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(54) 12Cr alloy steel for a turbine rotor

(57) A turbine rotor material, that has sufficient corrosion resistance and stress corrosion cracking resistance and appropriate strength and toughness in a good balance, and a manufacturing method thereof are provided. The turbine rotor material is a 12Cr alloy steel that contains: C of 0.01 to 0.10%, Si of 0.01 to 0.50%, Mn of 0.1 to 1.0%, Cr of 9 to 13%, Ni of 2 to 7%, Mo of 0.3 to 3%, N of 0.01 to 0.10%, all in weight percent, and remains of Fe and incidental impurities.

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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention relates to a 12Cr alloy steel for a turbine rotor of a geothermal power generation turbine, steam power generation low pressure turbine or the like as well as to a manufacturing method of this alloy steel and a turbine rotor made of this alloy steel.

Description of the Prior Art

[0002] In a rotor material of a geothermal turbine, there is no large problem in the high temperature strength characteristic, as the geothermal steam temperature is usually about 300°C or less. Hence, as a rotor material of a low pressure steam turbine, it is usual to use a 3.5Ni-Cr-Mo-V steel that is excellent in the strength and toughness of 300°C or less or a rotor material of a modified type CrMoV steel that has an enhanced toughness. However, as these materials are short of a corrosion resistance, they cannot be said as having a sufficient characteristic, especially when they are used in a geothermal steam environment that is of a highly corrosive nature. Moreover, in the rotor material of the geothermal turbine or low pressure steam turbine, in addition to the general corrosion resistance, a stress corrosion cracking resistance is also an important factor of the material. Further, the 3.5Ni-Cr-Mo-V steel or the modified type CrMoV steel cannot necessarily be considered sufficient in the stress corrosion cracking resistance also.

[0003] On the other hand, as mentioned in the Japanese Patent No. 002115837 for example, the 12Cr steel is sometimes used for a high pressure rotor material or intermediate pressure rotor material of a steam turbine. But in this case, as the temperature of the steam used is about 600°C or more, such a component design that especially aims at securing a creep strength is carried out, wherein the components of the steam used are carefully controlled so that no specific problem may occur as to the corrosion ability. Nevertheless, this material is not very good in the toughness in the temperature range between room temperature and 300°C, such as in the geothermal steam or low pressure steam. Especially, differently from the high pressure rotor, in a large sized geothermal power generation turbine rotor or steam power generation low pressure turbine rotor, it is also important to ensure the toughness.

[0004] In the manufacture of the 12Cr steel to be used as the high pressure rotor material or intermediate pressure rotor material, segregation of alloy components is liable to occur at a central portion of steel ingot and it is usual to employ a special smelting by which the ingot once manufactured is re-smelted or an enriched portion of the alloy components is diluted in the solidifying process of the molten metal.

SUMMARY OF THE INVENTION

[0005] In view of the technological state of the prior art as mentioned above, it is an object of the present invention to provide a turbine rotor material that has a sufficient corrosion resistance and stress corrosion cracking resistance in a geothermal steam environment or in a dry and wet alternating environment of a low pressure steam turbine and also has an appropriate strength and toughness in a good balance between them as well as to provide a manufacturing method of this turbine rotor material.

[0006] In order to attain the mentioned object, the present invention provides a 12Cr alloy steel for a turbine rotor, a manufacturing method thereof and a turbine rotor made thereof, as follows.

[0007] In the first one of the present invention, provided is an alloy steel that has base components of the 12%Cr steel to stand a use even under a severe corrosion environment and is made by optimizing an addition quantity of various alloy elements, ensuring an appropriate strength and high toughness of the material and remarkably enhancing the corrosion resistance and stress corrosion cracking resistance. This alloy steel is particularly appropriate for making a rotor of a geothermal power generation turbine or steam power generation low pressure turbine that is mainly used under the temperature of 300°C or less.

[0008] To be more concrete, C (carbon) quantity is reduced so as to ensure the toughness and corrosion resistance and Ni (nickel) is added more than in the conventional case so as to ensure the hardenability that is lowered thereby. The addition of Ni aims also at leaving an appropriate quantity of austenitic phase in the metal base so as to enhance the toughness, corrosion resistance and stress corrosion cracking resistance. Moreover, addition of V (vanadium), that is added in the conventional high temperature 12%Cr rotor material, is avoided so as to maintain the toughness.

[0009] That is, in the first one of the present invention, the 12Cr alloy steel for a turbine rotor is characterized in containing C of 0.01 to 0.10%, Si (silicon) of 0.01 to 0.50%, Mn (manganese) of 0.1 to 1.0%, Cr (chromium) of 9 to 13%, Ni of 2 to 7%, Mo (molybdenum) of 0.3 to 3% and N (nitrogen) of 0.01 to 0.10%, all in weight percent, and remains of Fe (iron) and incidental impurities.

[0010] The 12Cr alloy steel according to the present invention is first melted in an electric furnace etc. for making an ingot. The ingot is then heated to the temperature of 1,000 to 1,200°C for a hot forging. After the material is sufficiently forged, it is formed in a rotor shape. This material is then heated to the temperature of 900 to 1,100°C to be applied with quenching and subsequently applied with tempering in the temperature range of 500 to 700°C. Thereby, the material is adjusted to a predetermined material strength.

[0011] Mentioned below is the reason why the respective alloy components are so limited. All the component percentages in the following description mean the weight percent.

(1) C (carbon)

[0012] C largely changes the material strength and toughness in the low temperature and also gives a large influence on the corrosion resistance and stress corrosion cracking resistance. If the C quantity exceeds 0.1%, the corrosion resistance, stress corrosion cracking resistance and toughness are largely lowered. Thus, the upper limit value is set to 0.1%. On the other hand, if the C quantity is below 0.01%, the strength is hardly ensured. Thus, the lower limit value is set to 0.01%. Preferably, C is 0.03 to 0.08%.

(2) Si (silicon)

[0013] While Si is a useful element as a deoxidizing agent, it accelerates growth of columnar crystal to promote segregation at the time of solidification and also it melts into the base metal to thereby invite lowering of toughness. Hence, the upper limit value is set to 0.5%. Also, if the Si quantity is extremely reduced, it invites an insufficiency of deoxidation and increase of manufacturing cost. Thus, the lower limit value is set to 0.01%. Preferably, Si is 0.05 to 0.3%.

(3) Mn (manganese)

[0014] Mn is added as a deoxidation agent. Also, when it combines with harmful S (sulfur) in the steel, it forms MnS (manganese sulfide) that has the effect to prevent hot cracks etc. As a minimum quantity by which such effect can be expected, the lower limit value is set to 0.1%. Also, as addition of too much quantity invites lowering of toughness, the upper limit value is set to 1.0%. Preferably Mn is 0.3 to 0.8%.

(4) Cr (chromium)

[0015] Cr is the most important element for enhancing the mechanical property, corrosion resistance and stress corrosion cracking resistance. If it is less than 9%, sufficient corrosion resistance and stress corrosion cracking resistance cannot be obtained. If it exceeds 3%, segregation tendency becomes large and flowability of molten metal and forgiability in manufacturing become worse. Hence, the appropriate addition range is set to 9 to 13%. Preferably, Cr is 10 to 12%.

(5) Ni (nickel)

[0016] Ni is an important element that suppresses generation of harmful δ ferrite and enhances hardenability. Also, the addition of Ni has the effect to leave an appropriate quantity of austenitic phase in the base metal to thereby enhance the toughness, corrosion resistance and stress corrosion cracking resistance. In order to obtain such an effect, addition of 2% or more is necessary. On the other hand, if it exceeds 7%, quantity of austenite becomes too much, so that the 0.2% yield strength lowers and stability against dimension changes in the long term use deteriorates. Hence, addition of Ni is set to 2 to 7%. Preferably, Ni is 4 to 6%.

(6) Mo (molybdenum)

[0017] Mo is added for enhancing the strength and corrosion resistance and preventing occurrence of temper brittleness. In order to obtain this effect, addition of 0.3% is necessary. But if it exceeds 3%, lowering of toughness is invited. Thus, Mo is set to 0.3 to 3%. Preferably, Mo is 0.8 to 1.8%.

(7) N (nitrogen)

[0018] N is a useful element for enhancing the hardenability and ensuring the strength without lowering the corrosion resistance. As the minimum quantity needed therefor is 0.01%, this is set as the lower limit value. On the other hand, if addition of N exceeds 0.1%, it harms the toughness and generates defects due to gas pores when the molten metal solidifies. Thus, the upper limit value is set to 0.1%. Preferably, N is 0.03 to 0.08%.

(8) V (vanadium)

[0019] V forms a carbon nitride that has the effect to enhance the material strength, especially the creep strength. Hence, V is an essential element for the 12Cr steel for a high temperature turbine rotor. However, the present invention has no specific object to ensure the high temperature strength and it is possible to realize the strength in the temperature range of use by effecting addition of other elements in good balances. Moreover, addition of V may lead to deterioration of the toughness. Hence, no addition of V is done in the present invention. If V is included as an inevitable element, it is left as allowable.

[0020] In the second one of the present invention, in addition to the components of the above-mentioned first invention, the 12Cr alloy steel is added with a small quantity of elements to thereby enhance the material characteristic as a steam power generation low pressure turbine rotor. That is, in the present second invention, the 12Cr alloy steel for a turbine rotor is characterized in containing, in addition to the components of the first invention, any one or more of rare earth elements of 0.003 to 0.03%, Ca (calcium) of 0.001 to 0.009% and B (boron) of 0.0005 to 0.005%, all in weight percent.

[0021] The reason why the newly added small quantity elements are so limited will be described below.

(9) Rare earth elements

[0022] Rare earth elements spheroidize intervening matters to finely disperse them and suppress growth of columnar crystal when the molten metal solidifies. Thereby, the effect to prevent a macro segregation of harmful impurity elements can be obtained. When a special smelting, such as an electroslag re-smelting in the manufacture of the 12Cr steel for a high temperature turbine, is carried out, the cleanliness is high, that is, the quantity of intervening matters is small, and the effect of addition of the rare earth elements is not so large. But in the case of usual smelting and ingot making process in which intervening matters exist to some extent, addition of rare earth elements is useful. Addition of 0.003% or less is not effective and, reversely, addition in excess of 0.03% rather increases the quantity of intervening matters. Hence, the appropriate quantity of addition of rare earth elements is set to 0.003 to 0.03%.

(10) Ca (calcium)

[0023] Ca is also an element that functions like the rare earth elements. Addition of 0.001% or less is not effective and, reversely, addition in excess of 0.009% rather increases the quantity of intervening matters. Hence, the appropriate quantity of addition of Ca is set to 0.001 to 0.009%.

(11) B (boron)

[0024] If appropriately added, B functions to stabilize crystal grain boundaries and has the effect to prevent selective corrosion of the grain boundaries. If the quantity of addition is 0.0005% or less, there is no substantial effect and if it is 0.05% or more, it will rather weaken the binding force of the grain boundaries. Thus, the addition quantity is set to 0.0005 to 0.005%. Preferably, B is 0.001 to 0.003%.

[0025] In the third one of the present invention, the upper limit of the quantity of harmful impurities in the components of the first and second inventions is defined. That is, in the present third invention, the quantity of impurity elements in the incidental impurities of the alloy steel of the first and second inventions is controlled so as to be as follows: that is, P (phosphorous) of 0.012% or less, S of 0.003% or less, Cu (copper) of 0.08% or less, Al (aluminum) of 0.012% or less, As (arsenic) of 0.008% or less, Sn (tin) of 0.008% or less and Sb (antimony) of 0.003% or less, all in weight percent.

[0026] It is a matter of course that these impurities are preferably to be lower for the mechanical characteristic and corrosion characteristic of the steel material. But, those elements for which the allowable quantity of content as impurities in the steel material is standardized are P and S only. As P and S make the steel material brittle, their allowable quantity has already been defined for most kinds of steel. But if the quantity of P and S is lowered more than needed by putting importance on the material characteristic, the smelting process becomes complicated to invite cost increase of the material.

[0027] The inventors here have put eyes on, and elaborated on, the study of the stress corrosion cracking resistance of the 12%Cr steel used especially for a geothermal power generation turbine rotor or steam power generation low pressure turbine rotor. This resulted in finding a fact that a very small quantity of micro-impurities gives a large influence on the stress corrosion cracking resistance. It was also found that, as the impurities, not only P and S but also Al, As, Sn, Sb, etc. give bad influences. Heretofore, it has been only vaguely recognized that the micro-impurities are better to be lower and no allowable quantity thereof has been concretely disclosed. The inventors here have precisely studied these impurities and succeeded in concretely defining the allowable quantity of impurities by judging existence of cracks caused by the stress corrosion cracking tests in the actual geothermal steam.

(12) P (phosphorous)

[0028] P is an impurity brought from the steel making material and lowers the toughness of the steel material. Further, it tends to cause segregation of grain boundaries to lower the binding force of the grain boundaries. This also lowers the characteristic of the stress corrosion cracking resistance. On the other hand, if P is reduced more than needed, the smelting process becomes complicated to invite cost increase of the material. Thus, as a value that neither invites a large cost increase nor damages the stress corrosion cracking resistance characteristic, the upper limit is set to 0.012%. Preferably, P is 0.008% or less.

(13) S (sulfur)

[0029] S is an element that causes hot cracks when it segregates in the grain boundaries. In order to avoid this, Mn is added to fix S as MnS, but if a large quantity of MnS exists, it becomes a starting point of the stress corrosion cracks or an extending path of the cracks, resulting in lowering the stress corrosion cracking resistance. On the other hand, if S is reduced more than needed, the smelting process becomes complicated to invite cost increase of the material. Thus, as a value that neither invites a large cost increase nor damages the stress corrosion cracking resistance characteristic, the upper limit is set to 0.005%. Preferably, S is 0.003% or less.

(14) Al (aluminum)

[0030] Al is brought mainly from deoxidation agent in the steel making process. Al forms intervening matters of oxide type in the steel material to lower the toughness. If it exists too much, it may act as a starting point of the stress corrosion cracks. As the result of stress corrosion cracking tests, the upper limit value is set to 0.015%. Preferably, Al is 0.01% or less.

(15) As (arsenic), Sn (tin) and Sb (antimony)

[0031] As, Sn and Sb are impurities mixed in from the steel making material. All of them segregate in the crystal grain boundaries and lowers the grain boundary strength. This results in lowering the toughness as well as the stress corrosion cracking resistance. As the result of stress corrosion cracking tests, the upper limit values of content of these impurities are set to 0.008% (preferably 0.005%) for As, 0.008% (preferably 0.005%) for Sn and 0.005% (preferably 0.002%) for Sb.

[0032] In the fourth one of the present invention, in order to appropriately control the quantity of austenitic phase in the alloy steel of the above first to third inventions, the Cr equivalent weight is employed and the range thereof is limited so as to obtain characteristics of high toughness and appropriate stress corrosion cracking resistance. That is, in the present fourth invention, the 12Cr alloy steel for a turbine rotor of the first to third inventions is characterized in that the Cr equivalent weight shown by "[Cr%] + 2[Si%] + 1.5[Mo%] - 2[Ni%] - [Mn%] - 15[C% + N%]" is -2.0 or more and +8.0 or less.

[0033] Every alloy steel of the first to third inventions is that which exhibits a finely mixed two phase structure that contains fine austenite in the martensite structure. This results in obtaining characteristics of high toughness and appropriate stress corrosion cracking resistance. This austenitic phase contains a reversely transformed austenite that re-precipitates by tempering, in addition to the residual autstenite that has not been transformed at the time of quenching. The quantity of austenite depends on the extent of the thermal stability of the austenitic phase and the thermal stability is governed by the quantity of alloy elements. Thus, in order to fix an aim, the Cr equivalent weight is introduced so as to limit the preferable component range.

[0034] The fifth one of the present invention relates to a manufacturing method of the 12Cr alloy steel for a turbine rotor that is characterized in that, in the manufacturing process of the alloy steel of the first to fourth inventions, when the molten metal, adjusted to predetermined chemical components, is cast in a mold for making a steel ingot, there is carried out neither an adjustment of chemical components in the solidifying process of the molten metal nor a re-smelting treatment of the steel ingot that is once solidified.

[0035] In the manufacture of the 12Cr alloy steel used as a high pressure rotor material or intermediate pressure rotor material, as segregation of alloy components is liable to occur in the central portion of the ingot, it is usual to perform a special smelting that re-smelts the ingot that has been once manufactured or dilutes an enriched portion of the alloy elements in the solidifying process of the molten metal. However, when the special smelting process is employed, the resulting increase of manufacturing cost of the material is a large problem.

[0036] The main object to perform the special smelting is to sufficiently smelt the alloy elements so as to make the material less segregated and to enhance the toughness and high temperature strength (especially the creep strength). On the other hand, as the target of the 12%Cr steel of the present invention is the steel that is used in the low temperature range of 300°C or less, there is no need to pay a high attention to the high temperature strength. Also, as much of Ni is added as an element to enhance the toughness, it is presumed that the toughness can be ensured even if a small quantity of segregation occurs.

[0037] In view of the above circumstances, the inventors here have manufactured test pieces of which sizes correspond to the actual products manufactured by the usual smelting and ingot making process without using the special smelting process and studied the mechanical characteristic, corrosion resistance and stress corrosion cracking resistance of the steel ingot central portion in which the segregation is liable to occur. Moreover, these test results have been compared with the results obtained by small smelted test pieces for which there is no need of worry of segregation, and the effectiveness of the present invention has been judged.

[0038] The sixth one of the present invention proposes, in the heat treatment process of the alloy steel of the first to fifth inventions, to perform heat treatment that stabilizes the austenitic phase. That is, according to the present sixth invention, in the heat treatment process of the alloy steel of the first to fifth inventions, it is characterized in that there is performed tempering two times or more in the temperature range of 500 to 700°C (preferably 550 to 650°C) after quenching. Thereby, a manufacturing method of the 12Cr alloy steel for a turbine rotor that stabilizes the austenitic phase can be obtained.

[0039] As mentioned above, the material of the present invention (hereinafter referred to as "the invented material") is that which exhibits a finely mixed two phase structure that contains fine austenite in the martensite structure. This results in obtaining characteristics of high toughness and appropriate stress corrosion cracking resistance. But if the stability of austenitic phase is low, there arises a phenomenon in which the austenitic phase in use is gradually transformed to the martensite. The transformation from the austenitic phase to the martensite accompanies volume expansion. If this is repeated, dimension changes are invited or local stress is caused and this results in hindering a safe operation of the turbine.

[0040] Thus, as the result of elaborated studies on the heat treatment method to perform tempering after quenching, it was found that stability of the austenitic phase is remarkably enhanced by performing tempering treatments repeatedly two times or more in the above-mentioned temperature range.

[0041] In the seventh one of the present invention, the turbine rotor is characterized in being made of the alloy steel of the first to sixth inventions. Especially, when the alloy steel of the first to sixth inventions is used for the geothermal power generation turbine rotor or steam power generation low pressure turbine rotor, the effectiveness of the material becomes clear.

BRIEF DESCRIPTION OF THE DRAWINGS

[0042]

Fig. 1 is a graph showing the relation between Cr equivalent weight of 12Cr alloy steel of the present invention and SCC crack length.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0043] Herebelow, the present invention will be described more concretely based on embodiments thereof. However, the present invention is by no means limited to the embodiments only.

(Example 1)

[0044]

[Table 1]

Chemical components of the invented materials and comparison materials used in Example 1

Example 1	No.	C	Si	Mn	Ni	Cr	Mo	N	REM	Ca	B	P	S	Al	As	Sn	Sb	Fe
Invented material	01	0.04	0.30	0.29	3.9	12.8	1.52	0.047				0.014	0.005	0.015	0.004	0.003	0.002	Remains
Invented material	02	0.04	0.26	0.55	5.0	11.8	1.15	0.061				0.007	0.003	0.009	0.005	0.003	0.001	Remains
Invented material	03	0.07	0.28	0.49	5.8	10.5	1.13	0.044				0.008	0.002	0.010	0.005	0.003	0.002	Remains
Invented material	04	0.07	0.28	0.47	4.8	9.8	0.74	0.070				0.010	0.002	0.009	0.006	0.004	0.001	Remains
Comparison material	05	0.04	1.02	0.51	1.5	12.4	1.14	0.007				0.010	0.001	0.008	0.006	0.003	0.001	Remains
Comparison material	06	0.15	0.30	0.52	4.5	7.9	0.04	0.008				0.008	0.006	0.014	0.005	0.004	0.002	Remains
Comparison material	07	0.05	0.31	1.95	7.5	10.4	0.74	0.056				0.010	0.001	0.008	0.005	0.003	0.002	Remains

[Table 2]

Materials characteristics of the invented materials and comparison materials used in Example 1

Example 1	No.	0.2% Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction of area (%)	Room temperature impact absorbing energy (J)	50% FATT (°C)	Corrosion rate (mm/year)	SCC Crack length (μm)
Invented material	01	719	840	26.3	68	106	-125	0.001	no crack
Invented material	02	736	894	28.1	69.2	136	-164	0.0012	no crack
Invented material	03	751	863	27.1	68.5	115	-148	0.0015	no crack
Invented material	04	740	855	26.4	68.9	123	-136	0.0021	19
Comparison material	05	725	832	18.4	55.7	102	-48	0.0017	62
Comparison material	06	719	860	29	68.2	90	14	0.0058	106
Comparison material	07	621	831	30.2	72	110	-121	0.0034	45

[0045] The chemical components of the invented materials (Test piece Nos. 01 to 04) and comparison materials

(Test piece Nos. 05 to 07) used for the present Example 1 are shown in Table 1. Each of the test piece materials is melted using a 50 kg vacuum melting furnace, forging corresponding to an actual rotor cylinder portion is done and then heat treatment that simulates a central portion of an actual rotor of a cylinder diameter of 1,600 mmϕ is applied.

[0046] Tempering is done two times in the temperature range of 500 to 700°C and temperature appropriate for making the 0.2% yield strength of 730±25 MPa is set for each kind of the steel. Incidentally, as to the comparison material No. 07, the target strength could not be obtained, even though the tempering was done by the temperature of 500°C.

[0047] Table 2 shows the mechanical characteristic, corrosion rate, stress corrosion cracking (SCC) crack length, etc. of the test pieces of Example 1. The target of the mechanical property is to obtain the following: the 0.2% yield strength of 637 MPa or more (preferably 700 MPa or more), tensile strength of 740 MPa or more (preferably 830 MPa or more), elongation of 16% or more, reduction of area of 45% or more, room temperature impact absorbing energy of 30J or more (preferably 80J or more) and Charpy impact test fracture appearance ductility-brittleness transition temperature (FATT) of 40°C or less (preferably -60°C or less).

[0048] As to the corrosion test, the test pieces are exposed for two years to the actual geothermal steam to thereby obtain the thinned quantity by the corrosion and this is converted to the yearly corrosion rate. The target of the corrosion rate is set to 0.003 mm/year or less.

[0049] In the stress corrosion cracking test, the test piece used is made such that a V type notch (notch apex radius R: 0.2 mm) of depth 1.25 mm and length 8 mm is worked in the central portion of the test piece having the dimension of 8×108×5 mm and the test piece is kept bent so that tensile stress of 90 to 95% of the 0.2% yield strength acts on the vicinity of the notch portion. The test piece is kept in the actual geothermal steam for two years and the existence of crack and crack length are examined by observation of the fracture appearance immediately below the notch. In the stress corrosion cracking test, the target of the crack length is set to 30 μm or less for two years.

[0050] The present invented materials achieve the target of all of the mechanical characteristic, corrosion rate and SCC crack length. On the other hand, in all of the comparison materials, the SCC crack lengths are longer than the target value and it is found that the comparison materials are inferior in the stress corrosion cracking resistance. Also, the comparison material 06 does not attain the target of the yearly corrosion rate and the comparison material 07 does not attain the target of the 0.2% yield strength and yearly corrosion rate.

[0051] From the above, it becomes clear that, by using the components shown in Claim 1 of the present invention, such an alloy steel as has all of the mechanical characteristic, corrosion resistance and stress corrosion cracking resistance that are necessary for a geothermal power generation turbine rotor or steam power generation low pressure turbine rotor can be obtained.

(Example 2)

[0052]

Table 3

Chemical components of the invented materials and comparison materials used in Example 2

Example 2	No.	C	Si	Mn	Ni	Cr	Mo	N	REM	Ca	B	P	S	Al	As	Sn	Sb	Fe
Invented material	08	0.07	0.28	0.51	4.8	9.7	0.72	0.066	0.012			0.010	0.002	0.007	0.004	0.004	0.002	Remains
Invented material	09	0.07	0.30	0.49	4.9	9.7	0.72	0.071		0.014		0.010	0.001	0.007	0.004	0.003	0.001	Remains
Invented material	10	0.07	0.28	0.49	4.8	9.8	0.75	0.072	0.005		0.002	0.009	0.001	0.009	0.006	0.004	0.001	Remains
Invented material	11	0.07	0.31	0.50	4.8	9.7	0.74	0.069		0.016	0.003	0.008	0.002	0.009	0.005	0.004	0.002	Remains

Table 4

Materials characteristics of the invented materials and comparison materials used in Example 2

Example 2	No.	0.2% Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction of area (%)	Room temperature impact absorbing energy (J)	50% FATT (°C)	Corrosion rate (mm/year)	SCC Crack length (µm)
Invented material	08	736	860	27.7	70.5	136	-144	0.0011	no crack
Invented material	09	741	859	26.3	67	139	-142	0.0009	no crack
Invented material	10	748	843	25.8	65.7	120	-132	0.0015	no crack
Invented material	11	739	841	26.4	67.6	115	-134	0.0012	no crack

[0053] The chemical components of the invented material (Test piece Nos. 08 to 11) used for the present Example

2 are shown in Table 3. The test piece materials are made on the basis of the chemical components of the invented material 04 of Example 1 and is added with appropriate quantity of any one or more of the rare earth elements, Ca and B. Each of the test piece materials is melted using a 50 Kg vacuum melting furnace, forging corresponding to an actual rotor cylinder portion is done and then heat treatment that simulates a central portion of an actual rotor of a cylinder diameter of 1,600 mmϕ is applied.

[0054] Tempering is done two times in the temperature range of 500 to 700°C and temperature appropriate for making the 0.2% yield strength of 730±25 MPa is set for each kind of the steel.

[0055] Table 4 shows the mechanical characteristic, corrosion rate and stress corrosion cracking (SCC) crack length of the test piece materials of Example 2.

[0056] Corrosion test and stress corrosion cracking test are done by the method as described with respect to Example 1.

[0057] It is observed that all of the mechanical characteristics of the base material (see Table 2) and those of the present invented materials (Test piece Nos. 08 to 11) show good characteristic, there is seen no bad influence caused by adding any one or more of the rare earth elements, Ca and B and excellent mechanical characteristic is maintained as it is. If the corrosion rate of the base material (see Table 2) and those of the present invented materials (Test piece Nos. 08 to 11) are compared with each other, those of the present invented materials show smaller values. This means that the corrosion resistance is enhanced. To be noted is an enhancement of the stress corrosion cracking resistance. While the SCC crack length of the base material is 19 μm, by adding any one or more of the rare earth elements, Ca and B, there is seen no crack in any of the test pieces.

[0058] From the above, it becomes clear that, by using the components shown in Claim 2 of the present invention, such an alloy steel as has the mechanical characteristic and corrosion resistance and especially has the stress corrosion cracking resistance as well that are necessary for a geothermal power generation turbine rotor or steam power generation low pressure turbine rotor can be obtained.

(Example 3)

[0059]

[Table 5]

Chemical components of the invented materials and comparison materials used in Example 3

Example 3	No.	C	Si	Mn	Ni	Cr	Mo	N	REM	Ca	B	P	S	Al	As	Sn	Sb	Fe
Invented material	12	0.07	0.30	0.49	4.9	9.9	0.75	0.069				0.009	0.002	0.008	0.005	0.004	0.001	Remains
Comparison material	13	0.08	0.28	0.45	4.9	9.9	0.72	0.068				0.020	0.001	0.009	0.005	0.010	0.001	Remains
Comparison material	14	0.07	0.29	0.45	4.9	9.8	0.74	0.071				0.008	0.007	0.016	0.005	0.010	0.001	Remains
Comparison material	15	0.07	0.30	0.48	4.9	9.8	0.71	0.066				0.007	0.001	0.010	0.012	0.003	0.006	Remains
Comparison material	16	0.07	0.28	0.51	4.8	9.8	0.73	0.069	0.005		0.002	0.018	0.008	0.009	0.006	0.004	0.001	Remains

[Table 6]

Materials characteristics of the invented materials and comparison materials used in Example 3

Example 3	No.	0.2% Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction of area (%)	Room temperature impact absorbing energy (J)	50% FATT (°C)	Corrosion rate (mm/year)	SCC Crack length (μm)
Invented material	12	735	859	27	66.7	130	-133	0.0022	21
Comparison material	13	741	854	27.1	67	112	-104	0.0039	69
Comparison material	14	733	853	26.5	66.5	109	-110	0.0025	51
Comparison material	15	739	860	25.9	65.7	92	-77	0.0046	90
Comparison material	16	742	866	25.3	63.1	116	-96	0.0045	42

[0060] The chemical components of the present invented material (Test piece No. 12) and the comparison materials

(Test piece Nos. 13 to 16) used for the present Example 3 are shown in Table 5. The present invented material (Test piece No. 12) is that which is re-melted aiming at the chemical components of the invented material 04 of Example 1 and the comparison materials (Test piece Nos. 13 to 15) are those in which the level of the quantity of impurities of the present invented material (Test piece No. 12) is enhanced. Also, the comparison material (Test piece No. 16) is that in which the level of the quantity of impurities of the invented material (Test piece No. 10) is enhanced.

[0061] Each of the test pieces is melted using a 50 Kg vacuum melting furnace, forging is done corresponding to an actual rotor cylinder portion and then heat treatment that simulates a central portion of an actual rotor of a cylinder diameter of 1,600 mmϕ is applied.

[0062] Tempering is done two times in the temperature range of 500 to 700°C and temperature appropriate for making the 0.2% yield strength of 730±25 MPa is set for each kind of the steel.

[0063] Table 6 shows the mechanical characteristic, corrosion rate and stress corrosion cracking (SCC) crack length of the test piece materials of Example 3.

[0064] Corrosion tests and stress corrosion cracking tests are done by the method mentioned in Example 1.

[0065] While all of the mechanical characteristics of the present invented material (Test piece No. 12) and comparison materials (Test piece Nos. 13 to 15) attain the target value, the latter has the lower room temperature impact absorbing energy and higher Charpy impact test fracture appearance ductility-brittleness transition temperature. Hence, it is found that the toughness tends to become lower. As to the corrosion rate, while the comparison material (Test piece No. 14) clears the target value, the comparison materials (Test piece Nos. 13 and 15) do not satisfy the target value. Moreover, with respect to the SCC crack length, none of the comparison materials (Test piece Nos. 13 to 15) satisfies the target value.

[0066] From the above, it is clear that, by controlling the quantity of impurities in the invented material shown in Claim 1 to be adjusted to a predetermined quantity or less, the corrosion resistance or stress corrosion cracking resistance can be enhanced.

[0067] Next, the materials characteristic of the invented material (Test piece No. 10) and comparison material (Test piece No. 16) is considered. With respect to the mechanical characteristic, the comparison material (Test piece No. 16) has the higher ductility-brittleness transition temperature, which shows that the toughness is lowered. The corrosion rate of the comparison material (Test piece No. 16) shows a value as high as three times of the invented material (Test piece No. 10) and does not satisfy the target value. Also, while no SCC crack is caused in the invented material (Test piece No. 10), a crack of 42 μm is caused in the comparison material (Test piece No. 16), resulting in failing to satisfy the target value.

[0068] From the above, it is clear that, by controlling the quantity of impurities in the invented material shown in Claim 2 to be adjusted to a predetermined quantity or less, the corrosion resistance or stress corrosion cracking resistance can be enhanced.

[0069] As mentioned above, it becomes clear that, by effecting the control of impurities as shown in Claim 3 of the present invention, such an alloy steel as has the mechanical characteristic as well as the corrosion resistance or stress corrosion cracking resistance, that are necessary for a geothermal power generation turbine rotor or steam power generation low pressure turbine rotor can be obtained.

(Example 4)

[0070]

[Table 7]

Relation between chromium equivalent weight and SCC crack length of the invented materials (Example 4)

Cr Equivalent Weight	SCC Crack Length (μm)
6.29	0
1.98	0
-1.05	0
-0.7	19
11.94	62
-3.33	106
-5.66	45

[0071] The relation between the Cr equivalent weight and SCC crack length of the invented materials (Test piece

Nos. 01 to 04) and comparison materials (Test piece Nos. 05 to 07) used in Example 1 is summarized in Table 7 and Fig. 1.

[0072] While there are proposed various equations that show the Cr equivalent weight, the inventors here consider, based on the past manufacturing results of many large type steel ingots, that the following equation is appropriate for the manufacture of a large type steel ingot for a turbine rotor etc.:

$$\text{Cr equivalent weight} = [\text{Cr}\%] + 2[\text{Si}\%] + 1.5[\text{Mo}\%] - [\text{Mn}\%] - 15[\text{C}\% + \text{N}\%]$$

[0073] From Fig. 1, it is found that, in order to obtain the target SCC crack of 30 μm, the Cr equivalent weight is necessary to be -2.0 or more and +8.0 or less.

[0074] As mentioned above, it becomes clear that, by effecting the control of the quantities of alloy components so as to make the Cr equivalent weight of the invented material fall within an appropriate range, such an alloy steel as has the enhanced stress corrosion cracking resistance that is an important factor of materials for a geothermal power generation turbine rotor or steam power generation low pressure turbine rotor can be obtained.

(Example 5)

[0075]

[Table 8]

Chemical components of the invented materials and comparison materials used in Example 5

Example 5	No.	C	Si	Mn	Ni	Cr	Mo	N	REM	Ca	B	P	S	Al	As	Sn	Sb	Fe
Invented material	central portion	0.05	0.27	0.57	5.1	11.8	1.16	0.060				0.010	0.001	0.008	0.006	0.003	0.001	Remains
Invented material	outer surface	0.04	0.26	0.55	5.0	11.8	1.15	0.061				0.009	0.001	0.007	0.005	0.003	0.001	Remains

[Table 9]

Materials characteristics of the invented materials and comparison materials used in Example 5

Example 5	No.	0.2% Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction of area (%)	Room temperature impact absorbing energy (J)	50% FATT (°C)	Corrosion rate (mm/year)	SCC Crack length (μm)
Invented material	12	752	883	24.3	60.1	130	-156	0.0018	no crack
Comparison material	13	722	879	26.1	63.7	138	-160	0.0014	no crack

[0076] The chemical components of the present invented material used for Example 5 are shown in Table 8. The sample is of the size corresponding to an actual rotor for a geothermal turbine and the ingot of about 95 tons in weight is made by the usual ingot making process without using the special smelting and special ingot making process in which the ingot once made is re-smelted or an enriched portion of the alloy elements is diluted in the solidification process of the molten metal. The ingot is applied with forging and heat treatment that correspond to the manufacturing process of an actual rotor. The test pieces are taken from a radial directional central portion and surface layer portion of the resulted rotor shape material to be used for the chemical component analysis (Table 8) and various materials tests.

[0077] The materials test result is shown in Table 9. While the corrosion tests and stress corrosion cracking tests are carried out by the method mentioned in Example 1, the test period is set to 6 months. Every characteristic satisfies the target value. This makes it clear that, when a large type steel ingot, like that for a turbine rotor, is manufactured using the invented material, a sufficient characteristic can be obtained even without using the special smelting and special ingot making process in which the ingot once manufactured is re-smelted or the enriched portion of the alloy elements is diluted in the solidification process of the molten metal. That is, it is shown that, by using the invented material, the geothermal power generation turbine rotor and steam power generation low pressure turbine rotor can be manufactured less costly.

(Example 6)

[0078]

[Table 10]

Influence of the tempering treatment given on the austenite quantity of the invented material No. 2 (Example 6)

Number of times of tempering	Austenite quantity after tempering (volume %)	Austenite quantity after subzero treatment (volume %)
1	34	20
2	36	35
3	35	35

Tempering temperature: 600°C
Invented material: No. 2 is tested.

[Table 11]

Influence of the tempering treatment given on the austenite quantity of the invented material No. 11 (Example 6)

Number of times of tempering	Austenite quantity after tempering (volume %)	Austenite quantity after subzero treatment (volume %)
1	29	16
2	30	30
3	31	30

Tempering temperature: 575°C
Invented material: No. 11 is tested.

[0079] Using the invented material 02 that is used for Example 1, studies are done on the stability of austenitic phase following the repeated tempering treatments after the quenching treatment and the result thereof is shown in Table 10. In the tests, tempering is done at the temperature of 600°C after quenching and then the first measurement of the austenite quantity is done at the room temperature. Subsequently, the test piece is put into liquid nitrogen to be kept therein for one hour (the subzero treatment). Then, the test piece is returned to the room temperature and the second measurement of the austenite quantity is done. Then, again the tempering is done at 600°C, the third measurement of the austenite quantity is done at the room temperature and the test piece is kept in the liquid nitrogen for one hour and is returned to the room temperature. Thereafter, the fourth measurement of the austenite quantity is done. Further, the same procedures of the tempering and subsequent keeping in the liquid nitrogen are repeated and then the fifth and sixth measurements, respectively, of the austenite quantity are done. The austenite quantity is obtained by comparing the peak sizes of the X-ray diffraction.

[0080] While the austenite quantity after the first tempering is 34%, it is reduced to 20% by the subzero treatment. This shows that the austenitic phase that is thermally unstable is transformed to the martensite in the subzero treatment. As the transformation from the austenitic phase to the martensite accompanies volume expansion, if this is repeated, dimension changes arise or local stresses are caused. This hinders stable operation of the turbine. The austenite quantity after the second tempering is 36% and even if this is applied with the subzero treatment, that quantity is 35% that is not much changed. The test pieces applied with the third tempering exhibit the similar results. This shows that the austenitic phase is thermally stabilized by applying the tempering two times or more.

[0081] Using the invented material 11 that is used for Example 2, studies are done on the stability of austenitic phase following the repeated tempering treatments after the quenching treatment and the result thereof is shown in Table 11. In the tests, tempering is done at the temperature of 575°C after quenching and then the first measurement of the austenite quantity is done at the room temperature. Subsequently, the test piece is put into liquid nitrogen to be kept therein for one hour (the subzero treatment). Then, the test piece is returned to the room temperature and the second measurement of the austenite quantity is done. Then, again the tempering is done at 575°C, the third measurement of austenite quantity is done at the room temperature and the test piece is kept in the liquid nitrogen for one hour and is returned to the room temperature. Thereafter, the fourth measurement of the austenite quantity is done. Further, the same procedures of the tempering and subsequent keeping in the liquid nitrogen are repeated and then the fifth and sixth measurements, respectively, of the austenite quantity are done. The austenite quantity is obtained by comparing the peak sizes of the X-ray diffraction.

[0082] While the austenite quantity after the first tempering is 29%, it is reduced to 16% by the subzero treatment. This shows that the austenitic phase that is thermally unstable is transformed to the martensite in the subzero treatment. The austenite quantity after the second tempering is 30% and even if this is applied with the subzero treatment, that quantity is 30% that is not changed. The test pieces applied with the third tempering exhibit the similar results. This shows that the austenitic phase is thermally stabilized by applying the tempering two times or more.

[0083] As mentioned above, it becomes clear that, by performing the tempering treatments two times or more in the temperature range of 500 to 700°C (preferably 550 to 650°C), the austenitic phase of the invented material is stabilized, aged dimension changes in the turbine operation can be prevented and a stable turbine operation is ensured.

[0084] The 12Cr alloy steel of the present invention has both the material strength and the ductility and toughness that are necessary as a large type rotor material and, moreover, has the appropriate corrosion resistance and the extremely high stress corrosion cracking resistance. By using this material for a geothermal turbine rotor, construction of such a geothermal power generation plant as stably generates power even by the geothermal steam of the severe corrosive condition becomes possible and supply of power becomes possible with emission of CO_2 being suppressed and with no bad influence being given on the global environment.

[0085] Also, by using the invented material for the low pressure turbine rotor of the steam turbine, reliability thereof is enhanced, number of times of the periodical inspection etc. can be reduced and power generation of high efficiency can be carried out.

Claims

1. A 12Cr alloy steel for a turbine rotor, **characterized in** containing: C of 0.01 to 0.10%, Si of 0.01 to 0.50%, Mn of 0.1 to 1.0%, Cr of 9 to 13%, Ni of 2 to 7%, Mo of 0.3 to 3%, N of 0.01 to 0.10%, all in weight percent, and remains of Fe and incidental impurities.

2. A 12Cr alloy steel for a turbine rotor as claimed in Claim 1, **characterized in** further containing any one or more of rare earth elements of 0.003 to 0.03%, Ca of 0.001 to 0.009% and B of 0.0005 to 0.005%, all in weight percent.

3. A 12Cr alloy steel for a turbine rotor as claimed in Claim 1 or 2, **characterized in that** a quantity of impurity elements of said incidental impurities is controlled so as to contain: P of 0.0012% or less, S of 0.005% or less, Al of 0.015% or less, As of 0.008% or less, Sn of 0.008% of less and Sb of 0.005% or less, all in weight percent.

4. A 12Cr alloy steel for a turbine rotor as claimed in Claim 1 or 2, **characterized in that** a Cr equivalent weight shown by "[Cr%] + 2[Si%] + 1.5[Mo%] - 2[Ni%] - [Mn%] - 15[C% + N%]" is -2.0 or more and +8.0 or less.

5. A 12Cr alloy steel for a turbine rotor as claimed in Claim 3, **characterized in that** a Cr equivalent weight shown by "[Cr%] + 2[Si%] + 1.5[Mo%] - 2[Ni%] - [Mn%] - 15[C% + N%]" is -2.0 or more and +8.0 or less.

6. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 1 or 2, **characterized in**

that, in a manufacturing process of said alloy steel, there is carried out neither an adjustment of chemical components in a solidifying process of molten metal when said molten metal, adjusted to predetermined chemical components, is cast in a mold for making a steel ingot nor a re-smelting treatment of said steel ingot once solidified.

7. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 3, **characterized in that**, in a manufacturing process of said alloy steel, there is carried out neither an adjustment of chemical components in a solidifying process of molten metal when said molten metal, adjusted to predetermined chemical components, is cast in a mold for making a steel ingot nor a re-smelting treatment of said steel ingot once solidified.

8. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 4, **characterized in that**, in a manufacturing process of said alloy steel, there is carried out neither an adjustment of chemical components in a solidifying process of molten metal when said molten metal, adjusted to predetermined chemical components, is cast in a mold for making a steel ingot nor a re-smelting treatment of said steel ingot once solidified.

9. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 1 or 2, **characterized in that**, in a heat treatment process of said alloy steel, there are carried out tempering treatments two times or more in a temperature range of 500 to 700°C after a quenching treatment.

10. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 3, **characterized in that**, in a heat treatment process of said alloy steel, there are carried out tempering treatments two times or more in a temperature range of 500 to 700°C after a quenching treatment.

11. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 4, **characterized in that**, in a heat treatment process of said alloy steel, there are carried out tempering treatments two times or more in a temperature range of 500 to 700°C after a quenching treatment.

12. A manufacturing method of a 12Cr alloy steel for a turbine rotor as mentioned in Claim 5, **characterized in that**, in a heat treatment process of said alloy steel, there are carried out tempering treatments two times or more in a temperature range of 500 to 700°C after a quenching treatment.

13. A turbine rotor **characterized in** being made of an alloy steel mentioned in Claim 1 or 2.

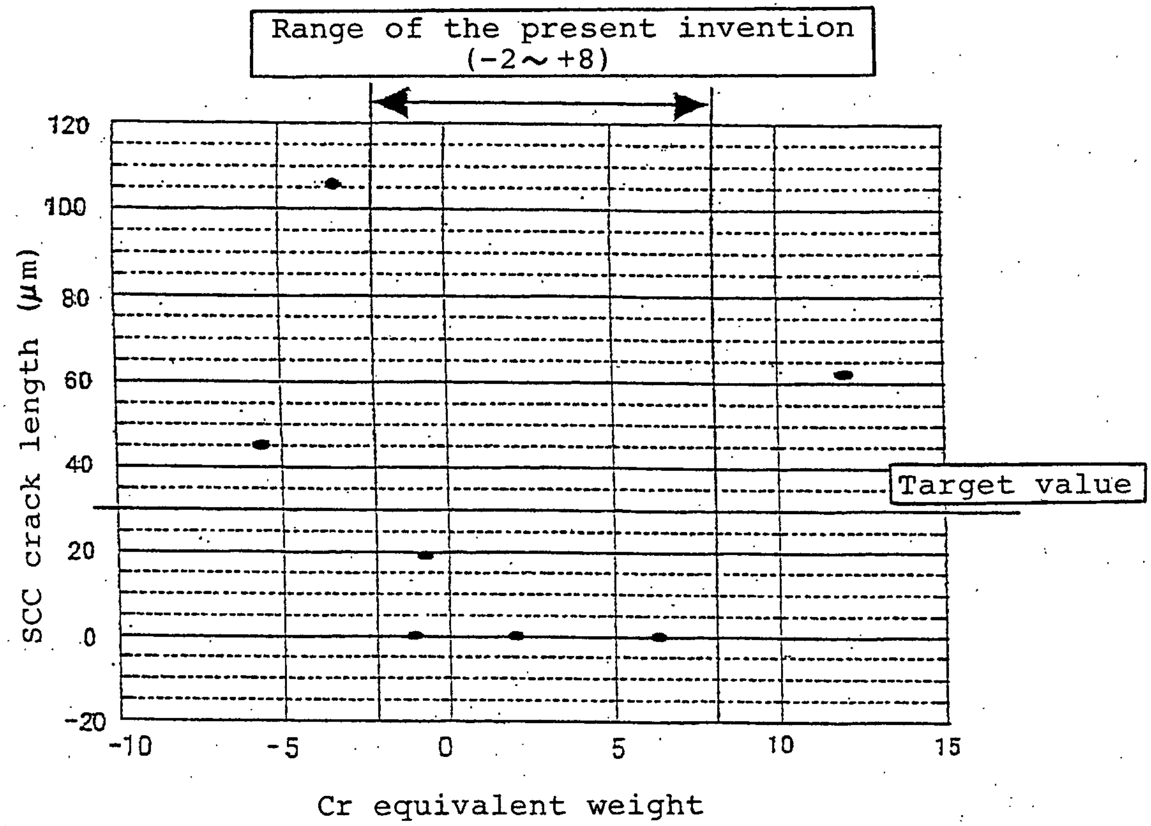
14. A turbine rotor **characterized in** being made of an alloy steel mentioned in Claim 3.

15. A turbine rotor **characterized in** being made of an alloy steel mentioned in Claim 4.

16. A turbine rotor **characterized in** being made of an alloy steel mentioned in Claim 5.

17. A turbine rotor **characterized in** being made of an alloy steel mentioned in Claim 6.

Fig. 1


Range of the present invention
(-2～+8)
Target value
SCC crack length (μm)
120
100
80
60
40
20
0
-20
-10
-5
0
5
10
15
Cr equivalent weight