(54) **Low-alloy heat-resistant steel, process for producing the same, and turbine rotor**

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Acier faiblement allié, sa méthode de fabrication et rotor de turbine

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Description

BACKGROUND OF THE INVENTION

5   1. FIELD OF THE INVENTION

[0001]   The present invention relates to low-alloy heat-resistant steels which show excellent performance as heat-resistant structural members, particularly as turbine rotor members, and relates to processes for producing the low-alloy heat-resistant steels. The present invention also relates to turbine rotors in which the low-alloy heat-resistant

10   steels are used.

2. DESCRIPTION OF RELATED ART

[0002]   Conventionally, as heat-resistant steels for high-temperature turbine rotor members for use in steam turbine

15   plants for thermal electric power generation, CrMoV steels, which belong to low alloys, and 12Cr steels, which belong to high-Cr steels, have been exclusively used (see Japanese Patent Applications, First Publications (Kokai), Nos. Sho 60-165359 and Sho 62-103345). Of these, the use of CrMoV steel is restricted to plants having a steam temperature up to 566°C because of its limited high-temperature strength. Moreover, cooling of the rotor may be required depending on the steam temperature, which is disadvantageous in that it complicates the plant. In order to improve the creep

20   properties at high temperatures, use of an ingot obtained by an electroslag remelting method has been proposed (see Japanese Patent Application, First Publication, No. Sho 60-70125). On the other hand, 12Cr steels are superior to CrMoV steels in the high-temperature strength and can hence be used in plants having a steam temperature up to 600°C. However, 12Cr steels are disadvantageous in that the production of the material is difficult and costly.

[0003]   However, in recent years, further improvement in the energy efficiency has been desired, and if it is intended

25   to raise the operational temperature of a steam turbine, a steel of a conventional type is insufficient in mechanical properties at high temperatures, particularly in terms of creep strength. Accordingly, need for developing a material which is durable in use at higher steam temperatures has been growing. Conventionally, a CrMoV steel is used after quenching the CrMoV steel heated to a temperature of about 950°C. A higher heating temperature before quenching results in a higher strength of the material because precipitation of a pro-eutectoid ferrite phase, which is soft, is in-

30   hibited, and dissolution of the strengthening elements in a solid solution is promoted. However, another problem arises in that a higher heating temperature before quenching causes creep embrittlement of the material. Therefore, the heating temperature before quenching cannot be raised. Although attempts have been made in which elements such as cobalt, niobium, and tantalum, were additionally used in order to inhibit the precipitation of the pro-eutectoid ferrite phase, a satisfactory material has not yet been obtained.

35   **[0004]**   US-A-5611 873 discloses a turbine rotor formed of steel of a composition having, by weight, a carbon content of from 0.10 to 0.35%, a silicon content of not more than 0.3%, a manganese content of not more than 1.0%, a nickel content of from 1.0 to 2.0%, a chromium content of from 1.5 to 3.0%, a molybdenum content of from 0.9 to 1.3%, a vanadium content of from 0.10 to 0.35%, a niobium content of from 0.01 to 0.15%, a tungsten content of from 0.1 to 1.5%, and the balance of iron and inevitable impurities, the inevitable impurities having a phosphorus content of not

40   more than 0.005%, a sulphur content of not more than 0.001%, an arsenic content of not more than 0.008%, aN antimony content of not more than 0.004%, and a tin content of riot more than 0.008%.

BRIEF SUMMARY OF THE INVENTION

45   **[0005]**   Accordingly, the preferred aim of the present invention is to provide a heat-resistant steel which can be quenched after heating to a higher temperature, has a toughness equivalent to or higher than that of a conventional CrMoV steel, and has excellent creep properties such as a high creep rupture property, according to a creep test on an unnotched test piece, and inhibition of creep embrittlement. Another preferred aim of the present invention is to provide a turbine rotor comprising this novel heat-resistant steel.

50   **[0006]**   The present inventors have diligently carried out research, and found that impurities greatly affect the properties of a steel at high temperatures, particularly the creep embrittlement resistance. As a result, the present inventors found that a low-alloy heat-resistant steel and a turbine rotor which can be quenched after heating to a high temperature of at least 1000°C, having a high toughness as explained below, and having excellent properties at high temperatures such as not being subject to creep embrittlement, can be obtained not only by mixing alloy components with predeter-

55   mined proportions, but also by minimizing the amount of trace impurity elements which are harmful, such as phosphorus, sulfur, copper, aluminum, arsenic, tin, and antimony. The present inventors have thus achieved the present invention.

[0007]   First, of the high-temperature properties, the creep rupture strength of a notched test piece will be described.

When a stress is applied to a steel product at a high temperature, even if the stress is comparatively small, the steel product plastically deforms very gradually to become elongated, and finally the elongation proceeds rapidly narrowing a part of the steel product, which results in rupture in the steel product. This phenomenon is called "creep" or "creep rupture phenomenon". This phenomenon is believed to occur due to viscous flow at crystal grain boundaries and dislocation within crystals. In a high-temperature creep test, a constant static load is applied to a material for a long time at a high temperature, and the time elapsed before rupture is measured. As a test piece, a round bar having a constant cross section is used. The measuring method is defined by JIS Z-2271 and JIS Z-2272. The measuring methods defined by the JIS standards are for creep tests on unnotched test pieces, and test pieces which are finished by smoothly shaving between gauge marks in the portion to be measured are used in these methods.

[0008] In contrast, in a creep test on a notched test piece, a test piece having a notch between gauge marks is used. The cross section of the portion to be stretched and subject to measurement is set to be the same as the cross section of the part subject to the measurement in a creep test on an unnotched test piece, and the stress is determined. In a creep test on an unnotched test piece, a tensile stress which is applied gradually elongates the distance between gauge marks, and narrows the portion between the gauge marks, which finally will rupture. In contrast, if a notch is formed in a test piece, a stress which counteracts deformation of the notched portion is produced such that the stress surrounds the notched portion (this stress is a so-called "multiaxial stress"), and the test piece finally ruptures without being elongated. In general, with a highly ductile material, the lapse of time before rupture tends to be long because deformation is restricted by the notch. However, depending on the type of steel, embrittlement of some materials gradually proceeds during creep tests, and creep rupture may occur in such a material without deformation (by occurrence of voids or by formation of cracks from connected voids). In this case, a notched test piece ruptures in a shorter time than an unnotched test piece due to the concentrated stress. Such a phenomenon is called "notch softening", which can be used as an index for expressing creep embrittlement. That is to say, by conducting creep rupture tests on an unnotched test piece and a notched test piece under the same conditions such as stress and temperature, and comparing the times elapsed before creep rupture, the level of creep embrittlement can be clearly demonstrated.

[0009] Since a turbine rotor is subjected to high temperatures for a long time under a stress during its operation, deterioration in the strength of the material with age is of concern. The quality of turbine rotor members has been hitherto evaluated only by high-temperature creep tests on unnotched test pieces, as defined by the Japanese Industrial Standards or the like. However, the present inventors have found a method of evaluating high-temperature strength properties of the material, particularly the creep embrittlement resistance, in a high-temperature creep test on a notched test piece. In addition, the present inventors have found that trace impurities which are harmful greatly affect creep embrittlement. As a result, the present inventors succeeded in developing a material which can be quenched after heating to a high temperature of 1000°C or higher, which is inhibited from producing precipitation of a pro-eutectoid ferrite phase, and which is not subject to creep embrittlement, by minimizing the amount of trace impurity elements which are harmful, such as phosphorus, sulfur, copper, aluminum, arsenic, tin, and antimony.

[0010] That is to say, an alloy according to a first aspect of the present invention is a low-alloy heat-resistant steel comprising:

carbon in an amount of 0.20 to 0.35% by weight,
silicon in an amount of 0.005 to 0.35% by weight,
manganese in an amount of 0.05 to 1.0% by weight,
nickel in an amount of 0.05 to 0.2% by weight,
chromium in an amount of 0.8 to 2.5% by weight,
molybdenum in an amount of 0.1 to 1.5% by weight,
tungsten in an amount of 0.1 to 2.5% by weight,
vanadium in an amount of 0.05 to 0.3% by weight,
phosphorus in an amount not larger than 0.012% by weight or no phosphorus,
sulfur in an amount not larger than 0.005% by weight or no sulfur,
copper in an amount not larger than 0.10% by weight or no copper,
aluminium in an amount not larger than 0.01% by weight or no aluminium,
arsenic in an amount not larger than 0.01 by weight or no arsenic,
tin in an amount not larger than 0.01 by weight or no tin, and
antimony in an amount not larger than 0.003% by weight or no antimony,

the balance being iron and unavoidable impurities.

[0011] Tungsten is added to a conventional CrMoV steel with the intention of improving the creep properties. Furthermore, by limiting the permissible amounts of phosphorus, sulfur, copper, aluminium, arsenic, tin, and antimony impurities, which are harmful in causing creep embrittlement, to low levels, the creep embrittlement resistance is particularly improved.

[0012]   The alloy of the first aspect of the invention may further comprise cobalt in an amount of 0.1 to 3.5% by weight.

[0013]   In this embodiment of the first aspect of the invention, cobalt is further added with the intention of improving the toughness of the alloy. Furthermore, like the alloy of the basic invention, by limiting the permissible amounts of phosphorus, sulfur, copper, aluminium, arsenic, tin, and antimony impurities, which are harmful in causing creep embrittlement, to low levels, the creep embrittlement resistance is particularly improved.

[0014]   The alloy of the first aspect of the invention may further comprise at least one of niobium in an amount of 0.01 to 0.15% by weight, tantalum in an amount of 0.01 to 0.15% by weight, nitrogen in an amount of 0.001 to 0.05% by weight, and boron in an amount of 0.001 to 0.015% by weight.

[0015]   In this embodiment of the first aspect of the invention, a trace amount of at least one type of element selected from niobium, tantalum, nitrogen, and boron is further added with the intention of further improving particularly the creep properties of an unnotched test piece. Furthermore, like the alloy of the first aspect, by limiting the permissible amounts of phosphorus, sulfur, copper, aluminium, arsenic, tin, and antimony impurities, which are harmful in causing creep embrittlement, to low levels, the creep embrittlement resistance is particularly improved.

[0016]   The alloy of the first aspect of the invention may further comprise cobalt in an amount of 0.1 to 3.5% by weight, and at least one of niobium in an amount of 0.01 to 0.15% by weight, tantalum in an amount of 0.01 to 0.15% by weight, nitrogen in an amount of 0.001 to 0.05% by weight, and boron in an amount of 0.001 to 0.015% by weight.

[0017]   In this embodiment of the first aspect of the invention, cobalt and a trace amount of at least one type of element selected from niobium, tantalum, nitrogen, and boron are further added with the intention of improving the toughness as well as further improving particularly the creep properties of an unnotched test piece. Furthermore, as in the case of alloy of the invention, the creep embrittlement resistance is intended to be improved.

[0018]   In any embodiments of low-alloy heat-resistant steel according to the invention, the amount of pro-eutectoid ferrite phase may be not larger than 10% by volume.

[0019]   By controlling the amount of pro-eutectoid ferrite phase, which is soft, at a low level, the strength of the material is ensured, and the toughness, the creep rupture strength, and the creep embrittlement resistance are improved.

[0020]   A process for producing a low-alloy heat resistant steel comprises the steps of:

   forging and molding an ingot having a composition according to any one of the embodiments of the first aspect of the invention,
   quenching the ingot after it is heated to 1000°C or higher, and
   tempering the ingot at a temperature of 600 to 750°C.

[0021]   By heating the ingot to 1000°C or higher, the amount of pro-eutectoid ferrite phase can be restricted, and the properties at high temperatures are improved due to thorough dissolution of reinforcing elements in the alloy matrix.

[0022]   A further aspect of the present invention is a turbine rotor comprising a low-alloy heat-resistant steel as in any one of the first to fourth aspects. In particular, this turbine rotor is superior to a conventional turbine in creep embrittlement resistance, and is durable in use at high temperatures.

[0023]   The low-alloy heat-resistant steel according to the present invention can be easily manufactured, has a yield strength and toughness which are equivalent to or greater than those of a conventional CrMoV steel, and has excellent high-temperature properties. In particular, since it is possible to quench the steel after it is heated to 1000°C or higher, and precipitation of pro-eutectoid ferrite phase is inhibited, creep embrittlement does not occur, and therefore this steel can be used at a high temperature and is very useful because it allows construction of power plants of high energy efficiency.

DETAILED DESCRIPTION OF THE INVENTION

[0024]   In the following, the reason for limiting the amount of each component in the alloy of the first aspect of the invention is described. The amounts of the components are expressed hereinafter on the basis of weight percentages, unless otherwise specified.

[0025]   Carbon (C): Carbon has the effect of increasing the material strength as well as ensuring the hardenability during the heat treatment. In addition, carbon forms a carbide and contribute to improvement of the creep rupture strength at high temperatures. In the alloys according to the present invention, the lower limit of the carbon content is 0.20% since a carbon content of less than 0.02% does not impart sufficient material strength to the alloy. On the other hand, an excessive carbon content deteriorates the toughness, and while the alloy is being used at a high temperature, carbon nitride aggregates to form coarse grains, which cause degradation in the creep rupture strength and creep embrittlement. Accordingly, the upper limit of the carbon content is 0.35%. A particularly preferred range within which both material strength and the toughness are imparted to the alloy is from 0.25 to 0.30%.

[0026]   Silicon (Si): Si is an element which is effective as a deoxidizer but embrittles the alloy matrix. When a deoxidizing effect is desired, an Si content of up to 0.35% is permissible. However, in the manufacture of the material

according to the present invention, there are some cases in which the deoxidizing effect of silicon is not strongly desired, depending on the manufacturing method. In such a case, the silicon content can be minimized. However, since extreme reduction of silicon requires a careful selection of materials, and therefore bring about a higher cost, the lower limit of the silicon content is 0.005%. Accordingly, the range of the silicon content is from 0.005 to 0.35%. A preferable range is from 0.01 to 0.30%.

[0027] Manganese (Mn): Manganese functions as a deoxidizer as well as having the effect of preventing hot cracks during forging. In addition, manganese has the effect of enhancing the hardenability during heat treatment. However, since too large a manganese content deteriorates the creep rupture strength, the upper limit of the manganese content is 1.0%. However, since limiting the manganese content to less than 0.05% requires careful selection of materials and excessive refining steps, and therefore brings about a higher cost, the lower limit of the manganese content is 0.05%. Accordingly, the range of the manganese content is from 0.05 to 1.0%, preferably from 0.1 to 0.8%.

[0028] Nickel (Ni): Nickel particularly has the effect of enhancing the toughness as well as enhancing the hardenability during the heat treatment and improving the tensile strength and the yield strength. If the nickel content is less than 0.05%, these effects are not discernible. On the other hand, a large amount of nickel added reduces the long-term creep rupture strength. For the alloy of the present invention, improvement of the hardenability, the toughness, and the like by the addition of nickel is not strongly counted on, but instead in order to eliminate the harmful effect of nickel on the long-term creep rupture strength, the upper limit of the nickel content is 0.2%. Taking account of the balance between this harmful effect and the effect of enhancing the toughness, the range of the nickel content is from 0.05 to 0.2%, preferably from 0.08 to 0.20%.

[0029] Chromium (Cr): Chromium enhances the hardenability of the alloy during the heat treatment as well as contributing to improvement of the creep rupture strength by forming a carbide and/or a carbonitride, and improving the antioxidation effect by dissolving in the matrix of the alloy. In addition, chromium has the effect of strengthening the matrix itself and improving the creep rupture strength. A chromium content of less than 0.8% does not provide a sufficient effect, and a chromium content exceeding 2.5% has the adverse effect of reducing the creep rupture strength. Accordingly, the range of the chromium content is from 0.8 to 2.5%, preferably from 1.0 to 1.5%.

[0030] Molybdenum (Mo): Molybdenum enhances the hardenability of the alloy during the heat treatment as well as improving the creep rupture strength by dissolving in the matrix of the alloy or in a carbide and/or a carbonitride. If the molybdenum content is less than 0.1%, these effects are not sufficiently discernible. Addition of molybdenum exceeding 2.0% has the adverse effect of deteriorating the toughness and brings about a higher cost. Accordingly, the molybdenum content is from 0.1 to 1.5%, preferably 0.5 to 1.5%.

[0031] Vanadium (V): Vanadium enhances the hardenability of the alloy during the heat treatment as well as improving the creep rupture strength by forming a carbide and/or a carbonitride. A vanadium content of less than 0.05% does not provide a sufficient effect. In addition, a vanadium content exceeding 0.3% has the opposite effect of deteriorating the creep rupture strength. Accordingly, the vanadium content is from 0.05 to 0.3%, preferably from 0.15 to 0.25%.

[0032] Tungsten (W): Tungsten dissolves in the matrix of the alloy or a carbide to improve the creep rupture strength. If the tungsten content is less than 0.1%, the above effect is not sufficient. If the tungsten content exceeds 2.5%, there is a possibility of segregation in the alloy, and a ferrite phase tends to emerge, which deteriorates the strength. Accordingly, the tungsten content is from 0.1 to 2.5%, preferably 1.0 to 2.4%.

[0033] Next, an explanation with regard to phosphorus, sulfur, copper, aluminum, arsenic, tin, and antimony, which are harmful impurities, will be given. It goes without saying that the less of these impurities are present, the better for the mechanical properties of the steel product. However, elements for which permissible amounts contained as impurities in a steel product are standardized are only phosphorus and sulfur, which are inevitably transferred from the materials used for steel production. Since phosphorus and sulfur embrittle the steel product, permissible amounts of phosphorus and sulfur are established for most types of steel products, which are at considerably high levels in view of difficulty of the refining processes. As a result of diligent research aimed at improvement of the high-temperature properties of a CrMoV steel for turbine rotors, particularly improvement of the creep rupture strength of a notched test piece, the present inventors have found that trace impurities greatly affect the creep rupture strength of a notched test piece. As such impurities, not only phosphorus and sulfur, but also copper, aluminum, arsenic, tin, antimony, and the like were also found to have harmful effects. The present inventors have studied these impurities in detail, and decided to specifically quantify the permissible amounts in an effort to achieve a rupture time of 10,000 hours or longer in a creep test on a notched test piece under the conditions of a temperature of 600°C and a stress of 15 kgf/mm^2.

[0034] Phosphorus (P), Sulfur (S): Both phosphorus and sulfur are impurities transferred from materials for steel production, and are harmful impurities which noticeably deteriorate the toughness of the steel product by forming a phosphide or a sulfide therein. In the research conducted by the inventors, it was found that phosphorus and sulfur also adversely affect the high-temperature properties. Phosphorus tends to be segregated, and secondarily causes segregation of carbon which embrittles the steel product. It was also found that phosphorus greatly affects the embrittlement when a high load is applied at a high temperature over a long time. Since extreme reduction of phosphorus and sulfur is a large burden on the steel production process, the upper limits of phosphorus and sulfur were sought

such that the rupture time in a creep test on a notched test piece is 10,000 hours or longer. As a result, it has been determined that the upper limit of phosphorus is 0.012%, and the upper limit of sulfur is 0.005%. More preferably, phosphorus is 0.010% or less, and sulfur is 0.002% or less.

[0035] Copper (Cu): Copper is diffused along crystal grain boundaries in the steel product, and embrittles the steel product. Copper particularly degrades high-temperature properties. In view of the results of creep tests on notched test pieces, it has been determined that the upper limit of the copper content is 0.10%. More preferably, the copper content is 0.04% or less.

[0036] Aluminum (Al): Aluminum is brought into steel mainly from deoxidizers during the steel production process, and forms an oxide-type inclusion in the steel product, which embrittles it. In view of the results of creep tests on notched test pieces, it has been determined that the upper limit of the aluminum content is 0.01%. More preferably, the copper content is 0.005% or less.

[0037] Arsenic (As), Tin (Sn), Antimony (Sb): It is often the case that arsenic, tin, and antimony are brought into the steel from materials for steel production. They are precipitated along crystal grain boundaries, which deteriorates the toughness of the steel product. Arsenic, tin, and antimony are aggregated in crystal grain boundaries particularly at high temperatures, and accelerate the embrittlement. In view of the results of creep tests on notched test pieces, the upper limits of these impurities are 0.01% for arsenic, 0.01% for tin, and 0.003% for antimony. More preferably, the arsenic content is 0.007% or less, the tin content is 0.007% or less, and the antimony content is 0.0022% or less.

[0038] Next, the reason for limiting the amount of each component in the alloy of a further embodiment of the invention is described. Since the reasons for limiting the amounts of the components and the impurities which have been explained above are the same for the alloy of this embodiment, the reason for limiting the amount of cobalt only is explained here.

[0039] Cobalt (Co): Cobalt dissolves in the matrix of the alloy, and strengthens the matrix itself as well as inhibiting the precipitation of the ferrite phase. In addition, cobalt has an effect of improving the toughness, and thus is effective in keeping the balance between the hardness and the toughness. If the amount of cobalt added is less than 0.1%, the above effects are not discernible. If the amount of cobalt added exceeds 3.5%, precipitation of carbides is accelerated, which leads to deterioration of the creep properties. Accordingly, a permissible range of the cobalt content is from 0.1% to 3.5%, and more preferably from 0.5% to 2.5%.

[0040] Next, the reason for limiting the amount of each component in the alloys of still further embodiments of the invention is described. Since the reasons for limiting the amounts of the components and the impurities which have been explained for the alloys detailed above are the same for the alloys of those further embodiments, the reasons for limiting the amounts of niobium, tantalum, nitrogen, and boron only are explained here.

[0041] Niobium (Nb): Niobium enhances the hardenability of the alloy as well as improving the creep rupture strength by forming a carbide and/or a carbonitride. In addition, niobium restricts the growth of crystal grains during heating at high temperatures, and contributes to homogenization of the alloy structure. If the amount of niobium added is less than 0.01%, the effects are not discernible. An amount of niobium added exceeding 0.15% will bring about noticeable deterioration of the toughness as well as causing formation of coarse grains of the carbide or the carbonitride of niobium during use of the alloy, which deteriorates long-term creep rupture strength. Accordingly, it has been determined that a permissible niobium content is from 0.01% to 0.15%, preferably 0.05 to 0.1%.

[0042] Tantalum (Ta): Tantalum, in a manner similar to niobium, enhances the hardenability of the alloy as well as improving the creep rupture strength by forming a carbide and/or a carbonitride. If the amount of tantalum added is less than 0.01%, the effects are not discernible. An amount of tantalum added exceeding 0.15% will bring about noticeable deterioration of the toughness as well as causing formation of coarse grains of the carbide or the carbonitride of niobium during use of the alloy, which deteriorates long-term creep rupture strength. Accordingly, it has been determined that a permissible tantalum content is from 0.01% to 0.15%, preferably 0.05 to 0.1%.

[0043] Nitrogen (N): Nitrogen together with carbon is bonded to alloy elements and forms carbonitrides, which contribute to improvement of the creep rupture strength. If the amount of nitrogen added is less than 0.001%, nitrides cannot be formed, and thus the above effects are not discernible. If the amount of nitrogen added exceeds 0.05%, carbonitrides are aggregated to form coarse grains, and thus a sufficient creep strength cannot be obtained. Accordingly, it has been determined that a permissible nitrogen content is from 0.001 to 0.05%, preferably 0.005 to 0.01%.

[0044] Boron (B): Boron enhances the hardenability as well as contributing to improvement of the creep rupture strength by increasing the grain boundary strength. If the amount of boron added is less than 0.001%, the above effects are not discernible. If the amount of boron added exceeds 0.015%, an adverse effect of deteriorating the hardenability occurs. Accordingly, it has been determined that the permissible boron content is from 0.001% to 0.015%, preferably 0.003 to 0.010%.

[0045] Next, the structure of the low-alloy steel according to the invention as observed by an optical microscope is described.

[0046] The low-allow steel of the present invention is normally used after it is heated to a high temperature of 950°C or higher and quenched, and then tempered at a temperature of 580 to 680°C. In order to increase the high-temperature

creep strength, there is a method in which the temperature of heating before quenching is increased to sufficiently dissolve the strengthening elements in the steel as a solid solution. However, a heating temperature of 1000°C or higher before quenching a conventional CrMoV steel causes so-called creep embrittlement, by which the material becomes brittle. Accordingly, the heating temperature before quenching a conventional CrMoV steel is from 950 to 970°C. On the other hand, if the heating temperature before quenching a system of components in which amounts of strengthening elements such as tungsten and molybdenum are increased is within a range of 950 to 970°C, the strength of the material cannot be ensured since a soft ferrite phase is precipitated in large amounts, and yet the high-temperature creep strength does not reach a satisfactory level. However, when the ferrite phase precipitated is in a small amount and is finely distributed, the harmful effects are small.

[0047]   As a result of diligent research in measures to prevent creep embrittlement, the present inventors have found that trace impurities of phosphorus, sulfur, copper, aluminum, arsenic, tin, and antimony greatly affect creep embrittlement. Since creep embrittlement originates from these trace impurities, it was discovered that by limiting the amount of these trace impurities to low levels, creep embrittlement does not occur even if the temperature of heating before quenching is increased to 1000°C or higher. If the temperature of heating before quenching is increased to 1000°C or higher, the strengthening elements are sufficiently dissolved in the matrix of the alloy, and in addition precipitation of the ferrite phase is restricted so that the strength of the material is increased and the creep properties according to tests on an unnotched test piece are further improved. The effects from the reduction of the ferrite phase become discernible when the ferrite phase is 10% or less in the structure viewed by an optical microscope. When the ferrite phase of 10% or less is finely distributed, there are no large harmful effects.

[0048]   The proportion of the ferrite phase in the light microscopic structure can be determined using an image analyzing device which is commonly used.

[0049]   Next, a process for producing a low-alloy heat-resistant steel of the present invention will be described.

[0050]   According to the process for producing a low-alloy heat-resistant steel of the present invention, first, as described above, a base material is produced by a melting process so as to have a predetermined alloy composition. A method for reducing the trace impurities is not particularly limited, and various known refining methods including careful selection of raw materials can be employed. Then, in the case where a turbine rotor member, for example, is manufactured, an alloy melt with a predetermined composition is cast by a known method to form a steel ingot, which is subjected to a predetermined forging/molding process to produce a material for the turbine rotor member. Then, this material is quenched after heating to a temperature between 1000°C and 1100°C, preferably between 1030°C and 1070°C, and is tempered at a temperature between 600°C and 750°C, preferably 650°C and 700°C. If the heating temperature before quenching is lower than 1000°C, a great amount of soft ferrite phase is precipitated because dissolution of the strengthening elements is insufficient, and the strength is not increased. if the heating temperature before quenching exceeds 1100°C, coarse crystal grains are formed, which deteriorates the toughness. If the tempering temperature is lower than 600°C, the tempering is insufficient, and the high-temperature creep strength is deteriorated while the desired toughness cannot be obtained. If the tempering temperature exceeds 750°C, the tensile strength and the yield strength are deteriorated. The range of the tempering temperature is appropriately chosen such that the 0.2% yield strength will be about 63±2 kgf/mm^2. There are also no limitations on the means for quenching and tempering, and any known means can be appropriately chosen taking account of the use and size of the material.

Examples

[0051]   The present invention will be more specifically described with reference to the following examples.

[0052]   In the examples, all test pieces were prepared by a melting process using a 50 kg vacuum high-frequency furnace, and forging at a heating temperature of 1200°C. Heat treatments of the test pieces used in the various evaluation tests were carried out by hardening the test pieces under conditions which simulated the central part of an oil-quenched rotor having a drum diameter of 1,200 mm, and then tempering them at a temperature which had been determined so as to give a 0.2% yield strength of about 63±2 kgf/mm^2. However, some test pieces did not achieve this target yield strength.

Example 1

[0053]   In Table 1, chemical compositions of materials tested in Example 1 (Samples Nos. 1 to 6) and of comparative materials (Samples Nos. 7 to 14) are shown. The amounts of pro-eutectoid ferrite phase in each material quenched after heating to 950°C, 1000°C, and 1050°C were quantified using an image analyzing device, and the results are shown in Table 2. In addition, the 0.2% yield strength, the Charpy impact absorbed energy, and the creep rupture time at 600°C under 15 kgf/mm^2 for each material quenched after heating to 1050°C were measured for notched and unnotched test pieces, and the results are also shown in Table 2.

[0054]   Each of Samples Nos. 7 to 9 of Comparative Example A exhibited insufficient strength even though the trace

impurity contents were reduced, mainly because the amounts of carbon, silicon, and manganese were inappropriate. Each of Samples Nos. 7 and 8 had a large amount of pro-eutectoid ferrite phase, having reduced hardenability, and exhibited an insufficient strength. Sample No. 9 exhibited an inferior toughness. Each of Samples Nos. 10 and 11 of Comparative Example B had an insufficient creep strength according to the test using an unnotched test piece even though the trace impurity contents were reduced, since the amounts of nickel, chromium, molybdenum, tungsten, vanadium, and the like were inappropriate. Samples Nos. 12 and 13 of Comparative Example C satisfied the desired level of the main components of the present invention. However, since the trace impurity contents were large, the materials of Samples Nos. 12 and 13 were brittle, causing creep embrittlement, although they exhibited long rupture times in the creep tests using the unnotched test pieces.

[0055]   In contrast, in the examples of the present invention, the amounts of pro-eutectoid ferrite phase are reduced remarkably in Samples Nos. 2 to 6 which were quenched after heating to 1000°C, and the yield strength, the toughness, and the creep properties of Samples Nos. 2 to 6 were all excellent. In particular, in creep tests using these samples with notches which were quenched after heating to 1050°C, the samples did not break even after 12,000 hours, which indicates that creep embrittlement did not occur in these samples. (Sample 1 of Example 1 of Tables 1 and 2 falls outside the scope of the invention).

Example 2

[0056]   In Table 3, the chemical compositions of the materials tested in Example 2 are shown. Example 2 is based on the material of Sample No. 2 or 5 in Example 1, and furthermore in Example 2, cobalt or a trace element such as niobium, tantalum, nitrogen, and boron was added to the material of Sample No. 2 or 5, and trace impurities were restricted to low levels. In a manner similar to Example 1, the 0.2% yield strength, the Charpy impact absorbed energy, and the creep rupture time at 600°C under 15 kgf/mm^2 of each material quenched after heating to 1050°C were measured for notched and unnotched test pieces, and the results are shown in Table 4.

[0057]   From the results in Table 4, it is understood that the levels of the 0.2% yield strength and the Charpy impact absorbed energy of each material (Samples Nos. 15 to 21) of Example 2 are about the same as those of the materials in Example 1, but the creep properties were improved, and particularly the creep rupture time in the creep test using the unnotched test piece was prolonged greatly. In addition, it is understood that in Example 2 the amounts of pro-eutectoid ferrite phase were reduced in the test pieces which were quenched after heating to 1000°C, and creep embrittlement did not occur in the test pieces which were quenched after heating to 1050°C since the trace impurities were restricted to low levels.

Table 1

	Sample No.	Chemical Composition (wt%)

	Sample No.	C	Si	Mn	Ni	Cr	Mo	W	V	P	S	Cu	Al	As	Sn	Sb	Fe
Example 1	1	0.23	0.24	0.11	0.26	1.95	1.46	0.59	0.25	0.008	0.002	0.04	0.004	0.005	0.005	0.0015	balance
	2	0.26	0.05	0.09	0.08	1.46	0.54	2.40	0.25	0.006	0.001	0.03	0.003	0.006	0.005	0.0012	balance
	3	0.26	0.09	0.75	0.10	1.40	0.99	2.00	0.19	0.008	0.001	0.01	0.002	0.006	0.004	0.0022	balance
	4	0.27	0.29	0.18	0.19	1.23	1.02	1.52	0.21	0.010	0.002	0.02	0.005	0.004	0.006	0.0013	balance
	5	0.27	0.07	0.20	0.08	1.35	1.21	2.40	0.23	0.005	0.002	0.02	0.004	0.007	0.005	0.0011	balance
	6	0.31	0.03	0.23	0.09	1.04	0.52	2.42	0.24	0.006	0.001	0.01	0.003	0.006	0.005	0.0015	balance
	7	0.14	0.25	0.10	0.11	1.19	1.02	1.49	0.24	0.008	0.002	0.02	0.004	0.006	0.006	0.0016	balance
	8	0.17	0.06	0.69	0.08	0.75	0.51	2.42	0.01	0.009	0.002	0.03	0.002	0.006	0.005	0.0013	balance
	9	0.41	0.40	0.25	0.27	1.14	0.52	3.04	0.24	0.007	0.002	0.01	0.002	0.005	0.005	0.0012	balance
Comparative Example A	10	0.27	0.32	1.23	0.20	1.92	0.48	0.002	0.17	0.006	0.001	0.03	0.003	0.007	0.004	0.0020	balance
	11	0.24	0.18	0.22	0.47	2.97	0.02	1.03	0.01	0.009	0.001	0.02	0.004	0.007	0.006	0.0021	balance
Comparative Example B	12	0.34	0.30	0.75	0.42	1.04	1.27	0.003	0.25	0.020	0.008	0.15	0.005	0.028	0.020	0.0036	balance
Comparative Example C	13	0.26	0.06	0.11	0.09	1.44	0.54	2.41	0.25	0.015	0.001	0.03	0.003	0.008	0.005	0.0039	balance
	14	0.27	0.07	0.20	0.08	1.35	1.21	2.40	0.23	0.019	0.002	0.02	0.012	0.007	0.005	0.0034	balance

Table 2

| | Sample No. | Amount of pro-eutectoid ferrite (volume %) Heating temperature before quenching (°C) | | | Material quenched after heating to 1050°C | | | | Note |
		950	1000	1050	0.2% Yield (kgf/mm²)	Charpy impact absorbed energy (kgf-m)	600°C-15kgf/mm² Creep rupture time (h) Unnotched test piece	Notched test piece	
Example 1	1	34	7	0	61.2	6.9	4,830	Not broken in 12,000	
	2	32	3	0	63.5	6.2	6,995	Not broken in 12,000	
	3	15	0	0	62.8	5.3	5,662	Not broken in 12,000	
	4	14	0	0	61.7	4.9	5,269	Not broken in 12,000	
	5	26	8	0	64.3	4.2	7,783	Not broken in 12,000	
	6	18	5	0	63.7	4.0	7,155	Not broken in 12,000	
Comparative Example A	7	55	37	28	55.4	9.0	1,562	Not broken in 5,000	Insufficient strength even after tempering at 600°C
	8	40	23	16	58.8	7.6	1,092	Not broken in 5,000	Insufficient strength even after tempering at 600°C
	9	13	2	0	64.1	0.8	3,844	6,456	Insufficient toughness
Comparative Example B	10	0	0	0	62.7	4.4	3,168	Not broken in 5,000	Insufficient strength of unnotched test piece
	11	15	2	0	61.6	7.1	1,513	Not broken in 5,000	Insufficient strength of unnotched test piece
Comparative Example C	12	0	0	0	62.5	3.0	3,250	2,010	Embrittlement of notched test piece; insufficient strength of unnotched test piece
	13	36	8	0	61.9	2.5	6,823	6,597	Embrittlement of notched test piece
	14	23	3	0	63.6	2.4	7,604	7,031	Embrittlement of notched test piece

Table 3

Sample No.		C	Si	Mn	Ni	Cr	Mo	W	V	Nb	Ta	Co	N	B	P	S	Cu	Al	As	Sn	Sb	Fe
													Chemical Composition (wt%)									
15	Example 2	0.26	0.05	0.09	0.09	1.45	0.53	2.39	0.25	0.06					0.006	0.001	0.03	0.003	0.006	0.005	0.0012	balance
16		0.26	0.05	0.10	0.08	1.44	0.54	2.39	0.25		0.09			0.004	0.007	0.001	0.03	0.002	0.005	0.005	0.0012	balance
17		0.27	0.08	0.20	0.08	1.35	1.22	2.39	0.23	0.06	0.05			0.006	0.005	0.001	0.01	0.002	0.006	0.007	0.0014	balance
18		0.26	0.07	0.19	0.10	1.34	1.20	2.40	0.24	0.07					0.007	0.001	0.02	0.002	0.007	0.006	0.0013	balance
19		0.27	0.08	0.20	0.09	1.35	1.20	2.38	0.24			1.48	0.008		0.006	0.001	0.01	0.002	0.006	0.006	0.0013	balance
20		0.27	0.07	0.20	0.08	1.33	1.20	2.42	0.24	0.08		0.98	0.006		0.005	0.002	0.02	0.004	0.007	0.005	0.0011	balance
21		0.27	0.08	0.22	0.08	1.34	1.20	2.39	0.23			2.04	0.009		0.007	0.001	0.02	0.002	0.007	0.005	0.0010	balance

Table 4

| Sample No. | Amount of pro-eutectoid ferrite (volume %) Heating temperature before quenching (°C) | | | Material quenched after heating to 1050°C | | | |
	950	1000	1050	0.2% Yield (kgf/mm²)	Charpy impact absorbed energy (kgf-m)	600°C-15kgf/mm² Creep rupture time (h) Unnotched test piece	Notched test piece
15	41	9	0	63.0	5.6	7,652	Not broken in 12,000
16	27	3	0	61.6	5.2	7,885	Not broken in 12,000
17	33	8	0	63.3	3.9	8,843	Not broken in 12,000
18	19	5	0	62.2	4.0	8,499	Not broken in 12,000
19	20	3	0	63.3	5.0	8,064	Not broken in 12,000
20	21	0	0	64.0	4.8	9,189	Not broken in 12,000
21	17	0	0	62.5	5.1	8,570	Not broken in 12,000

Example 2

Claims

1. A low-alloy heat-resistant steel comprising:

carbon in an amount of 0.20 to 0.35% by weight,
silicon in an amount of 0.005 to 0.35% by weight,
manganese in an amount of 0.05 to 1.0% by weight,
nickel in an amount of 0.05 to 0.2% by weight,
chromium in an amount of 0.8 to 2.5% by weight,
molybdenum in an amount of 0.1 to 1.5% by weight,
tungsten in an amount of 0.1 to 2.5% by weight,
vanadium in an amount of 0.05 to 0.3% by weight,
phosphorus in an amount not larger than 0.012% by weight or phosphorus

sulfur in an amount not larger than 0.005% by weight or no sulfur,
copper in an amount not larger than 0.10% by weight or no copper,
aluminium in an amount not larger than 0.01% by weight or no aluminium,
arsenic in an amount not larger than 0.01% by weight or no arsenic,
tin in an amount not larger than 0.01% by weight or no tin, and
antimony in an amount not larger than 0.003% by weight or no antimony,

the balance being iron and unavoidable impurities.

2. A low-alloy heat-resistant steel according to claim 1 and further comprising cobalt in an amount of 0.1 to 3.5% by weight, the addition being made at the expense of iron.

3. A low-alloy heat-resistant steel according to claim 1 and further comprising at least one of niobium in an amount of 0.01 to 0.15% by weight, tantalum in an amount of 0.01 to 0.15% by weight, nitrogen in an amount of 0.001 to 0.05% by weight, and boron in an amount of 0.001 to 0.15% by weight, these additions being made at the expense of iron.

4. A low-alloy heat-resistant steel according to claim 1 and further comprising cobalt in an amount of 0.1 to 3.5% by weight, and at least one of niobium in an amount of 0.01 to 0.15% by weight, tantalum in an amount of 0.01 to 0.15% by weight, nitrogen in an amount of 0.001 to 0.05% by weight, and boron in an amount of 0.001 to 0.015% by weight, these additions being made at the expense of iron.

5. A low-alloy heat-resistant steel according to any one of claims 1 to 4, wherein the amount of pro-eutectoid ferrite phase is not larger than 10% by volume.

6. A process for producing a low-alloy heat-resistant steel, the process comprising the step of:

forging and molding an ingot having a composition as in any one of claims 1 to 5,
quenching the ingot after it is heated to 1000°C or higher, and
tempering the ingot at a temperature of 600 to 750°C.

7. A turbine rotor comprising a low-alloy heat-resistant steel as in any one of the claims 1 to 5.

8. A turbine rotor comprising a low-alloy heat-resistant steel produced by the process as in claim 6.

Patentansprüche

1. Niedriglegierter, hitzebeständiger Stahl, umfassend;

Kohlenstoff in einer Menge von 0,20 bis 0,35 Gew.-%,
Silizium in einer Menge von 0,005 bis 0,35 Gew.-%,
Mangan in einer Menge von 0,05 bis 1,0 Gew.-%,
Nickel in einer Menge von 0,05 bis 0,2 Gew.-%,
Chrom in einer Menge von 0,8 bis 2,5 Gew.-%,
Molybdän in einer Menge von 0,1 bis 1,5 Gew.-%,
Wolfram in einer Menge von 0,1 bis 2,5 Gew.-%,
Vanadium in einer Menge von 0,05 bis 0,3 Gew.-%,
Phosphor in einer Menge von nicht über 0,012 Gew.-% oder keinen Phosphor,
Schwefel in einer Menge von nicht über 0,005 Gew.-% oder keinen Schwefel,
Kupfer in einer Menge von nicht über 0,10 Gew.-% oder kein Kupfer,
Aluminium in einer Menge von nicht über 0,01 Gew.-% oder kein Aluminium,
Arsen in einer Menge von nicht über 0,01 Gew.-% oder kein Arsen,
Zinn in einer Menge von nicht über 0,01 Gew.-% oder kein Zinn, und
Antimon in einer Menge von nicht über 0,003 Gew.-% oder kein Antimon,

wobei der Rest aus Eisen und unvermeidlichen Verunreinigungen besteht.

2. Niedrigleglerter, hitzebeständiger Stahl nach Anspruch 1, der weiters Kobalt in einer Menge von 0,1 bis 3,5 Gew.-% umfasst, wobei der Zusatz auf Kosten von Eisen erfolgt.

3. Nieriglegierter, hitzebeständiger Stahl nach Anspruch 1, der weiters zumindest eines von Niob in einer Menge von 0,01 bis 0,15 Gew.-%, Tantal in einer Menge von 0,01 bis 0,15 Gew.-%, Stickstoff in einer Menge von 0,001 bis 0,05 Gew.-% und Bor in einer Menge von 0,001 bis 0,15 Gew.-% umfasst, wobei diese Zusätze auf Kosten von Eisen erfolgen.

4. Niedriglegierter, hitzebeständiger Stahl nach Anspruch 1, der weiters Kobalt in einer Menge von 0,1 bis 3,5 Gew.-% und zumindest eines von Niob in einer Menge von 0,01 bis 0,15 Gew.-%, Tantal in einer Menge von 0,01 bis 0,75 Gew.-%, Stickstoff in einer Menge von 0,001 bis 0,05 Gew.-% und Bor in einer Menge von 0,001 bis 0,015 Gew.-% erfolgt, wobei diese Zusätze auf Kosten von Eisen erfolgen.

5. Niedriglegierter, hitzebeständiger Stahl nach einem der Ansprüche 1 bis 4, worin die Menge an pro-eutektolder Ferritphase nicht über 10 Vol.-% liegt.

6. Verfahren zur Herstellung von niedriglegiertem, hitzebeständigem Stahl, wobei das Verfahren folgende Schritte umfasst:

das Schmieden und Formen eines Barrens mit einer Zusammensetzung nach einem der Ansprüche 1 bis 5,
das Abschrecken des Barrens, nachdem er auf 1.000 °C oder darüber erhitzt worden ist, und
das Anlassen des Barrens bei einer Temperatur von 600 bis 750 °C.

7. Turbinenrotor, der niedriglegierten, hitzebeständigen Stahl nach einem der Ansprüche 1 bis 5 umfasst.

8. Turbinenrotor, der nach einem Verfahren nach Anspruch 6 hergestellten niedriglegierten, hitzebeständigen Stahl umfasst.

Revendications

1. Acier faiblement allié résistant à la chaleur comprenant :

du carbone dans une quantité de 0,20 à 0,35 % en poids,
du silicium dans une quantité de 0,005 à 0,35 % en poids,
du manganèse dans une quantité de 0,05 à 1,0 % en poids,
du nickel dans une quantité de 0,05 à 0,2 % en poids,
du chrome dans une quantité de 0,8 à 2,5 % en poids,
du molybdène dans une quantité de 0,1 à 1,5 % en poids,
du tungstène dans une quantité de 0,1 à 2,5 % en poids,
du vanadium dans une quantité de 0,05 à 0,3 % en poids,
du phosphore dans une quantité qui n'est pas supérieure à 0,012 % en poids ou ne comprenant pas de phosphore,
du soufre dans une quantité qui n'est pas supérieure à 0,005 % en poids ou ne comprenant pas de soufre,
du cuivre dans une quantité qui n'est pas supérieure à 0,10 % en poids ou ne comprenant pas de cuivre,
de l'aluminium dans une quantité qui n'est pas supérieure à 0,01 % en poids ou ne comprenant pas d'aluminium,
de l'arsenic dans une quantité qui n'est pas supérieure à 0,01 % en poids ou ne comprenant pas d'arsenic,
de l'étain dans une quantité qui n'est pas supérieure à 0,01 % en poids ou ne comprenant pas d'étain, et
de l'antimoine dans une quantité qui n'est pas supérieure à 0,003 % en poids ou ne comprenant pas d'antimoine,
l'équilibre étant assuré par du fer et des impuretés inévitables.

2. Acier faiblement allié résistant à la chaleur selon la revendication 1 et comprenant en outre du cobalt dans une quantité de 0,1 à 3,5 % en poids, l'addition étant effectuée aux dépens du fer,

3. Acier faiblement allié résistant à la chaleur selon la revendication 1 et comprenant en outre au moins l'un parmi le niobium dans une quantité de 0,01 à 0,15 % en poids, le tantale dans une quantité de 0,01 à 0,15 % en poids,

l'azote dans une quantité de 0,001 à 0,05 % en poids, le bore dans une quantité de 0,001 à 0,15 % en poids, ces additions étant effectuées aux dépens du fer.

4. Acier faiblement allié résistant à la chaleur selon la revendication 1 et comprenant en outre du cobalt dans une quantité de 0,1 à 3,5 % en poids, et au moins l'un parmi le niobium dans une quantité de 0,01 à 0,15 % en poids, le tantale dans une quantité de 0,01 à 0,15 % en poids, l'azote dans une quantité de 0,001 à 0,05 % en poids, et le bore dans une quantité de 0,001 à 0,015 % en poids, ces additions étant effectuées aux dépens du fer.

5. Acier faiblement allié résistant à la chaleur selon l'une quelconque des revendications 1 à 4, dans lequel la quantité d'une phase de ferrite proeutectoïde n'est pas supérieure à 10 % en volume.

6. Procédé pour la production d'un acier faiblement allié résistant à la chaleur, le procédé comprenant les étapes consistant à :

    forger et mouler un lingot ayant une composition telle que définie dans l'une quelconque des revendications 1 à 5,
    tremper le lingot après qu'il ait été chauffé à 1 000°C ou à une température supérieure, et
    faire un revenu du lingot à une température de 600 à 750°C.

7. Rotor de turbine comprenant un acier faiblement allié résistant à la chaleur tel que défini dans l'une quelconque des revendications 1 à 5.

8. Rotor de turbine comprenant un acier faiblement allié résistant à la chaleur produit suivant le procédé tel que défini dans l'une quelconque des revendications 1 à 6.