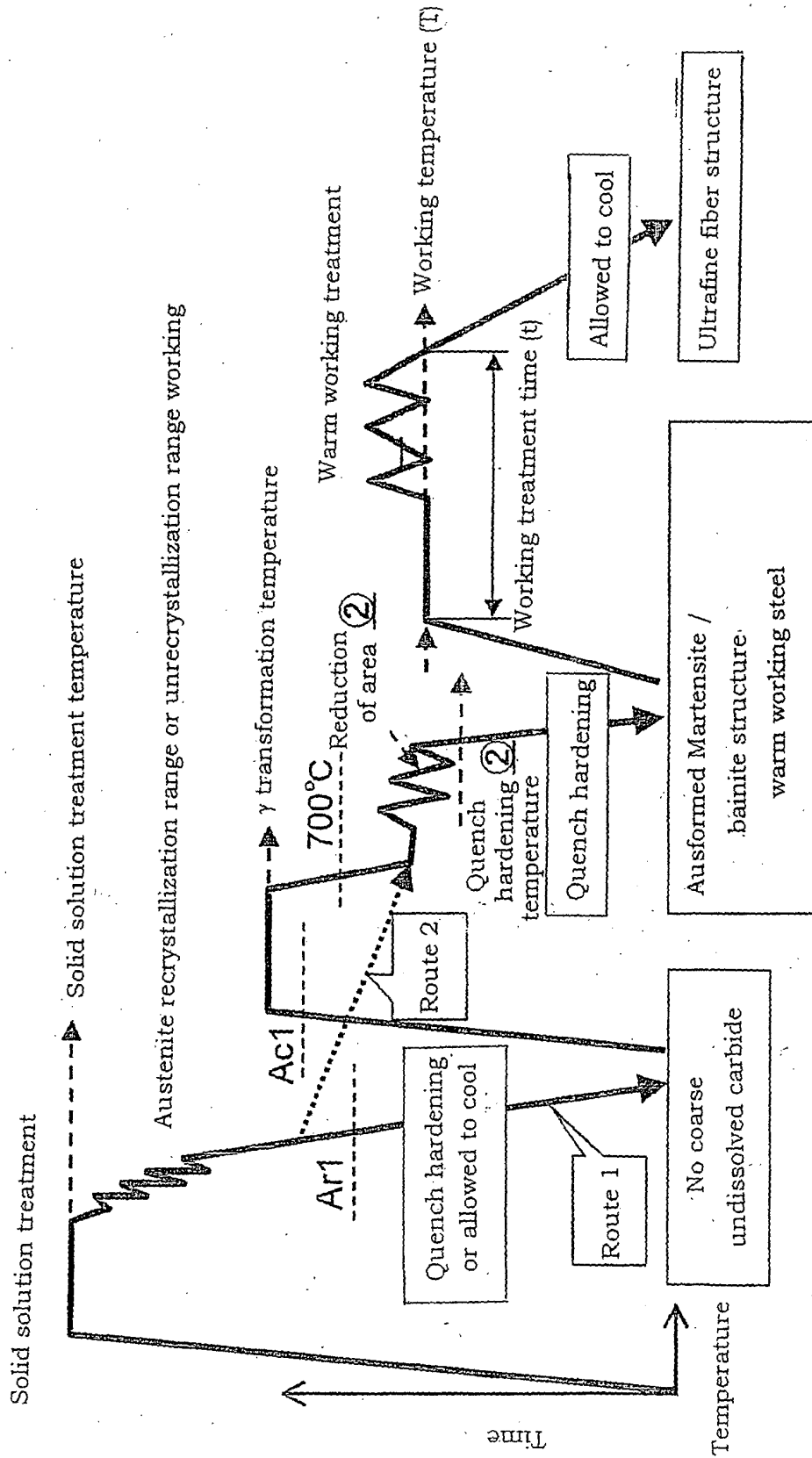


Fig. 4

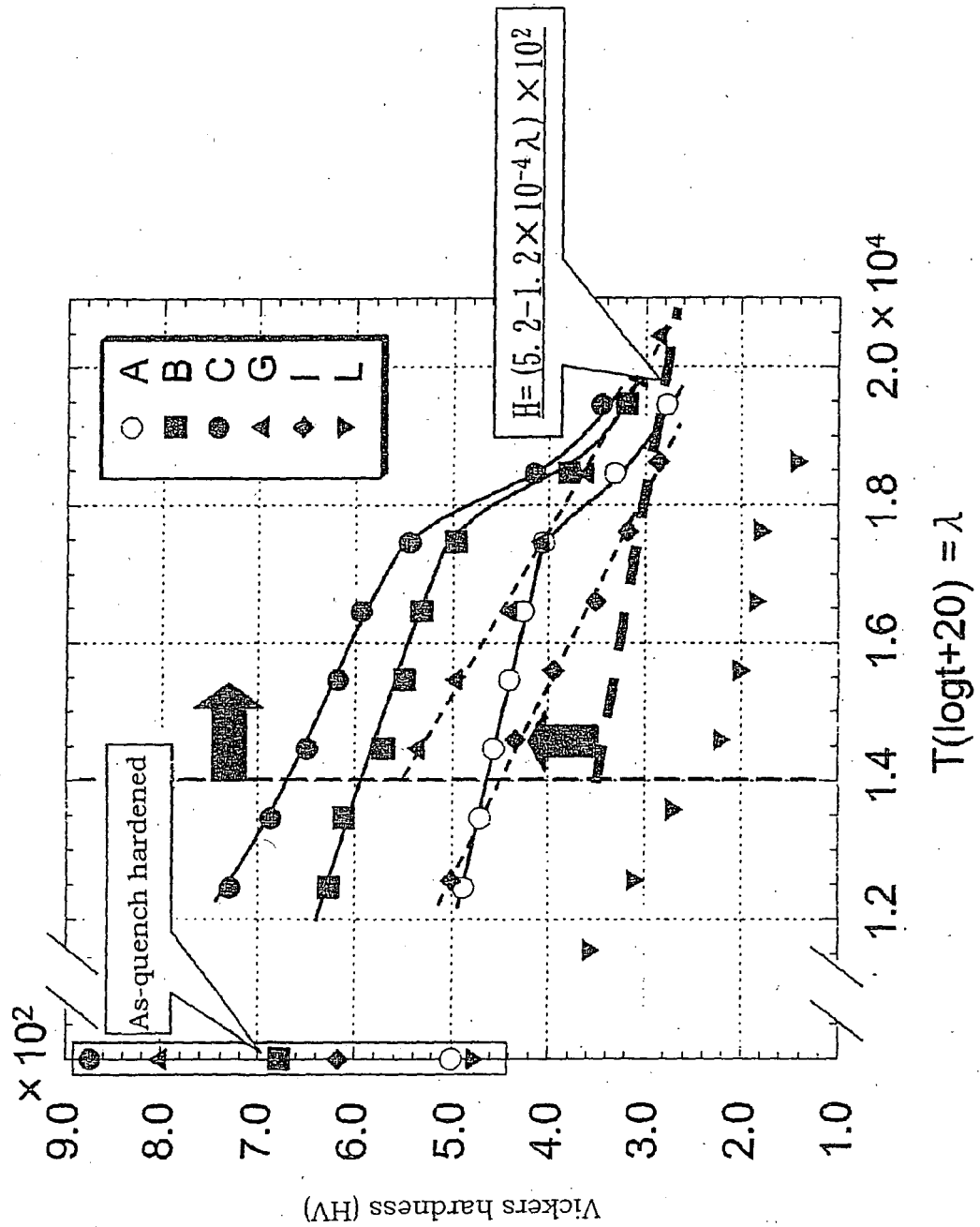


Fig. 5

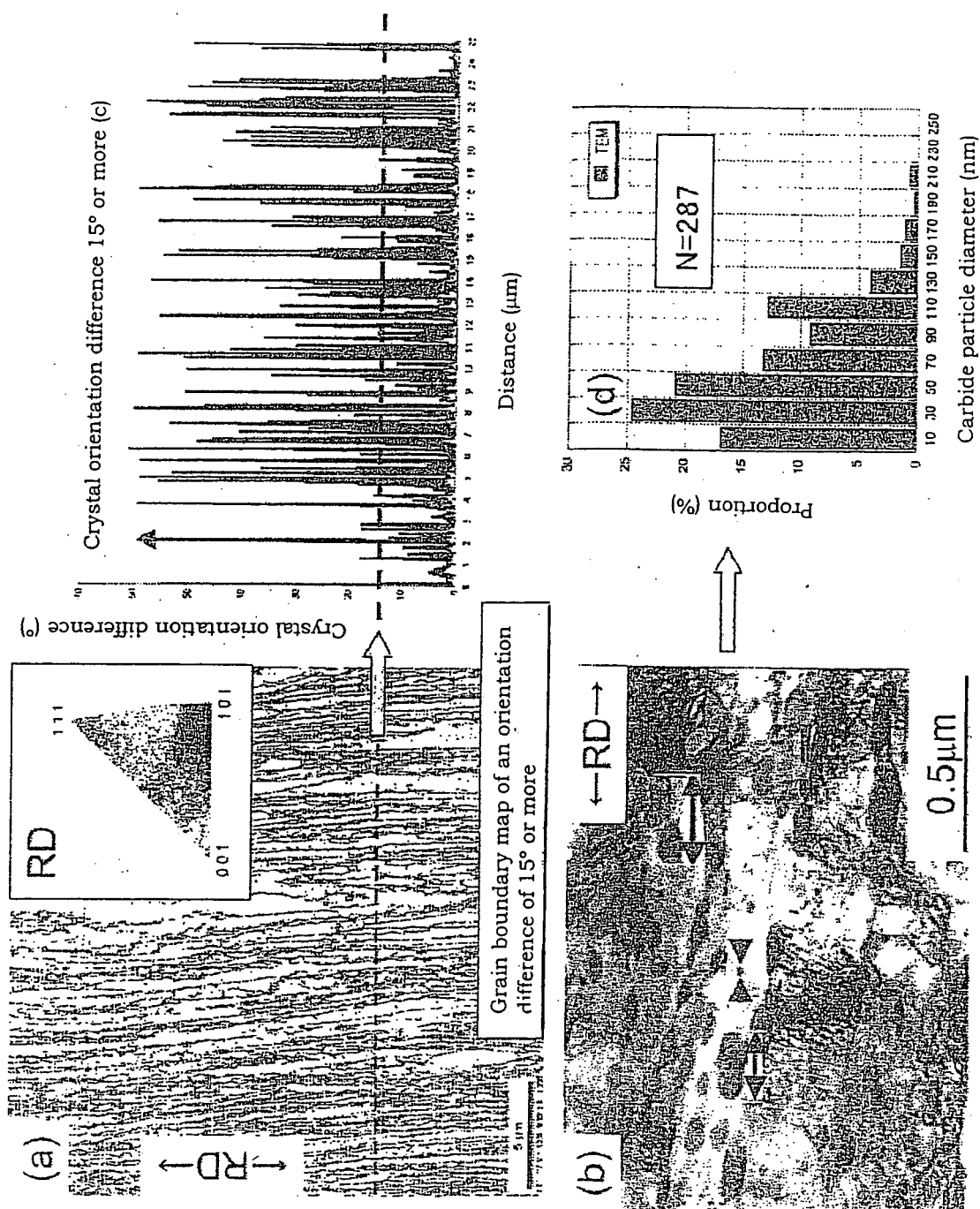


Fig. 6

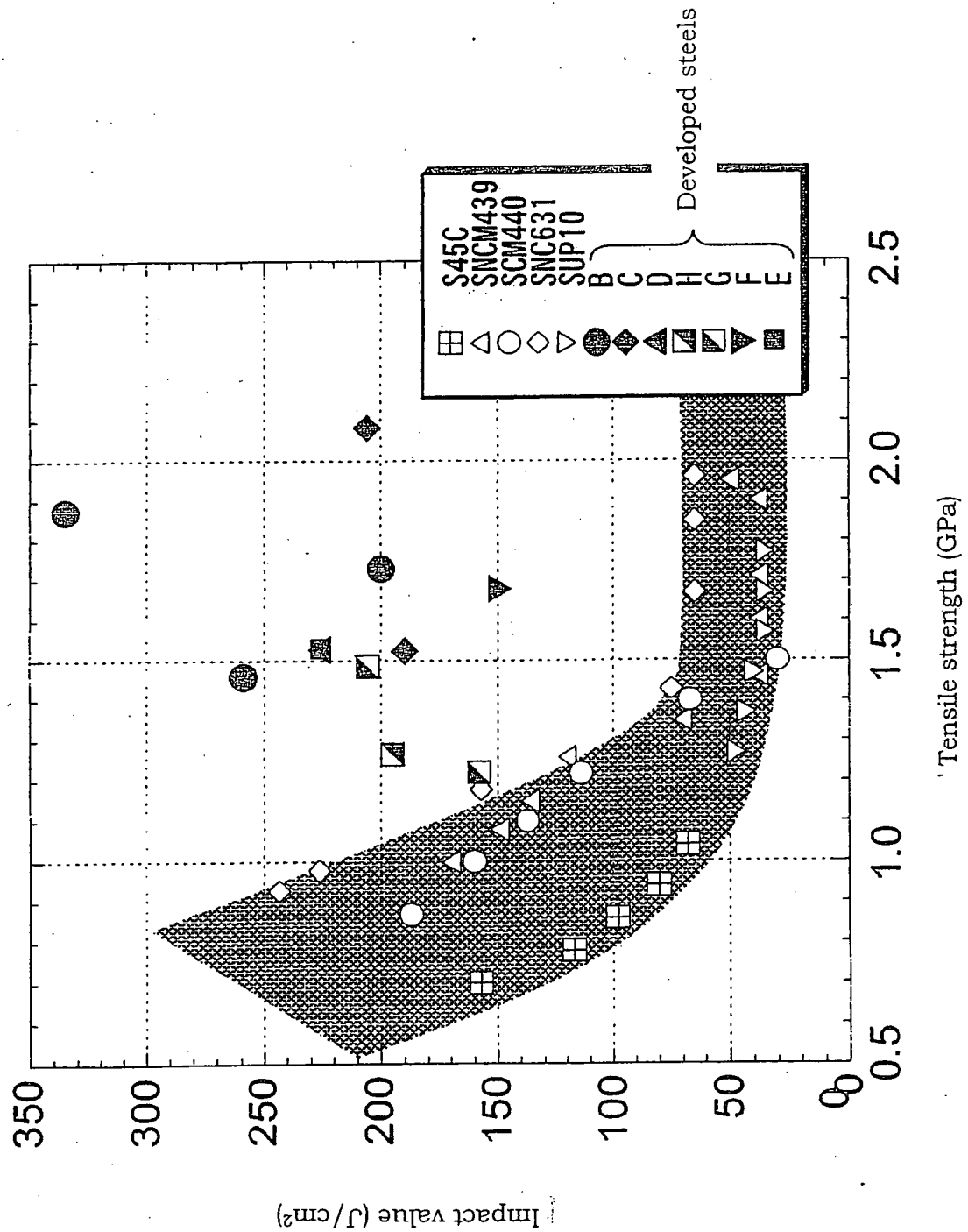


Fig. 7

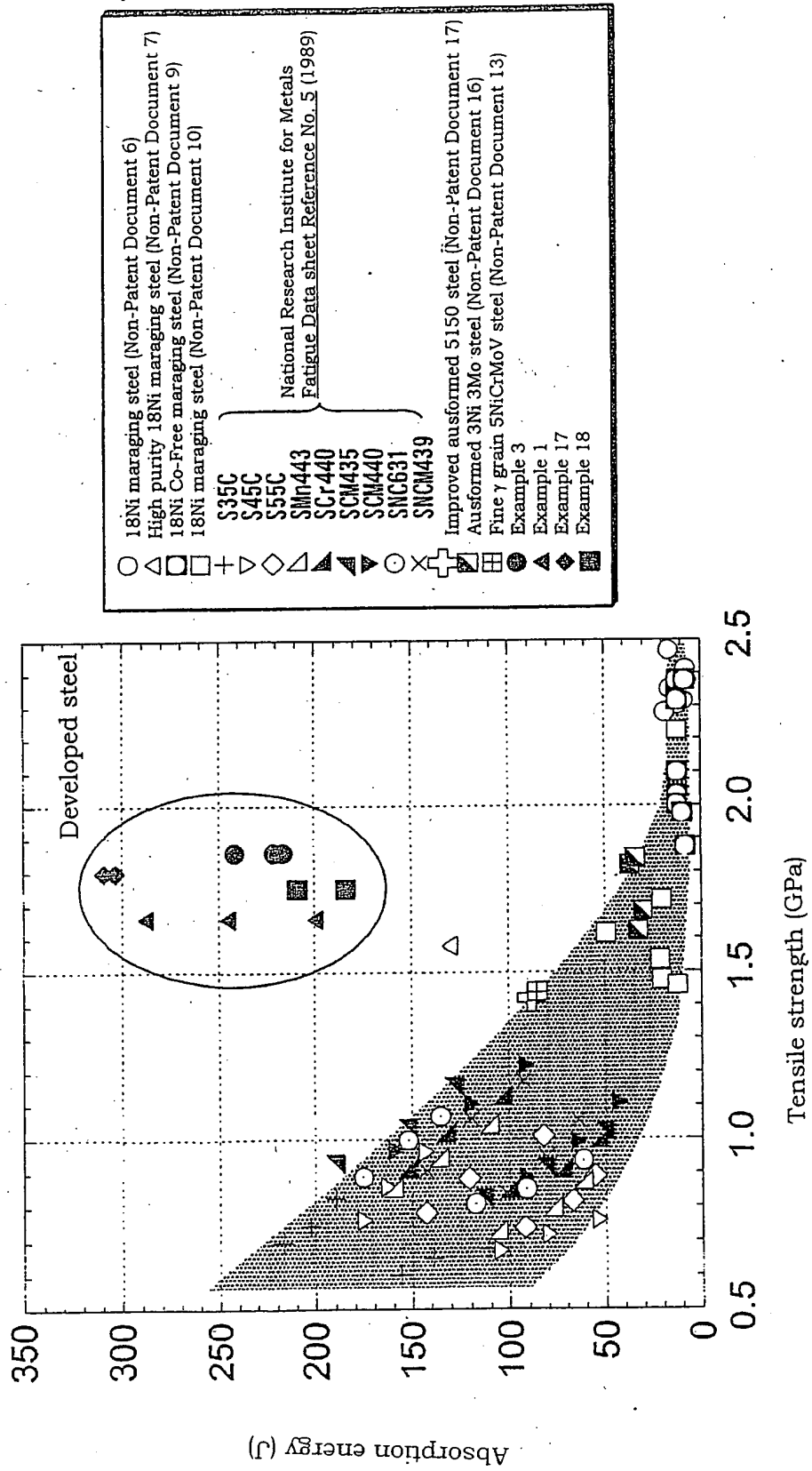


Fig. 8

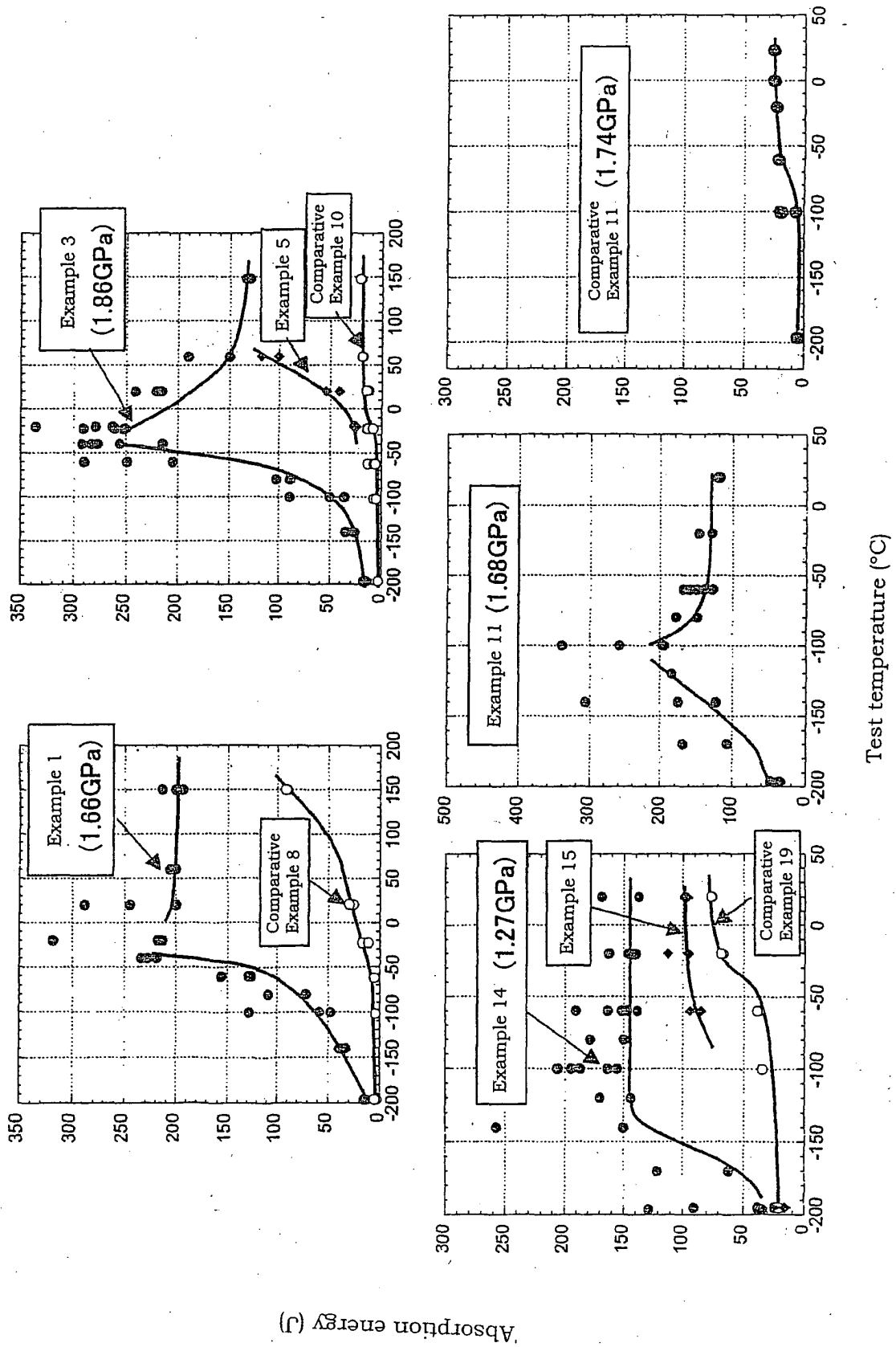


Fig. 9

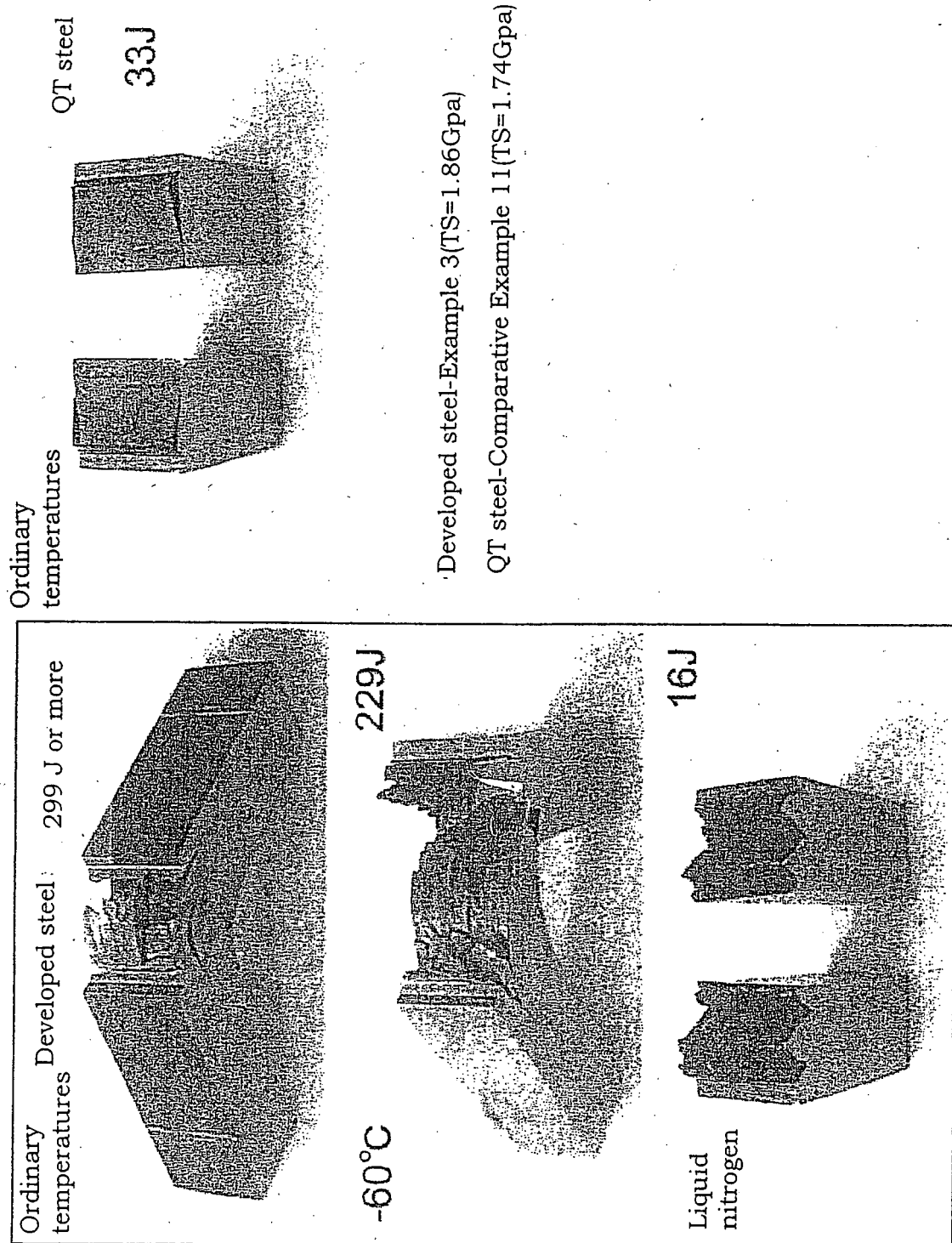


Fig. 10

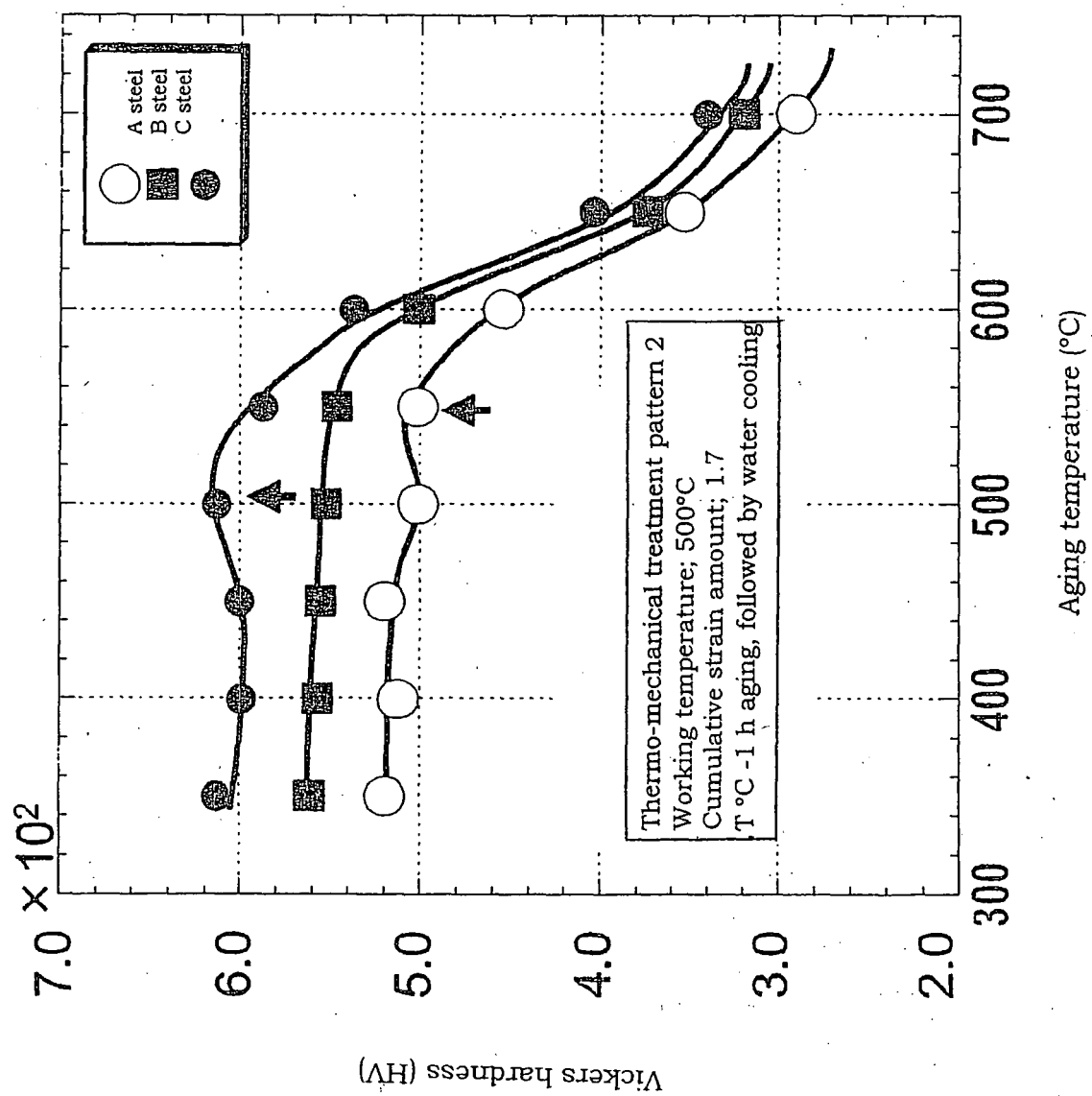


Fig. 11

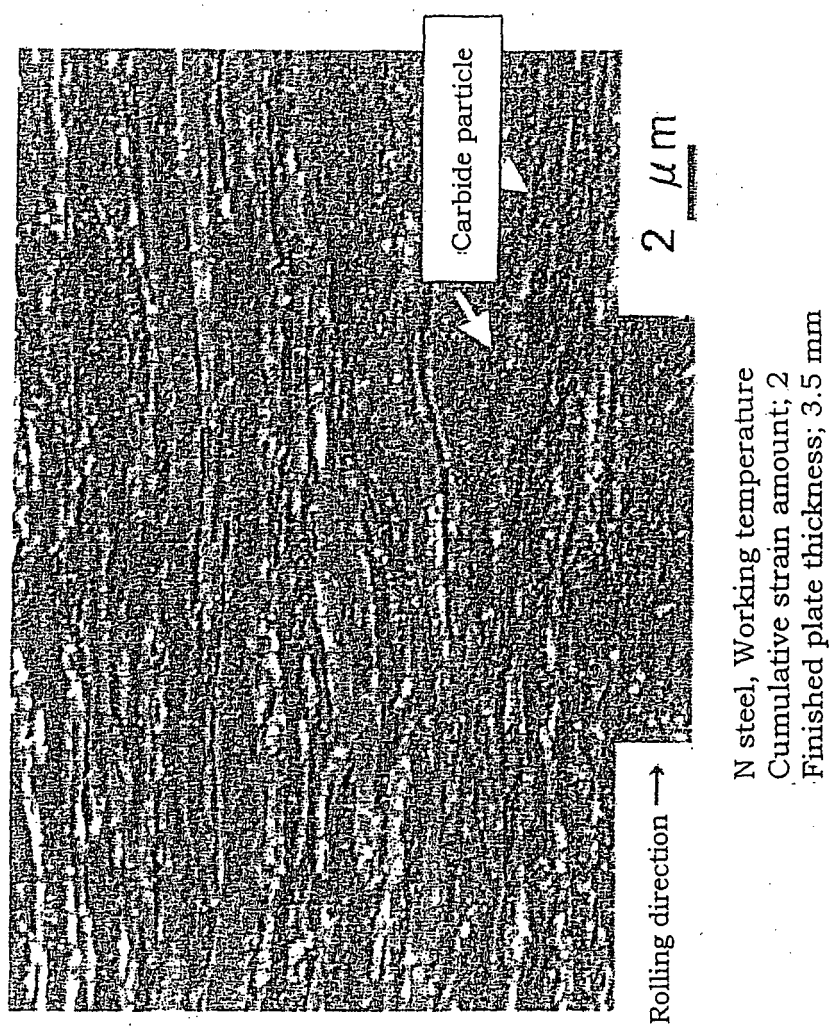
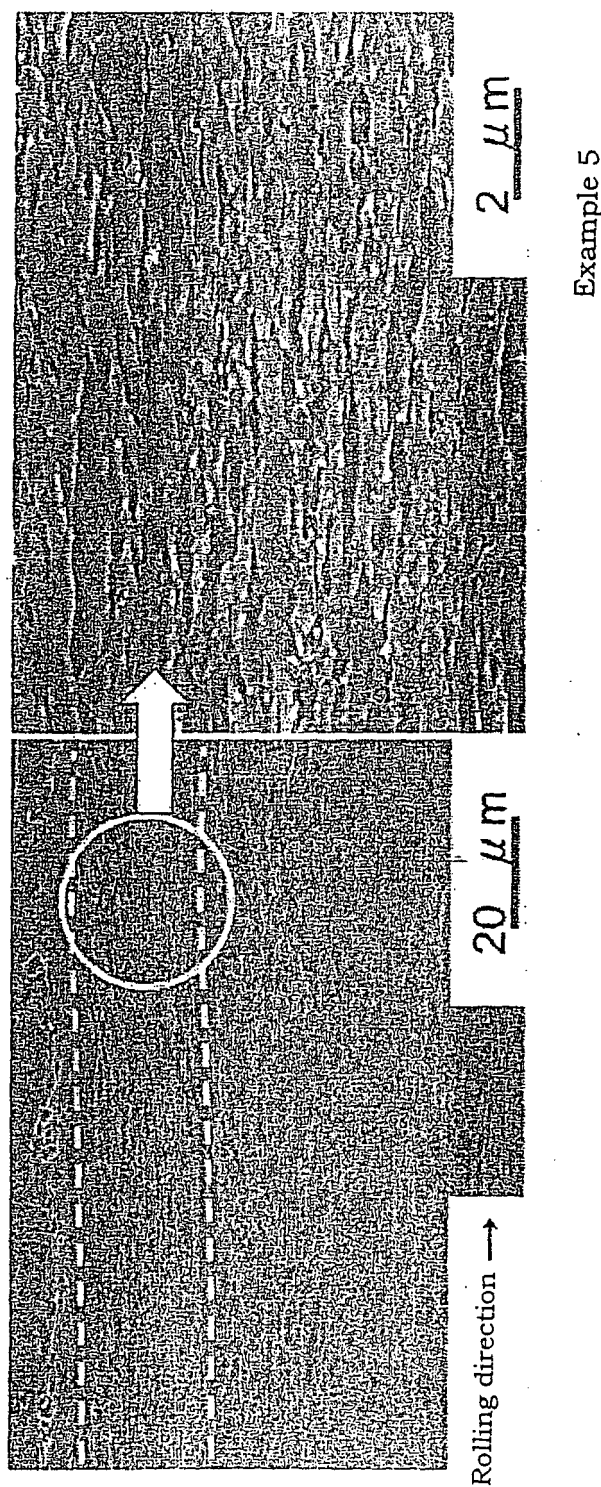


Fig. 12



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/323248

A. CLASSIFICATION OF SUBJECT MATTER

C21D8/06(2006.01) i, C22C38/00(2006.01) i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C21D8/06, C22C38/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2007

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

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X A	JP 11-71633 A (Nippon Steel Corp.), 16 March, 1999 (16.03.99), Claims; Par. Nos. [0011], [0018], [0031]; table 1; table 2, the lowest part (Family: none)	1-7 8-15
A	JP 61-37339 A (Minebea Co., Ltd.), 22 February, 1986 (22.02.86), Claims (Family: none)	1-15
A	JP 64-87746 A (Kobe Steel, Ltd.), 31 March, 1989 (31.03.89), Claims & EP 330752 A1 & KR 93-5075 B & CA 1334923 A	1-15

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

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Date of the actual completion of the international search

11 January, 2007 (11.01.07)

Date of mailing of the international search report

23 January, 2007 (23.01.07)

Name and mailing address of the ISA/

Japanese Patent Office

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REFERENCES CITED IN THE DESCRIPTION

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