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(54) HEAT-RESISTING STEEL AND METHOD OF MANUFACTURING THE SAME

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(57) ABSTRACT

Provided is a heat-resisting steel, which can be operated stably under a high-temperatures steam environment and which provides an excellent economic advantage. The particular heat-resisting steel comprises 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

HEAT-RESISTING STEEL AND METHOD OF MANUFACTURING THE SAME

CROSS-REFERENCE TO RELATED APPLICATIONS

[0001] This application is based upon and claims the benefit of priority from the prior Japanese Patent Application No. 2002-087042, filed Mar. 26, 2002, the entire contents of which are incorporated herein by reference.

BACKGROUND OF THE INVENTION

[0002] 1. Field of the Invention

[0003] The present invention relates to a composition of a metal member used under a high-temperature environment, particularly, to a heat-resisting steel used for forming a steam turbine in such as a power station.

[0004] 2. Description of the Related Art

[0005] The metal materials used under a high-temperature environment in a power station include low-alloy heat-resisting steels such as 1Cr-1Mo-0.25V steel and high-Cr heat-resisting steels such as 12Cr-1Mo-VNbN steel. These steels are widely used nowadays. In recent years, the steam temperature has become higher and higher in thermal power stations. In this connection, high-Cr heat-resisting steel having a high mechanical strength and excellent in, for example, resistance to the environment has come to be used widely. The use of such a high-strength steel has made it possible to construct power stations of higher performance.

[0006] However, not only a high thermal efficiency but also excellent economic advantages tend to be required for thermal power stations in recent years. Also, it is indispensable for the materials used for constructing a power station to exhibit mechanical properties and workability favorably comparable to conventional construction materials and to produce excellent economic advantages.

[0007] An object of the present invention is to provide a heat-resisting steel, which can be operated stably under a high-temperature steam environment and which is capable of providing excellent economic advantages, and to provide a method of manufacturing the particular heat-resisting steel.

BRIEF SUMMARY OF THE INVENTION

[0008] According to a first aspect of the present invention, there is provided a heat-resisting steel, comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

[0009] It is desirable for the heat-resisting steel according to the first aspect of the present invention to further comprise 0.002 to 0.008% by mass of N.

[0010] It is also desirable for the heat-resisting steel according to the first aspect of the present invention to further comprise 0.001 to 0.004% by mass of B.

[0011] Further, it is desirable for the heat-resisting steel according to the first aspect of the present invention to further comprise 0.002 to 0.008% by mass of N and 0.001 to 0.004% by mass of B.

[0012] According to a second aspect of the present invention, there is provided a heat-resisting steel, comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

[0013] It is desirable for the heat-resisting steel according to the second aspect of the present invention to further comprise 0.002 to 0.008% by mass of N.

[0014] According to a third aspect of the present invention, there is provided a heat-resisting steel having precipitates of M_7C_3 type, MX type and $M_{23}C_6$ type, which are precipitated within the crystal grains or at the crystal grain boundaries as a result of a hot forging treatment, an annealing treatment, a normalizing treatment, a quenching treatment and a tempering treatment applied in the order mentioned to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the sum of the precipitates falling within a range of 0.5% to 2.0% by mass.

[0015] According to a fourth aspect of the present invention, there is provided a heat-resisting steel having precipitates of M_7C_3 type, MX type and $M_{23}C_6$ type, which are precipitated within the crystal grains or at the crystal grain boundaries as a result of a hot forging treatment, an annealing treatment, a normalizing treatment, a quenching treatment and a tempering treatment applied in the order mentioned to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the sum of the precipitates falling within a range of 0.5% to 2.0% by mass.

[0016] According to a fifth aspect of the present invention, there is provided a method of manufacturing a heat-resisting steel, comprising manufacturing by an electros slag remelting process a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

[0017] According to a sixth aspect of the present invention, there is provided a method of manufacturing a heat-resisting steel, comprising manufacturing by an electros slag remelting process a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

[0018] According to a seventh aspect of the present invention, there is provided a method of manufacturing a heat-

resisting steel, comprising applying a quenching treatment to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the initiating (starting) temperature of the quenching treatment falling within a range of 970° C. to 1,020° C.

[0019] Further, according to an eighth aspect of the present invention, there is provided a method of manufacturing a heat-resisting steel, comprising applying a quenching treatment to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the initiating (starting) temperature of the quenching treatment falling within a range of 1,020° C. to 1,050° C.

[0020] It is desirable for the cooling rate in the quenching treatment not be lower than 100° C./hour.

[0021] Additional objects and advantages of the invention will be set forth in the description which follows, and in part will be obvious from the description, or may be learned by practice of the invention. The objects and advantages of the invention may be realized and obtained by means of the instrumentalities and combinations particularly pointed out hereinafter.

DETAILED DESCRIPTION OF THE INVENTION

[0022] In the present invention, the composition of the heat-resisting steel is very important as described below. In the following description, the symbol “%” represents “% by mass” unless otherwise specified.

[0023] (a) Carbon (C): Carbon (C) is useful for ensuring the hardenability and is also useful as a constituting element of the carbide contributing to the precipitation strengthening. The particular effects cannot be produced if the C content of the steel is less than 0.25%. On the other hand, if the C content of the steel exceeds 0.35%, coarsening of the carbide is promoted. Also, the tendency of segregation is enhanced in the coagulating stage of the ingot. Under the circumstances, the C content of the steel is defined to fall within a range of 0.25% to 0.35% in the present invention.

[0024] (b) Silicon (Si): Silicon (Si) is useful as a deoxidizer and serves to improve the resistance of the steel to steam oxidation. If the Si content is excessively high, however, the toughness of the steel is lowered, and the embrittlement of the steel is promoted. Therefore, it is desirable to suppress the Si content as much as possible. If the Si content exceeds 0.15%, the toughness of the steel is markedly reduced and, thus, the Si content of the steel is defined to be not higher than 0.15% in the present invention.

[0025] (c) Manganese (Mn): Manganese (Mn) is useful as a desulfurizing agent. If the Mn content of the steel is less than 0.2%, however, the desulfurizing effect cannot be obtained. On the other hand, if Mn is added in an amount exceeding 0.8%, the creep resistance of the steel is reduced.

Under the circumstances, the Mn content of the steel is defined to fall within a range of 0.2 to 0.8% in the present invention.

[0026] (d) Chromium (Cr): Chromium (Cr) has the effect of imparting resistance to oxidation and corrosion to the steel and is also useful as a constituting element of the precipitates contributing to the precipitation strengthening. In the steel of the present invention, Cr is mainly expected to have the effect of improving the toughness of the steel. If the Cr content of the steel is less than 1.6%, an improvement in the toughness of the steel cannot be expected. On the other hand, if the Cr content of the steel exceeds 1.9%, the resistance of the steel to softening by the tempering treatment is reduced so as to make the creep strength poor. Under the circumstances, the Cr content of the steel is defined to fall within a range of 1.6 to 1.9% in the present invention.

[0027] (e) Vanadium (V): Vanadium (V) contributes to the solid-solution strengthening and to the formation of fine carbo-nitrides. Since V has an effect similar to that produced by niobium (Nb), it is necessary to change the amount of V added according to the amount of Nb added.

[0028] Where Nb is not added, fine precipitates are sufficiently precipitated and the recovery of the matrix is suppressed in the case of adding V in an amount not less than 0.26%. On the other hand, if the V content of the steel exceeds 0.35%, the toughness of the steel is reduced. Also, coarsening of the carbo-nitrides is promoted. Under the circumstances, the V content of the steel is defined to fall within a range of 0.26 to 0.35% in the present invention.

[0029] Where both V and Nb are added together, a part of the V has an effect similar to that produced by Nb. Therefore, the effects described above can be expected by the addition of V in an amount not less than 0.23%. On the other hand, if the amount of V added exceeds 0.30%, the toughness of the steel is reduced, and the coarsening of carbo-nitrides is promoted. Under the circumstances, the V content of the steel in the case where Nb is added together with V is defined to fall within a range of 0.23 to 0.30% in the present invention.

[0030] (f) Tungsten (W): Tungsten (W) contributes to the solid-solution strengthening and is substituted in a carbide so as to contribute to the precipitation strengthening. In order to ensure W forming a solid solution in an amount required in the case where the steel is exposed for a long time at the high temperature, it is necessary to add W in an amount not less than 0.6%. However, if the W content of the steel exceeds 1.4%, the toughness of the steel is reduced, and ferrite formation is promoted. In addition, the ingot tends to be segregated. Under the circumstances, the W content of the steel is defined to fall within a range of 0.6 to 1.4% in the present invention.

[0031] (g) Molybdenum (Mo): Molybdenum (Mo) contributes to the solid-solution strengthening and is substituted in a carbide so as to contribute to the precipitation strengthening. In order to ensure Mo forming a solid solution in an amount required in the case where the steel is exposed for a long time at the high temperature, it is necessary to add Mo in an amount not less than 0.6%. However, if the Mo content of the steel exceeds 1.1%, the toughness of the steel is reduced, and ferrite formation is promoted. In addition, the ingot tends to be segregated. Under the circumstances, the

Mo content of the steel is defined to fall within a range of 0.6 to 1.1% in the present invention.

[0032] (h) Boron (B): The hardenability of the steel are improved by the addition of traces of boron (B). Also, carbo-nitride can be stabilized for a long time under high temperatures by the addition of traces of B. The particular effects can be produced by the addition of B in an amount not less than 0.001%. To be more specific, adding B in an amount not less than 0.001% has the effect of suppressing the coarsening of the carbide particles precipitated in the crystal grain boundaries and in the vicinity thereof. However, if the B content of the steel exceeds 0.004%, the formation of coarse particles is promoted. Under the circumstances, the B content of the steel is defined to fall within a range of 0.001 to 0.004% in the present invention.

[0033] (i) Nitrogen (N): Nitrogen (N) forms a nitride or a carbo-nitride so as to contribute to the precipitation strengthening. Also, N remaining in the mother phase contributes to the solid-solution strengthening. In the steel of the present invention, these effects cannot be recognized if the amount of N added is less than 0.002%. On the other hand, if the amount of N added exceeds 0.008%, coarsening of the nitride or carbo-nitride particles is promoted so as to reduce the creep resistance. Under the circumstances, the N content of the steel is defined to fall within a range of 0.002 to 0.008% in the present invention.

[0034] (j) Niobium (Nb): Niobium (Nb) forms fine carbo-nitride particles so as to contribute to the precipitation strengthening. The particular effect cannot be obtained if the amount of Nb added is less than 0.001%. On the other hand, if the amount of Nb added exceeds 0.008%, segregation is generated so as to increase the volume ratio of coarse Nb carbo-nitride particles that do not form a solid solution. Under the circumstances, the Nb content of the steel is defined to fall within a range of 0.001 to 0.008% in the present invention. In the steel of the present invention, an effect similar to that produced by the addition of Nb can be obtained by increasing the amount of V added.

[0035] (k) Nickel (Ni): Nickel (Ni) serves to improve the hardenability and toughness of the steel and has the effect of suppressing ferrite formation. The particular effects can be produced if Ni is added in an amount not less than 0.3%. If the amount of Ni added exceeds 0.6%, however, the creep resistance is reduced. Under the circumstances, the Ni content of the steel is defined to fall within a range of 0.3 to 0.6% in the present invention.

[0036] Incidentally, in adding the components described above and the main component of Fe, it is desirable to suppress as much as possible the impurities that are unavoidably mixed in.

[0037] (l) (Mo+W/2): The amount represented by (Mo+W/2) is defined to fall within a range of 1.3 to 1.4 in the present invention.

[0038] To reiterate, W and Mo contained in the steel of the present invention have the effects described in items (f) and (g) above. It should be noted in this connection that, where W and Mo are added together, the creep strength is improved and the tendency of segregation is prominently promoted compared with the case where Mo and W are added singly. In order to obtain a desired creep strength and to avoid segregation, it is necessary to define the amount of Mo and

W. In this case, it is appropriate to use an index called Mo equivalent. In the case of the steel of the present invention, the creep strength is reduced if the Mo equivalent is less than 1.3. On the other hand, if the Mo equivalent exceeds 1.4, segregation is unavoidably generated. Under the circumstances, the Mo equivalent is defined to fall within a range of 1.3 to 1.4 in the present invention.

[0039] An electroslag remelting process is employed in the method of the present invention for manufacturing a heat-resisting steel.

[0040] It should be noted in this connection that, in forming a large part such as a steam turbine rotor, the additive elements tend to be segregated when the molten metal is coagulated, or the coagulated texture tends to be heterogeneous. In general, a heat-resisting steel can be manufactured by a vacuum carbon deoxidizing method. However, it is possible to further improve the properties of the ingot by employing the electroslag remelting process.

[0041] The initiating (starting) temperature of the quenching treatment, i.e., the temperature at which the normalizing temperature is maintained, is specified in the present invention. In the heat-resisting steel of the present invention, the Nb carbo-nitride is the most stable precipitate that is present at the high temperature. If Nb carbo-nitride that does not form a solid solution remains in a large amount in the steel as a formed product while the normalizing heating is maintained, the precipitation amount of fine Nb carbo-nitride particles contributing to the precipitation strengthening in the subsequent tempering process is reduced. As a result, the mechanical characteristics of the steel are degraded.

[0042] Under the circumstances, in the steel containing Nb, it is necessary to set the initiating (starting) temperature of the quenching treatment at 1,020° C. or more in order to decrease the amount of Nb carbo-nitride that does not form a solid solution. However, if the initiating (starting) temperature of the quenching treatment exceeds 1,050° C., the crystal grains tend to be bulky. It follows that the initiating (starting) temperature of the quenching treatment is defined to fall within a range of 1,020° C. to 1,050° C. in the present invention.

[0043] On the other hand, when it comes to a steel in which the V content is increased without adding Nb, Nb carbo-nitride that does not form a solid solution is not formed so as to make it unnecessary to consider the presence of the particular formed product. Under the circumstances, the initiating (starting) temperature of the quenching treatment is defined to exceed the transformation point and to be the temperature at which the grain growth can be suppressed. To be more specific, the starting temperature of the quenching treatment is defined to fall within a range of 970° C. to 1,020° C.

[0044] In the present invention, it is appropriate to set the cooling rate in the quenching treatment at 100° C./hour or more.

[0045] In the heat-resisting steel of the present invention, the desired mechanical characteristics can be exhibited in the case where the matrix is formed of a bainite single phase. However, ferrite formation tends to be promoted in steel containing a relatively large amount of ferrite-forming elements like the steel of the present invention. In particular, the tendency of ferrite formation is markedly promoted in the

case where the cooling rate in the quenching treatment is low. Where ferrite is formed in the steel, Mo and W added as hardening elements are concentrated in the ferrite so as to reduce the creep strength and the toughness of the steel. It is particularly important to completely avoid ferrite formation in the core of a steel where a cooling rate tends to be slowed when it comes to a large ingot such as a turbine rotor material. Under the circumstances, in the heat-resisting steel of the present invention, the cooling rate in the quenching treatment is defined to be at least 100° C./hour, and preferably to fall within a range of 100° C./hour to 1,000° C./hour. Where the quenching treatment is carried out under the cooling rate defined in the present invention, it is possible to avoid ferrite formation even in the central portion of a large ingot. The quenching treatment is carried out by, for example, air hardening such as wind cooling, quenching with a refrigerant such as water spraying, or oil quenching.

[0046] In the present invention, the M₇C₃ type, MX type and M₂₃C₆ type precipitates are precipitated by heat treatment within the crystal grains or at the grain boundaries. It is appropriate for the amount of these precipitates to fall within a range of 0.5 to 2.0% by mass.

[0047] As a result of the precipitation strengthening function performed by the precipitates of the kinds referred to above, the creep rupture strength of the heat-resisting steel of the present invention is improved. Where the amount of the precipitates noted above is less than 0.5% by mass, the precipitation strengthening function is insufficient, resulting in failure of the steel to exhibit the desired creep rupture strength.

[0048] On the other hand, if the amount of the precipitates exceeds 2.0% by mass, the ratio of the coarse precipitate incapable of producing the strength maintaining effect is increased, resulting in failure of the steel to exhibit the desired creep rupture strength. Also, heat treatment at high temperatures for a long time is required in the case where the amount of precipitate exceeds 2.0% by mass. As a result, the inconvenience of the strength of the matrix itself being lowered is brought about. Under the circumstances, the sum of the M₇C₃ type, MX type and M₂₃C₆ type precipitates is defined in the present invention to fall within a range of 0.5 to 2.0% by mass.

[0049] The precipitate is measured as follows. Specifically, a sample is put in a mixed solution containing metha-

nol, acetyl acetone and tetramethyl ammonium chloride so as to dissolve the mother phase by electrolysis. Then, the dissolved mother phase is filtered and the residue is washed away, followed by measuring the mass. The result is indicated as “% by mass”. Further, M₇C₃, MX, M₂₃C₆, etc., are evaluated in respect of the residue by using, for example, an X-ray analysis.

[0050] It is possible to use the heat-resisting steel obtained by the means described above for forming a steam turbine rotor. In forming a steam turbine by using the steel of the present invention, it is possible to use a rod of the steel having a diameter of approximately 1 meter and length of approximately 10 meters. Where the heat treatment described above is applied to the steel having the composition described above, the steel can exhibit characteristics satisfactory for use as a material of a steam turbine rotor which is exposed to a maximum steam temperature of 566 to 593° C. during normal operation. However, the steel of the present invention is markedly softened when exposed to temperatures higher than 593° C., with the result that deformation of the steel tends to be promoted during operation. Also, at temperatures less than 566° C., it suffices to use conventional 1Cr-1Mo-0.25V steel.

[0051] The heat-resisting steel according to one embodiment of the present invention and the manufacturing method thereof will now be described with reference to Examples of the present invention.

EXAMPLE 1

[0052] The heat-resisting steel according to one embodiment of the present invention exhibits excellent characteristics. Specifically, 30 kg of a steel sample was melted by vacuum induction melting, followed by casting the molten steel so as to obtain a cast lump and subsequently subjecting the cast lump to hot rolling. Further, the hot-rolled steel was subjected to an annealing treatment, a normalizing treatment, a quenching treatment, and a tempering treatment in the order mentioned. Steel samples P1 to P27 shown in Table 1 represent Examples of the present invention directed to heat-resisting steel samples having a chemical composition falling within the range specified in the present invention. On the other hand, steel samples C1 to C9 shown in Table 1 represent Comparative Examples directed to steel samples having a composition failing to fall within the range specified in the present invention.

TABLE 1

Steel samples	C	Si	Mn	Ni	Cr	V	W	Mo	Nb	N	B	Fe	Mo + W/2
Examples													
P1	0.28	0.07	0.29	0.31	1.62	0.29	1.38	0.66	—	<0.002	—	Balance	1.350
P2	0.31	0.04	0.51	0.35	1.73	0.28	1.06	0.82	—	<0.002	—	Balance	1.350
P3	0.25	0.05	0.61	0.41	1.88	0.24	0.97	0.91	—	<0.002	—	Balance	1.395
P4	0.30	0.08	0.46	0.36	1.70	0.28	0.62	1.05	—	<0.002	—	Balance	1.360
P5	0.27	0.06	0.32	0.31	1.78	0.31	1.19	0.75	—	<0.002	—	Balance	1.345
P6	0.32	0.05	0.45	0.30	1.65	0.30	1.01	0.86	0.001	<0.002	—	Balance	1.365
P7	0.33	0.15	0.51	0.37	1.71	0.23	1.25	0.69	0.005	<0.002	—	Balance	1.315
P8	0.31	0.08	0.49	0.41	1.69	0.30	0.64	0.98	0.002	<0.002	—	Balance	1.300
P9	0.34	0.04	0.78	0.48	1.82	0.25	1.37	0.66	0.008	<0.002	—	Balance	1.345
P10	0.26	0.11	0.61	0.32	1.75	0.27	0.70	1.02	—	0.006	—	Balance	1.370
P11	0.29	0.04	0.31	0.41	1.79	0.29	1.39	0.64	—	0.006	—	Balance	1.335
P12	0.29	0.09	0.68	0.34	1.68	0.29	0.61	1.08	—	0.002	—	Balance	1.385

TABLE 1-continued

Steel samples	C	Si	Mn	Ni	Cr	V	W	Mo	Nb	N	B	Fe	Mo + W/2
P13	0.31	0.07	0.72	0.34	1.70	0.31	1.22	0.71	—	0.004	—	Balance	1.320
P14	0.31	0.09	0.59	0.42	1.72	0.27	1.01	0.88	0.003	0.005	—	Balance	1.385
P15	0.32	0.12	0.55	0.32	1.67	0.30	1.28	0.73	0.007	0.005	—	Balance	1.370
P16	0.25	0.05	0.31	0.31	1.78	0.28	1.16	0.75	0.001	0.002	—	Balance	1.330
P17	0.30	0.05	0.49	0.33	1.74	0.28	0.70	1.05	0.002	0.006	—	Balance	1.400
P18	0.27	0.15	0.76	0.48	1.85	0.25	0.82	0.96	0.004	0.008	—	Balance	1.370
P19	0.29	0.06	0.59	0.37	1.72	0.32	1.39	0.62	—	<0.002	0.001	Balance	1.315
P20	0.31	0.09	0.49	0.42	1.73	0.30	1.08	0.77	—	<0.002	0.002	Balance	1.310
P21	0.26	0.06	0.61	0.49	1.86	0.34	0.89	0.90	—	<0.002	0.004	Balance	1.345
P22	0.31	0.05	0.25	0.32	1.78	0.32	0.61	1.08	—	<0.002	0.002	Balance	1.385
P23	0.35	0.03	0.47	0.31	1.66	0.28	1.19	0.75	—	0.005	0.002	Balance	1.345
P24	0.33	0.05	0.59	0.33	1.73	0.29	0.69	0.99	—	0.005	0.001	Balance	1.335
P25	0.31	0.06	0.55	0.32	1.85	0.35	1.36	0.63	—	0.007	0.004	Balance	1.310
P26	0.32	0.10	0.49	0.45	1.79	0.28	0.82	0.89	—	0.005	0.001	Balance	1.300
P27	0.30	0.05	0.21	0.36	1.75	0.26	1.21	0.73	—	0.002	0.001	Balance	1.335
Comparative Examples													
C1	0.24*	0.05	0.68	0.44	1.22*	0.27	0.67	1.02	—	0.011*	—	Balance	1.355
C2	0.28	0.17*	0.51	0.63*	1.70	0.24	1.02	0.90	0.10*	<0.002	—	Balance	1.410*
C3	0.36*	0.06	0.82*	0.09*	1.95*	0.25*	0.68	1.01	—	0.006	—	Balance	1.350
C4	0.30	0.05	0.59	0.35	1.15*	0.28	—*	1.33*	—	<0.002	—	Balance	1.330
C5	0.23*	0.07	0.18*	0.45	1.73	0.32*	0.77	1.21*	0.04*	0.010*	—	Balance	1.595*
C6	0.27	0.20*	0.21	0.26*	1.76	0.36*	1.15	0.72	—	0.004	0.002	Balance	1.295*
C7	0.31	0.05	0.08*	0.02*	1.51*	0.27	0.58*	1.10	—	<0.002	—	Balance	1.390
C8	0.38*	0.05	0.48	0.27*	1.85	0.33	1.47*	0.61	—	<0.002	0.006*	Balance	1.345
C9	0.32	0.06	0.52	0.43	2.03*	0.29	1.36	0.55*	—	0.006	0.005*	Balance	1.230*

Note:
Values in*fail to fall within the range of the present invention.

[0053] In particular, steel sample C4 for the Comparative Example shown in Table 1 corresponds to the conventional steel called 1Cr-1Mo-0.25V steel. All the steel samples were adjusted to have a 0.02% proof stress at room temperature of about 650 to 690 Mpa, as shown in FIG. 2, on the

assumption that the steel is used for forming a turbine rotor. Also, the steel sample was subjected to a Charpy impact test by using a JIS (Japanese Industrial Standards) 4, 2-mm V-notch Charpy impact test piece. Table 2 also shows the result.

TABLE 2

Steel samples	0.02% proof stress at room temperature (MPa)	600° C. - 196 MPa Creep rupture time (h)	Impact absorption energy at 20° C. (J)
Example			
P1	685	1787	55
P2	670	1892	60
P3	690	1939	52
P4	665	1850	53
P5	657	1708	45
P6	685	1897	40
P7	662	1961	45
P8	673	1841	42
P9	669	1763	48
P10	651	1782	58
P11	668	1845	50
P12	670	1733	56
P13	663	1868	59
P14	652	1968	41
P15	676	2060	48
P16	665	2121	47
P17	684	1932	43
P18	675	1903	48
P19	658	2193	58
P20	680	2258	55
P21	672	2482	51
P22	670	2224	60
P23	685	2375	55
P24	655	2082	52

TABLE 2-continued

Steel samples	0.02% proof stress at room temperature (MPa)	600° C. - 196 MPa Creep rupture time (h)	Impact absorption energy at 20° C. (J)
P25	662	2548	53
P26	680	2306	58
P27	674	2038	50
Comparative Example			
C1	664	895	12
C2	674	920	18
C3	660	1587	33
C4	655	712	11
C5	658	1549	21
C6	657	1635	18
C7	670	1651	12
C8	678	1523	15
C9	668	981	45

[0054] As shown in Table 2, steel samples P1 to P27 for the Examples of the present invention having a composition falling within the range specified in the present invention exhibited an impact absorption energy of 40 to 60 J at 20° C. when the steel samples were adjusted to have substantially the same 0.02% proof stress. On the other hand, steel samples C1 to C8 for the Comparative Examples except steel sample C9 exhibited an impact absorption energy less than 40 J at 20° C., which was relatively less than that for the steel samples for the Examples of the present invention.

[0055] Also, a creep rupture test was applied to each of the steel samples shown in Table 1 at 600° C. and under a load of 196 MPa. Table 2 also shows the creep rupture time for each steel sample obtained from this test. Steel samples P1 to P27 for the Examples of the present invention were found to have a creep rupture time of 1,700 to 2,600 hours. On the other hand, the creep rupture time for steel samples C1 to C9 for the Comparative Examples was found to be 700 to 1,700 hours. To be more specific, steel samples C6 and C7 for the Comparative Examples exhibited a creep rupture time comparative to the steel samples for the Examples of the present invention. However, the impact absorption energy at 20° C. for steel samples C6 and C7 for the Comparative Examples was markedly lower than that of the steel samples for the Examples of the present invention.

[0056] Table 2 also shows that the creep rupture time is clearly shortened in steel having an Mo equivalent less than 1.3, such as steel sample C9, and steel having an Mo equivalent exceeding 1.4, such as steel sample C2. Also, the creep rupture time was found to be short in the case where the addition amounts of the other elements failed to fall within the ranges specified in the present invention, even if the Mo equivalent of the steel fell within a range of 1.3 to 1.4.

[0057] As pointed out above, where the steel samples are adjusted to have substantially the same 0.02% proof stress at room temperature, the heat-resisting steel of the present invention is superior to the steel samples for the Comparative Examples, in which the addition amounts of the elements fail to fall within the ranges specified in the present invention, in both impact absorption energy and creep rupture time. Also, the heat-resisting steel of the present invention exhibits characteristics superior to those of the steel sample C4 for the Comparative Example.

EXAMPLE 2

[0058] This Example is intended to clarify that, where a normalizing treatment is applied under a prescribed temperature range to the heat-resisting steel having the chemical composition falling within the range specified in the present invention, it is possible to decrease the coarse formed product so as to allow the manufactured steel to have a high texture cleanliness, and it is also possible to suppress coarsening of the crystal grains. Steel samples P5, P13 and P15 shown in Table 1 were used in Example 2. Also, these steel samples were prepared as in Example 1.

[0059] Each of steel samples P5 and P13 was subjected to a normalizing treatment at 950° C., 970° C., 1,020° C., and 1,030° C. On the other hand, steel sample P15 was subjected to a normalizing treatment at 970° C., 1,020° C. and 1,060° C. Test steel plates were taken from the steel samples after the normalizing treatment. After each test steel sample was polished, the cleanliness of the test steel sample was evaluated on the basis of the test method specified in JIS G 0555. Table 3 shows the result. Substances that were evaluated as being an inclusion include MnS, Nb carbo-nitride failing to form a solid solution, BN, etc.

TABLE 3

Steel samples	Examples	Normalizing temperature (° C.)	Sum of inclusion	Crystal grain size ratio
P5	Comparative Example method 1	950	0.017	1
	Example method 1	970	0.008	About 1
	Example method 2	1,020	0.008	About 0.75

TABLE 3-continued

Steel samples	Examples	Normalizing temperature (° C.)	Sum of inclusion	Crystal grain size ratio
P13	Comparative Example method 2	1,030	0.008	About 0.5
	Comparative Example method 3	950	0.017	1
	Example method 3	970	0.012	About 1
	Example method 4	1,020	0.008	About 0.75
P15	Comparative Example method 4	1,030	0.008	About 0.5
	Comparative Example method 5	970	0.017	1
	Example method 5	1,020	0.012	About 0.75
	Comparative Example method 6	1,060	0.012	About 0.25

[0060] As apparent from Table 3, the sum of the inclusion was 0.017 in the cases where each of steel samples P5 and P13 was subjected to a normalizing treatment at 950° C. and where steel sample P15 was subjected to a normalizing treatment at 970° C. Also, the sum of the inclusion was smaller than 0.012 in the cases where each of steel samples P5 and P13 was subjected to a normalizing treatment at temperatures not less than 970° C. and where steel sample P15 was subjected to a normalizing treatment at temperatures not less than 1,020° C. What should be noted is that the sum of the inclusion is reduced if the normalizing treatment is applied under temperatures exceeding the lower limit of the normalizing temperature range specified in the present invention. The reduction of the inclusion permits Nb, N, B, etc. to produce their effects prominently.

[0061] The grain size of each of the steel samples shown in Table 3 was measured by the test method specified in JIS G 0551. Table 3 also shows the grain size ratio, i.e., the value obtained by dividing the obtained grain size number for each steel sample by the grain size number of the steel sample having the lowest normalizing temperature. As shown in Table 3, the steel plates obtained by the Comparative Example methods 2 and 4, in which the normalizing treatment was applied at 1,030° C., exhibited a grain size ratio of about 0.5. On the other hand, the steel plate obtained by the Comparative Example method 6, in which the normalizing treatment was applied at 1,060° C., exhibited a grain size ratio of about 0.25. What should be noted is that the grains are markedly coarsened if the normalizing treatment is performed at a temperature exceeding the upper limit of the range of the normalizing temperatures (start-up temperature of the quenching treatment) specified in the present invention.

[0062] As pointed out above, the heat-resisting steel of the present invention in which the normalizing treatment is carried out within a prescribed temperature range permits

ensuring a high texture cleanliness and also permits suppressing the coarsening of the grains.

EXAMPLE 3

[0063] This Example is intended to clarify that it is possible to further improve the properties of the ingot in the case of employing the ESR (electroslag remelting process) for manufacturing an ingot of a heat-resisting steel having a chemical composition falling within the range specified in the present invention. The test steel samples were prepared to have a composition after casting equal to that of the steel sample P23 shown in Table 1. After the melting, the test steel sample was cast in a mold for the consumable electrode of the ESR, followed by re-melting the steel lump as the consumable electrode and subsequently applying a forging treatment. As a result, a steel rod was formed having a diameter of about 500 mm and a length of about 700 mm. Also, a steel rod of substantially the same shape was prepared by a vacuum carbon deoxidizing method. Each of these steel rods was subjected to a quenching treatment, which was started at 1,000° C. falling within the temperature range specified in the present invention, followed by applying a tempering treatment to the steel rod at 680° C. for 20 hours.

[0064] A tensile test was applied at room temperature to the surface layer and the central portion of each of these steel rods. Then, a 2-mm V-notch Charpy impact test was applied at 20° C. to the surface layer and the central portion of each of these steel rods. Table 4 shows the results. The two steel rods were adjusted at substantially the same 0.02% proof stress at room temperature and tensile strength. However, the steel rod prepared by the ESR was found to be slightly superior to the steel rod prepared by the vacuum carbon deoxidizing method in the elongation, draw and impact absorbing energy.

TABLE 4

Steel samples	Manufacturing method	Portion	0.02% proof stress (MPa)	Tensile strength (MPa)	Elongation (%)	Draw (%)	Impact absorbing energy at 20° C. (J)
P23	ESR	Surface layer	673	842	29	68	54
		Core	670	839	28	67	51
	VCD	Surface layer	669	834	24	61	48
		Core	668	828	23	59	44

ESR: Electroslag remelting process
VCO: Vacuum carbon deoxidizing method

[0065] The experimental data clearly support that the heat-resisting steel having a composition falling within the range specified in the present invention, which is prepared by employing the ESR method, exhibits further improved ductility and toughness, compared with the case where the ESR method is not employed in the manufacturing process.

EXAMPLE 4

[0066] This Example is intended to clarify that the heat-resisting steel having a composition falling within the range specified in the present invention exhibits appropriate characteristics in the case where prescribed amounts of the sum of M_7C_3 type, MX type and $M_{23}C_6$ type precipitates are ensured. Steel samples P2, P9, P12 and P21 shown in Table 1 were used as the test steel samples. These test steel samples were prepared as in Example 1. Also, the quenching treatment was started at 1,030° C. for steel sample P9 and at 1,010° C. for the other steel samples. After the quenching treatment, a tempering treatment was performed at temperatures ranging from 620° C. to 700° C. so as to measure the mass of the precipitate. Table 5 shows the mass % of the sum of the obtained precipitate for each steel sample. Further, a creep rupture time of the steel sample after the heat treatment was measured at 650° C. under a load of 98 MPa, and the impact absorbing energy at 20° C. was measured for each of the steel samples after the heat treatment. Table 5 also shows the results.

[0067] It has been found that the steel samples in which the amounts of the sum of M_7C_3 type, MX type and $M_{23}C_6$ type precipitates are less than 0.5% are short in the creep rupture time and low in the impact absorbing energy. On the other hand, the steel samples in which the amounts of the sum of M_7C_3 type, MX type and $M_{23}C_6$ type precipitates exceed 2.0% have been found to be short in the creep rupture time, though these steel samples have been found to have a high impact absorbing energy.

[0068] As apparent from the experimental data, the characteristics of the heat-resisting steel of the present invention depend on the amounts of the sum of M_7C_3 type, MX type and $M_{23}C_6$ type precipitates after the heat treatment. Also, where prescribed amounts of the sum of M_7C_3 type, MX type and $M_{23}C_6$ type precipitates are secured after the heat treatment, the heat-resisting steel becomes excellent in both creep rupture time and impact absorbing energy.

EXAMPLE 5

[0069] This Example is intended to clarify that a heat-resisting steel having a chemical composition falling within the range specified in the present invention exhibits an appropriate metal texture and good characteristics in the case of applying a quenching treatment to the heat-resisting steel at a prescribed cooling rate. Steel samples P2, P9, P12 and P21 shown in Table 1 were used as the test steel samples. These test steel samples were prepared as in Example 1. The quenching treatment was started at 1,030° C. for steel sample P9 and at 1,010° C. for the other steel samples. The cooling rate in the quenching treatment was set at 80° C./h or 100° C./h and the test samples were cooled to 300° C. or less.

[0070] Table 6 shows the situation in respect of ferrite formation after a quenching treatment for each of the test steel samples. Ferrite formation was recognized in all the test steel samples in the case of employing a cooling rate of 80° C./h. On the other hand, the texture of a bainite single phase was observed in the case of employing a cooling rate of 100° C./h.

[0071] Then, a tempering treatment was applied to the test steel sample after the quenching treatment so as to adjust the 0.02% proof stress at about 650 MPa. Further, an impact test was applied at 20° C. to each of these test steel samples by using a JIS 4, 2-mm V-notch Charpy impact test piece. Table 6 shows the results.

TABLE 5

Steel samples	Examples	Amount of precipitate after heat treatment (mass %)	650° C. - 98 MPa creep rupture time (h)	Impact absorbing energy at 20° C. (J)
P2	Comparative Example method 7	0.45	952	11
	Example method 6	0.64	1235	48
	Example method 7	0.93	1292	60
	Example method 8	1.88	1081	62
	Comparative Example method 8	2.21	687	88
P9	Comparative Example method 9	0.47	908	12
	Example method 9	0.75	1211	48
	Example method 10	1.25	1263	54
	Example method 11	1.73	1133	75
	Comparative Example method 10	2.08	758	105
P12	Comparative Example method 11	0.38	967	15
	Example method 12	0.61	1250	52
	Example method 13	1.03	1268	56
	Example method 14	1.67	1097	70
	Comparative Example method 12	2.30	826	80
P21	Comparative Example method 13	0.44	1145	11
	Example method 15	0.85	1905	48
	Example method 16	1.22	1973	51
	Example method 17	1.58	1643	70
	Comparative Example method 14	2.16	952	84

TABLE 6

Steel samples	Examples	Cooling rate (° C./h)	Ferrite formation	0.02% proof stress at room temperature (MPa)	Impact absorbing energy at 20° C. (J)
P2	Comparative Example method 15	80	Formed	646	35
	Example method 18	100	None	655	65
P9	Comparative Example method 16	80	Formed	652	28
	Example method 19	100	None	642	53
P12	Comparative Example method 17	80	Formed	660	31
	Example method 20	100	None	652	63
P21	Comparative Example method 18	80	Formed	648	28
	Example method 21	100	None	652	68

[0072] Ferrite formation was recognized in the steel sample prepared by employing the quenching treatment at a low cooling rate. Also, the particular steel sample was low in impact absorbing energy.

[0073] As apparent from the experimental data, ferrite formation can be avoided by increasing the cooling rate in the quenching treatment, thereby enabling the heat-resisting steel of the present invention to exhibit satisfactory characteristics.

[0074] As described above in detail, the present invention provides a heat-resisting steel, which can be operated stably under a high-temperature steam environment and which provides excellent economic advantages, and a method of manufacturing the particular heat-resisting steel.

[0075] Additional advantages and modifications will readily occur to those skilled in the art. Therefore, the invention in its broader aspects is not limited to the specific details and representative embodiments shown and described herein. Accordingly, various modifications may be made without departing from the spirit or scope of the general inventive concept as defined by the appended claims and their equivalents.

What is claimed is:

1. A heat-resisting steel, comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.
2. A heat-resisting steel according to claim 1, further comprising 0.002 to 0.008% by mass of N.
3. A heat-resisting steel according to claim 1, further comprising 0.001 to 0.004% by mass of B.
4. A heat-resisting steel according to claim 1, further comprising 0.002 to 0.008% by mass of N and 0.001 to 0.004% by mass of B.
5. A heat-resisting steel, comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.
6. A heat-resisting steel according to claim 5, further comprising 0.002 to 0.008% by mass of N.
7. A heat-resisting steel having precipitates of M₇C₃ type, MX type and M₂₃C₆ type, which are precipitated within the

crystal grains or at the crystal grain boundaries as a result of a hot forging treatment, an annealing treatment, a normalizing treatment, a quenching treatment and a tempering treatment applied in the order mentioned to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the sum of said precipitates falling within a range of 0.5% to 2.0% by mass.

8. A heat-resisting steel having precipitates of M₇C₃ type, MX type and M₂₃C₆ type, which are precipitated within the crystal grains or at the crystal grain boundaries as a result of a hot forging treatment, an annealing treatment, a normalizing treatment, a quenching treatment and a tempering treatment applied in the order mentioned to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the sum of said precipitates falling within a range of 0.5% to 2.0% by mass.

9. A method of manufacturing a heat-resisting steel, comprising manufacturing by an electroslag remelting process a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

10. A method of manufacturing a heat-resisting steel, comprising manufacturing by an electroslag remelting process a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities.

11. A method of manufacturing a heat-resisting steel, comprising applying a quenching treatment to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass of Ni, 1.6 to 1.9% by mass of Cr, 0.26 to 0.35% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and

unavoidable impurities, the initiating temperature of said quenching treatment falling within a range of 970° C. to 1,020° C.

12. A method of manufacturing a heat-resisting steel according to claim 11, wherein said steel further comprises 0.002 to 0.008% by mass of N.

13. A method of manufacturing a heat-resisting steel according to claim 11, wherein said steel further comprises 0.001 to 0.004% by mass of B.

14. A method of manufacturing a heat-resisting steel according to claim 11, wherein said steel further comprises 0.002 to 0.008% by mass of N and 0.001 to 0.004% by mass of B.

15. A method of manufacturing a heat-resisting steel, comprising applying a quenching treatment to a steel comprising 0.25 to 0.35% by mass of C, not more than 0.15% by mass of Si, 0.2 to 0.8% by mass of Mn, 0.3 to 0.6% by mass

of Ni, 1.6 to 1.9% by mass of Cr, 0.23 to 0.30% by mass of V, 0.6 to 1.1% by mass of Mo, 0.6 to 1.4% by mass of W, 0.001 to 0.008% by mass of Nb, 1.3 to 1.4% by mass of Mo+W/2, and the balance of Fe and unavoidable impurities, the initiating temperature of said quenching treatment falling within a range of 1,020° C. to 1,050° C.

16. A method of manufacturing a heat-resisting steel according to claim 15, wherein said steel further comprises 0.002 to 0.008% by mass of N.

17. A method of manufacturing a heat-resisting steel according to claim 11, wherein the cooling rate in said quenching treatment is set at 100° C./hour or more.

18. A method of manufacturing a heat-resisting steel according to claim 15, wherein the cooling rate in said quenching treatment is set at 100° C./hour or more.

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