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(54) Heat-resistant austenitic stainless steel and a production process thereof

(57) To provide a heat-resistant austenitic stainless steel having high-temperature strength and sag-resistance capable of resisting working temperatures of not less than 550°C as well as being low in cost, and a production process thereof. The steel consistent with the present invention contains not more than 0.1wt% C, less than 1.0wt% Si, 1.0wt% to 10.0wt% Mn, not more than 0.03wt% P, not more than 0.01wt% S, 0.01wt% to 3.0wt% Cu, 7.0wt% to 15.0wt% Ni, 15.0wt% to 25.0wt% Cr, 0.5wt% to 5.0wt% Mo, not more than 0.03wt% Al, 0.4wt% to 0.8wt% N, and the remainder substantially consisting of Fe and unavoidable impurities.

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Description

BACKGROUND OF THE INVENTION

1. Field of the Invention

[0001] The present invention relates to a heat-resistant austenitic stainless steel and a production process thereof, more specifically relates to a heat-resistant austenitic stainless steel suitable for a steel material for heat-resistant members used in exhaust systems of an automobile engine and an aeroengine, industrial manufacturing facilities and the like, and a production process thereof.

2. Description of Related Art

[0002] Conventionally, for heat-resistant members used in exhaust systems of an automobile engine and an aeroengine, industrial manufacturing facilities and the like, high-temperature strength and sag-resistance are required, and various metal materials are selectively used according to working temperatures. For example, in a relatively low-temperature range of not more than 350°C, an austenitic stainless steel (e.g., SUS304 and SUS316), a precipitation hardened stainless steel (e.g., SUS631J1) and the like are used. In addition, in a high-temperature range not less than 350°C, an Fe-based superalloy (e.g., SUH660 (A286)) and an Ni-based superalloy (e.g., Inconel 718 and Inconel X750) and the like are used.

[0003] On the other hand, improvement in engine performance and thermal efficiency and the like have been promoted recently, so that working temperatures of the members tend to rise. Therefore, a heat-resistant steel material which is low in cost and more excellent in the high-temperature strength and sag-resistance is strongly required. Among the above-described various metal materials, the conventional austenitic stainless steel and the precipitation hardened stainless steel are relatively low in cost; however, the working temperatures thereof are limited. On the other hand, the Fe-based or Ni-based superalloy satisfies a requirement for high-temperature strength and sag-resistance at not less than 550°C, so that a heat-resistant member capable of resisting working temperatures of up to about 700°C may be obtained. However, the heat-resistant member made from the superalloy causes increases in a melting cost and a process cost as well as a raw material cost, so that there arises a problem of high manufacturing costs.

[0004] To overcome the problem described above, various proposals have been made heretofore. For example, Japanese Patent Application Unexamined Publication No.Hei9-143633 discloses a martensitic stainless steel for a heat-resistant spring consisting of 11wt% to 14wt% Cr, 4.5wt% to 7.0wt% Ni, 1.0wt% to 3.0wt% Mo, 1.0wt% to 3.0wt% Al, 0.10wt% to 0.20wt% C, less than 10 × C wt% Nb, and Fe and unavoidable impurities (see claim 1 and paragraph 0023). In this reference, it is described that when the martensitic stainless steel having composition as above is subjected to cold rolling at not more than 70% after solution treatment, its 0.2% proof stress at temperatures of 350 to 550°C becomes 120 kgf/mm^2 (1176 MPa) or more.

[0005] Further, Japanese Patent Application Unexamined Publication No.2000-239804 discloses a stainless steel wire for a heat-resistant spring containing 0.04wt% to 0.40wt% C, 0.02wt% to 0.30wt% N, 0.24wt% to 0.60wt% C + N, 1.5wt% to 20.0wt% Mn, 17.0wt% to 19.0wt% Cr, 2.0wt% to 12.0wt% Ni and 0.5wt% to 2.0wt% Mo as well as at least one element selected from 0.8wt% Nb, 0.6wt% to 1.2wt% Si, 1.0wt% Ti and 1.0wt% W, and the remainder substantially consisting of Fe and unavoidable impurities (see paragraphs 0008 and 0009, and Tables 1 and 3). In this reference, it is described that a stainless steel wire which is excellent in the sag-resistance at 350 to 500°C is obtained by increasing a solution amounts of interstitial solute elements such as C and N, and a ferrite-stabilizing elements such as W and Mo.

[0006] Further, Japanese Patent Application Unexamined Publication No.2003-73784 discloses a heat-resistant steel wire containing 0.02wt% to 0.30wt% C, 0.02wt% to 3.5wt% Si, 0.02wt% to 2.5wt% Mn, 20wt% to 30wt% Ni, 15wt% to 25wt% Cr, 1.0wt% to 5.0wt% Ti and 0.002wt% to 1.0wt% Al as well as one or more elements selected from 0.1wt% to 2.0wt% Nb, 0.1wt% to 2.0wt% Ta and 0.1wt% to 4.0wt% Mo - the total content of Ti, Al, Nb and Ta is 2.0wt% to 7.0wt% -, and the remainder substantially consisting of Fe and unavoidable impurities (see claim 1 and paragraph 0053). In this reference, it is described that by controlling a structure of a γ phase being a matrix phase, a precipitation amount on an η phase (Ni_3Ti), and a form of a γ' phase ($Ni_3(Al, Ti, Nb)$), both of tensile strength and high-temperature sag-resistance at 450 to 600°C (especially at about 450°C) are attained.

[0007] Further, Japanese Patent Application Unexamined Publication No.2000-109955 discloses a heat-resistant stainless steel containing 0.02wt% to 0.30wt% C, 0.02wt% to 3.5wt% Si, 0.02wt% to 2.5wt% Mn, 10wt% to 50wt% Ni, 12wt% to 25wt% Cr, 1.0wt% to 5.0wt% Ti and 0.002wt% to 1.0wt% Al as well as one or more elements selected from 0.1wt% to 3.0wt% Nb, 0.001wt% to 0.01wt% B and 0.1wt% to 4.0wt% Mo - the total content of Ti, Al and Nb is 3.0wt% to 7.0wt% (see claim 1 and paragraph 0037). In this reference, it is described that bringing the weight percentage of an η phase (Ni_3Ti) and a γ' phase ($Ni_3(Al, Ti, Nb)$) into a predetermined range allows high-temperature tensile strength and the high-temperature sag-resistance at temperatures close to 600°C to improve.

[0008] Further, Japanese Patent Application Unexamined Publication No.2000-345268 discloses a high-heat-resistant alloy wire for a spring containing not more than 0.1wt% C, 18.0wt% to 21.0wt% Cr, 12.0wt% to 15.0wt% Co, 3.5wt% to 5.0wt% Mo, 2.0wt% to 4.0wt% Ti and 1.0wt% to 3.0wt% Al, and the remainder substantially consisting of Ni (see claim 1, and paragraphs 0022 and 0068). In this reference, it is described that a cold wire drawing process is performed to obtain the alloy wire with a worked austenitic structure where a grain size is predetermined, having surface roughness within a predetermined range and being not more than 5mm in diameter, and thereby the sag-resistance at not less than 600°C is improved.

[0009] Further, Japanese Patent Application Unexamined Publication No.Hei8-269632 discloses a high-strength and high-corrosion-resistant nitrogen-contained austenitic stainless steel consisting of not more than 0.1wt% C, not more than 1.0wt% Si, 5wt% to 10wt% Mn, not more than 0.01wt% S, 8wt% to 15wt% Ni, 15wt% to 25wt% Cr, 0.5wt% to 4wt% Mo and 0.3wt% to 1.0wt% N, and the remainder substantially consisting of Fe (see claim 1, and paragraph 0024). In this reference, it is described that dissolving nitrogen completely in solid solution through a solution heat treatment at not more than 1100°C allows room-temperature strength and corrosion resistance to improve.

[0010] Furthermore, Japanese Patent Application Unexamined Publication No.Hei9-279315 discloses an austenitic stainless steel for a metal gasket consisting of not more than 0.1wt% C, not more than 1.0wt% Si, 1.0wt% to 10.0wt% Mn, not more than 0.01wt% S, not more than 3.0wt% Cu, 7.0wt% to 15.0wt% Ni, 15.0wt% to 25.0wt% Cr, not more than 5.0wt% Mo, 0.35wt% to 0.8wt% N and not more than 0.02wt% Al, and the remainder substantially consisting of Fe (see claim 1, and paragraphs 0006 and 0029). In this reference, it is described that by increasing a content of N, and decreasing an Al-content restraining a solution amount of N to less than the predetermined amount, a metal gasket excellent in strength, high-temperature strength, sag-resistance and high-temperature oxidation resistance is obtained.

[0011] However, the materials disclosed in the above-mentioned Publications No.Hei9-143633 and No.2000-239804 are prepared for working temperatures of not more than 500°C, and not more than 550°C, respectively, so that they do not satisfy requirements for high-temperature strength and sag-resistance at temperatures higher than 550°C. Further, the amounts of nitrogen contained in these materials are 0.3wt% at the maximum (see Table 1 of No.2000-239804)

[0012] On the other hand, the materials disclosed in the above-mentioned Publications No.2003-73784, No. 2000-109955 and No.2000-345268 are prepared for working temperatures of not less than 550°C; However, costs of the materials rise up to the same as or more than that of the Fe-based superalloy (e.g., SUH660) since improvement in heat resistance is attempted in the respective materials by adding a large amount of Ni or Co so that precipitation on the γ' phase (Ni_3Al) is mainly reinforced.

[0013] Further, in the above-mentioned Publications No.Hei8-269632 and No.Hei9-279315, it is described that increasing the N-content in the austenitic stainless steels allows the room-temperature strength, the corrosion resistance, the high-temperature strength and the like to improve. In these Publications, it is described that those materials are useful for a component for which high corrosion resistance is required such as a self-tapping screw, a drill screw and a bolt used in the open air, an industrial area, a coastal area and the like, or for the metal gasket for an internal combustion engine; however, it is not disclosed definitely that those materials are useful for a heat-resistant member such as a heat-resistant spring which is used at working temperatures of not less than 550°C.

SUMMARY OF THE INVENTION

[0014] An object of the invention is to overcome the problems described above and to provide a heat-resistant austenitic stainless steel having high-temperature strength and sag-resistance capable of resisting working temperatures of not less than 550°C as well as being low in cost, and a production process thereof.

[0015] To achieve the objects and in accordance with the purpose of the present invention, a heat-resistant austenitic stainless steel consistent with the preferred embodiment of the present invention contains not more than 0.1wt% C, less than 1.0wt% Si, 1.0wt% to 10.0wt% Mn, not more than 0.03wt% P, not more than 0.01wt% S, 0.01wt% to 3.0wt% Cu, 7.0wt% to 15.0wt% Ni, 15.0wt% to 25.0wt% Cr, 0.5wt% to 5.0wt% Mo, not more than 0.03wt% Al, 0.4wt% to 0.8wt% N, and the remainder substantially consisting of Fe and unavoidable impurities.

[0016] In another aspect of the present invention, a production process of a heat-resistant austenitic stainless steel consistent with the preferred embodiment of the present invention includes the steps of applying solution treatment to the heat-resistant austenitic stainless steel consistent with the present invention, providing cold-working at a cold working ratio of 40% to 70% to the steel subjected to the solution treatment, and applying aging treatment at temperatures of 400°C to 650°C for not less than one minute to the steel subjected to the cold working.

[0017] The heat-resistant austenitic stainless steel consistent with the preferred embodiment of the present invention is low in cost since an addition amount of Ni is restrained. Further, an austenitic phase is stabilized since amounts of respective alloying elements such as Mn, Cr and Mo, which contribute to an increase in a solution amount of N, are kept in balance, and thereby the N-content is increased to the highest level above which N exceeds an amount of N-solubility in molten metal under the atmosphere. Furthermore, excellent high-temperature strength is attained through the aging treatment after the cold working. Moreover, the Al-content is made not more than 0.03wt%, so that generation of AlN which leads to decline in strength, toughness and ductility is suppressed. Therefore, by optimizing conditions of the cold working and the aging treatment, a heat-resistant member having high-temperature strength and sag-resistance approximately equal to those of an Fe-based superalloy is obtained.

[0018] Additional objects and advantages of the invention are set forth in the description which follows, are obvious from the description, or may be learned by practicing the invention. The objects and advantages of the invention may be realized and attained by the heat-resistant austenitic stainless steel and the production process thereof in the claims.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0019] A detailed description of one preferred embodiment of a heat-resistant austenitic stainless steel embodied by the present invention is provided below. The heat-resistant austenitic stainless steel consistent with the present invention is characterized as containing elements as provided below, and the remainder thereof substantially consisting of Fe and unavoidable impurities. Hereinafter, description will be given on the addition elements, ranges of addition amounts thereof, and reasons for limitation of the ranges.

(1) C: not more than 0.1wt%

[0020] C is an interstitial element which contributes to improvement in strength. Further, C acts to improve heat resistance by combining with Cr, Mo, W, V, Ti and Nb described later to form carbide. Therefore, it is preferable for the heat-resistant austenitic stainless steel to contain C so as to attain excellent high-temperature strength and sag-resistance. Specifically, a C-content is preferably not less than 0.001wt%, more preferably not less than 0.005wt%, and still more preferably not less than 0.010wt%.

[0021] Excessive addition of C, however, leads to decline in a solution amount of N. Further, formation of Cr carbide decreases an amount of Cr in solid solution in a matrix phase, and lowers oxidation resistance. Furthermore, formation of coarse primary carbide significantly degrades cold workability after solution treatment, and reduces ductility, too. Therefore, the C-content is preferably not more than 0.1wt%, more preferably not more than 0.05wt%, and still more preferably not more than 0.04wt%.

(2) Si: less than 1.0wt%

[0022] The present steel is characterized in that N may be dissolved in solid solution to the maximum solution amount. Si functions similarly to Al as a deoxidation element; however, since Al reacts with N and generates AlN to decrease a solution amount of N in the matrix phase, and the generated AlN significantly declines the high-temperature strength, toughness and ductility, it is preferable to use Si as the deoxidation element to reduce an Al-content in the steel. Specifically, an Si-content is preferably not less than 0.01wt%, more preferably not less than 0.05wt%, and still more preferably not less than 0.10wt%.

[0023] Excessive addition of Si, however, leads to decline in the toughness and ductility as well as interference with forging. Therefore, the Si-content is preferably less than 1.0wt%, more preferably not more than 0.7wt%, and still more preferably not more than 0.5wt%.

(3) Mn: from 1.0wt% to 10.0wt%

[0024] Mn is an austenite-stabilizing element which contributes to stabilization of an austenitic phase. Further, Mn is an important element which contributes to improvement in the strength since it significantly increases the solution amount of N. Furthermore, Mn is effective as deoxidation and desulfurization elements. Specifically, an Mn-content is preferably not less than 1.0wt%, more preferably not less than 3.0wt%, and still more preferably not less than 4.0wt%.

[0025] Excessive addition of Mn, however, lowers the oxidation resistance, degrades hot workability, and reduces the toughness and ductility. Therefore, the Mn-content is preferably not more than 10.0wt%, more preferably not more than 9.0wt%, and still more preferably not more than 8.0wt%.

(4) P: not more than 0.03wt%

[0026] P degrades the hot workability, and reduces intergranular strength, toughness and ductility. Therefore, a P-content is preferably small, specifically not more than 0.03wt%. Excessive reduction in P, however, causes a cost rise.

(5) S: not more than 0.01wt%

[0027] S reduces the toughness and ductility at the time of the cold working, and degrades the hot workability. Therefore, an S-content is preferably small, specifically not more than 0.01wt%. Excessive reduction in S, however, causes a cost rise.

(6) Cu: 0.01wt% to 3.0wt%

[0028] Cu is an austenite-stabilizing element which contributes to the stabilization of the austenitic phase. Further, Cu contributes to improvement in the toughness at the time of the cold working. Specifically, a Cu-content is preferably not less than 0.01wt%, and more preferably not less than 0.02wt%.

[0029] Excessive addition of C, however, reduces the solution amount of N as well as rises a solution temperature of Cr nitride to increase an amount of insoluble Cr nitride at the time of solution treatment, so that the high-temperature strength, toughness and ductility are lowered, and the cold and hot workability is degraded. Therefore, the Cu-content is preferably not more than 3.0wt%, more preferably not more than 2.5wt%, and still more preferably not more than 2.0wt%.

(7) Ni: 7.0wt% to 15.0wt%

[0030] Ni is an austenite-stabilizing element which contributes to the stabilization of the austenitic phase. Further, Ni contributes to the improvement in the high-temperature strength. Specifically, an Ni-content is preferably not less than 7.0wt%, and more preferably not less than 7.5wt%, and still more preferably not less than 8.0wt%.

[0031] Excessive addition of Ni, however, causes a cost rise, so that a material less expensive than an Fe-based superalloy such as SUH660 cannot be obtained. Further, the excessive addition reduces the solution amount of N as well as rises the solution temperature of Cr nitride to increase the amount of the insoluble Cr nitride at the time of the solution treatment, and thereby the high-temperature strength, toughness and ductility are lowered and the cold workability is degraded, significantly. Therefore, the Ni-content is preferably not more than 15.0wt%, more preferably not more than 14.0wt%, and still more preferably not more than 12.0wt%.

(8) Cr: 15.0wt% to 25.0wt%

[0032] Cr significantly increases the solution amount of N, and contributes to the improvement in the strength. Further, Cr is an important element which improves the oxidation resistance and corrosion resistance. Furthermore, Cr combines with C and N through aging treatment after the cold working so as to greatly contribute to the improvement in the high-temperature strength and the sag-resistance. Specifically, a Cr-content is preferably not less than 15.0wt%, and more preferably not less than 18.0wt%, and still more preferably not less than 21.0wt%.

[0033] However, excessive addition of Cr, being a ferrite-stabilizing element brings a ferrite-austenite duplex-phase structure, and promotes precipitation on a σ phase which leads to decline in the toughness and ductility. Therefore, the Cr-content is preferably not more than 25.0wt%, and more preferably not more than 24.0wt%.

(9) Mo: 0.5wt% to 5.0wt%

[0034] Mo is an element for increasing the solution amount of N, which improves the corrosion resistance, the high-temperature strength and the sag-resistance. Furthermore, similarly to Cr, Mo combines with C to form the carbide, and improves the heat resistance. Specifically, an Mo-content is preferably not less than 0.5wt%, and more preferably not less than 0.8wt%, and still more preferably not less than 1.0wt%.

[0035] Excessive addition of Mo, however, significantly degrades the cold workability since Mo combines with C to generate the coarse primary carbide. Further, the excessive addition lowers the oxidation resistance, and interferes with the hot working. Furthermore, the excessive addition lowers the toughness and ductility to cause embrittlement. Moreover, the excessive addition, rising the solution temperature of the Cr nitride to increase the amount of the insoluble Cr nitride at the time of the solution treatment, significantly lowers the high-temperature strength, toughness and ductility as well as degrades the cold workability. Therefore, the Mo content is preferably not more than 5.0wt%, and more preferably not more than 4.5wt%, and still more preferably not more than 4.0wt%.

(10) Al: not more than 0.03wt%

[0036] Similarly to Si and Mn, Al is highly effective as a deoxidation element; however, excessive addition of Al significantly lowers the high-temperature strength, toughness and ductility, and further, degrades the cold workability since Al combines with N to generate A1N, while the present steel is characterized in that N may be dissolved in solid solution to the maximum solution amount. Specifically, an Al-content is preferably not more than 0.03wt%, and more preferably not more than 0.025wt%, and still more preferably not more than 0.020wt%.

(11) N: 0.4wt% to 0.8wt%

[0037] N is the interstitial element which is one of the most important elements in the present invention, and highly effective in improving the strength and the corrosion resistance and stabilizing the austenitic phase. Further, N is highly effective in improving the high-temperature strength and the sag-resistance through the aging treatment after the cold working. Specifically, an N-content is preferably not less than 0.4wt%, and more preferably not less than 0.42wt%.

[0038] Excessive addition of N, however, causes N blow-hole, and further, significantly degrades the cold workability and reduces the toughness and ductility since the insoluble Cr nitride and a large amount of Ti, Nb and V nitride remain in the steel at the time of the solution treatment. Therefore, the N-content is preferably not more than 0.8wt%, and more preferably not more than 0.7wt%, and still more preferably not more than 0.6wt%.

[0039] Then, in addition to the above-described elements, the heat-resistant austenitic stainless steel consistent with the present invention may further include at least one element selected from W and Co. Hereinafter, descriptions will be given on ranges of addition amounts of W and Co, and reasons for limitation of the ranges.

(12) W: not more than 1.0wt%

[0040] W is an element for increasing the solution amount of N which contributes to improvement in the high-temperature strength and the sag-resistance. Further, similarly to Mo, W combines with C to form carbide, and improves the heat resistance. Specifically, a W-content is preferably not less than 0.01wt%, and more preferably not less than 0.05wt%, and still more preferably not less than 0.10wt%.

[0041] Excessive addition of W, however, generates the coarse primary carbide to significantly degrade the cold workability as in the case of Mo. Further, the excessive addition interferes with the forging, and reduces the toughness and ductility to cause embrittlement. Therefore, the W-content is preferably not more than 1.0wt%, and more preferably not more than 0.9wt%, and still more preferably not more than 0.8wt%.

(13) Co: not more than 5.0wt%

[0042] Co contributes to the improvement in the high-temperature strength and the sag-resistance. Specifically, a Co-content is preferably not less than 0.01wt%, and more preferably not less than 0.05wt%, and still more preferably not less than 0.10wt%.

[0043] Excessive addition of Co, however, causes a cost rise, so that a material less expensive than the Fe-based superalloy such as SUH660 cannot be obtained. Further, the excessive addition leads to the degradation in the cold workability. Therefore, the Co-content is preferably not more than 5.0wt%, and more preferably not more than 4.5wt%, and still more preferably not more than 4.0wt%.

[0044] Then, in addition to the above-described elements, the heat-resistant austenitic stainless steel consistent with the present invention may further include at least one element selected from Ti, Nb and V. Hereinafter, descriptions will be given on ranges of addition amounts of Ti, Nb and V, and reasons for limitation of the ranges.

(14) Ti: 0.03wt% to 0.5wt%

[0045] Ti combines with C and N, and contributes to the improvement in the high-temperature strength and refining of crystal grains. Specifically, a Ti-content is preferably not less than 0.03wt%, and more preferably not less than 0.035wt%, and still more preferably not less than 0.04wt%.

[0046] Excessive addition of Ti, however, causes a large amount of oxide, carbide and nitride to remain in the steel to degrade the cold workability. Further, the excessive addition decreases the effective solution amount of N to lower the high-temperature strength. Therefore, the Ti-content is preferably not more than 0.5wt%, and more preferably not more than 0.4wt%, and still more preferably not more than 0.3wt%.

(15) Nb: 0.03wt% to 0.5wt%

[0047] Similarly to Ti, Nb combines with C and N, and contributes to the improvement in the high-temperature strength and the refining of the crystal grains. Specifically, an Nb-content is preferably not less than 0.03wt%, and more preferably not less than 0.035wt%, and still more preferably not less than 0.04wt%.

[0048] Excessive addition of Nb, however, causes a large amount of oxide, carbide and nitride to remain in the steel to degrade the cold workability. Further, the excessive addition decreases the effective solution amount of N to lower the high-temperature strength. Therefore, the Nb-content is preferably not more than 0.5wt%, and more preferably not more than 0.4wt%, and still more preferably not more than 0.3wt%.

(16) V: 0.03wt% to 1.0wt%

[0049] Similarly to Ti and Nb, V combines with C and N, and contributes to the improvement in the high-temperature strength and the refining of the crystal grains. Specifically, a V-content is preferably not less than 0.03wt%, and more preferably not less than 0.04wt%, and still more preferably not less than 0.05wt%.

[0050] Excessive addition of V, however, causes a large amount of oxide and nitride to remain in the steel to degrade the cold workability. Further, the excessive addition decreases the effective solution amount of N to lower the high-temperature strength. Therefore, the V-content is preferably not more than 1.0wt%, and more preferably not more than 0.9wt%, and still more preferably not more than 0.8wt%.

[0051] Then, in addition to the above-described elements, the heat-resistant austenitic stainless steel consistent with the present invention may further include at least one element selected from B and Zr. Hereinafter, descriptions will be given on ranges of addition amounts of B and Zr, and reasons for limitation of the ranges.

(17) B: 0.001wt% to 0.010wt%

[0052] B contributes to the improvement in the high-temperature strength and the sag-resistance. Further, B is effective in improving the hot workability. Specifically, a B-content is preferably not less than 0.001wt%.

[0053] Excessive addition of B, however, contrarily degrades the hot workability. Therefore, the B-content is preferably not more than 0.010wt%, and more preferably not more than 0.008wt%, and still more preferably not more than 0.005wt%.

(18) Zr: 0.01wt% to 0.10wt%

[0054] Zr contributes to the improvement in the high-temperature strength and the sag-resistance. Specifically, a Zr-content is preferably not less than 0.01wt, and more preferably not less than 0.02wt%, and still more preferably not less than 0.03wt%.

[0055] Excessive addition of Zr, however, reduces the toughness and ductility. Therefore, the Zr-content is preferably not more than 0.10wt%, and more preferably not more than 0.09wt%, and still more preferably not more than 0.08wt%.

[0056] Then, in addition to the above-described elements, the heat-resistant austenitic stainless steel consistent with the present invention may further include at least one element selected from Ca and Mg. Hereinafter, descriptions will be given on ranges of addition amounts of Ca and Mg, and reasons for limitation of the ranges.

(19) Ca: 0.001wt% to 0.010wt%

[0057] Ca is effective in improving the hot workability, and is also effective in improving machinability. Specifically, a Ca-content is preferably not less than 0.001wt%.

[0058] Excessive addition of Ca, however, contrarily degrades the hot workability. Therefore, the Ca-content is preferably not more than 0.010wt%, and more preferably not more than 0.008wt%, and still more preferably not more than 0.005wt%.

(20) Mg: 0.001wt% to 0.010wt%

[0059] Mg is effective in improving the hot workability. Specifically, an Mg-content is preferably not less than 0.001wt%.

[0060] Excessive addition of Mg, however, contrarily degrades the hot workability. Therefore, the Mg-content is preferably not more than 0.010wt%, and more preferably not more than 0.008wt%, and still more preferably not more than 0.005wt%.

[0061] Among materials having the above-described composition, a material having a PN value of not less than 60 when expressed in the following Equation 1 is preferable for the heat-resistant austenitic stainless steel consistent with the present invention.

$$PN=2.4Mn-Cu-0.6Ni+3Cr+0.8Mo(wt\%) \qquad \text{Equation 1}$$

[0062] In order to increase the solution amount of N in the steel, addition amounts of the alloying elements such as Cr and Mn need to be made proper. For Equation 1, Mn, Cu, Ni, Cr and Mo are selected as an element which contributes to the solution amount of N, and contribution rates of the respective elements to the solution amount of N are obtained. When the PN value expressed by Equation 1 is not less than 60, it means that the solution amount of N capable of satisfying a requirement for a high-temperature property is secured. To obtain a material having an excellent high-temperature property, the PN value is more preferably not less than 62, and still more preferably not less than 64.

[0063] Next, a production process of the heat-resistant austenitic stainless steel excellent in the high-temperature property will be described. When the heat-resistant austenitic stainless steel consistent with the present invention consisting of the above-described composition is subjected to the solution treatment, the cold working and the aging treatment under predetermined conditions, a heat-resistant steel material excellent in the high-temperature strength and the sag-resistance is obtained.

[0064] The solution treatment is applied to a forged and rolled alloy for the purpose of uniforming the structure so that the cold workability is secured and Cr_2N precipitates while being refined and dispersed uniformly at the time of the aging treatment. As for the condition of the solution treatment, a condition necessary and sufficient for uniforming the structure may be applied. In the present invention, specifically, a temperature of the solution treatment is preferably 1000°C to 1150°C, and the time is preferably 0.1 hour to 2 hours.

[0065] After the solution treatment, the alloy is subjected to the cold working to be formed into a shape for a desired application such as a spring. A cold working ratio is preferably 40% to 70%. When the cold working ratio is below 40%, an increase in the strength by work hardening becomes small, and further, no increase can be attained at the succeeding aging treatment. As a result, primary hardness of 45HRC at room temperature cannot be secured, and a residual stress ratio in a relaxation test at 700 °C becomes 25% or less. Also in a case where the cold working ratio rises over 70%, the residual stress ratio falls, which is not preferable. Besides, a method for the cold working is not limited, and various methods such as wire drawing, cold rolling and swaging may be applied.

[0066] The aging treatment is applied to the alloy, which is cold-worked at 40 to 70% after the solution treatment, for the purpose of improving the strength and the sag-resistance. The aging treatment is preferably conducted for not less than 1 minute at 400°C to 650°C. Under the conditions other than the one above, the primary hardness of 45HRC at room temperature cannot be secured, and the residual stress ratio at 700 °C becomes 25% or less. An upper limit of the aging treatment time is not specified particularly; however, not more than 1 hour is recommended to avoid a cost rise in terms of industrial use.

[0067] By subjecting the material having the above-described composition under the above-described condition to the solution treatment, the cold working and the aging treatment, a heat-resistant austenitic stainless steels having the primary hardness of 45HRC at room temperature is obtained. By optimizing the material composition and the treatment conditions, a heat-resistant austenitic stainless steel having the primary hardness of 50HRC at room temperature is obtained.

[0068] Further, by optimizing the material composition and the treatment conditions, a heat-resistant austenitic stainless steel is obtained, which has hardness of not less than 45HRC at room temperature after 400-hour heat treatment at 600°C, and hardness of not less than 40HRC at room temperature after 400-hour heat treatment at 700°C.

[0069] Furthermore, by optimizing the material composition and the treatment conditions, a heat-resistant austenitic stainless steel is obtained, which has the residual stress ratio of not less than 25% after a 50-hour relaxation test at 700 °C.

[0070] The heat-resistant austenitic stainless steel consistent with the present invention is low in cost compared with the conventional Fe-based or Ni-based superalloys since the addition amount of Ni which causes a cost rise is restrained.

[0071] Further, the austenitic phase is stabilized, and the excellent high-temperature strength is attained through the aging treatment after the cold working since the amounts of the respective alloying elements such as Mn, Cr and Mo, which contribute to the increase of the solution amount of N, are kept in balance so as to increase the N-content to the highest level above which N exceeds an amount of N-solubility in molten metal under the atmosphere. Especially, by adjusting the amounts of the respective alloying elements so that the PN value becomes not less than 60, the solution amount of N necessary for satisfying the requirement for the high-temperature property may be secured. Moreover, the generation of AlN which leads to decline in the strength, toughness and ductility may be suppressed since the Al-content is made not more than 0.03wt%.

[0072] Furhter, by optimizing the conditions of the cold working after the solution treatment, and of the aging treatment, the heat-resistant austenitic stainless steel exhibits the high-temperature strength and the sag-resistance capable of resisting working temperatures of up to 700°C which is approximately equal to those of the Fe-based superalloy. Therefore, when the steel is applied to various heat-resistant members for which the high-temperature strength and the sag-resistance are required, an improvement in performance and thermal efficiency of machines and the like where the heat-resistant members are installed may be yielded while a cost rise is curbed.

[Examples]

[0073] Alloys having chemical compositions as listed in Table 1 attached hereto (Examples 1 to 14) were melted by using a high-frequency induction furnace, subjected to homogenization and heating, and made into a round bar of 24 mm in diameter by hot forging. Then, solution treatment was conducted where the bar was water-cooled after kept at 1100°C for 1 hour. Next, the bar was subjected to cold working at a cold working ratio of 60% to be formed into a round bar of 15.2 mm in diameter. Further, aging treatment was conducted where the bar was air-cooled after kept at 500°C for 1 hour.

[0074] From the resultant material, test pieces were taken and hardness tests (HRC) at room temperature and tensile tests (MPa) at 600°C and 700°C were conducted thereon. Further, hardness tests (HRC) at room temperature after kept at 600°C and 700°C for 400 hours were conducted, and residual stress ratios (%) in relaxation tests at 700°C where primary stress was made 530MPa was evaluated. The material with a greater residual stress ratio is more excellent in sag-resistance.

[0075] Incidentally, the test procedure is as follows.

The hardness test: Rockwell hardness measurement test (based on JIS Z2245)
The high-temperature tensile test: based on JIS G0567
The hardness test after long-time heat treatment at a high temperature: Rockwell hardness measurement test (based on JIS Z2245)
The relaxation test: based on JIS Z2276

[0076] Further, the same tests were conducted on SUH660 (Comparative Example 1) as a currently-used typical material. A production process of SUH660 before cold working was the same as that of Examples 1 to 14. Further, the cold working was conducted at a cold working ratio of 50%, and SUH660 was formed into a round bar of 17 mm in diameter. Furthermore, for aging treatment, the bar was air-cooled after kept at 720°C for 4 hours.

[0077] Furthermore, the same tests were conducted on a low-Mo material (Comparative Example 2), a high-Mo material (Comparative Example 3), a low-Cr, low-N and low-PN material (Comparative Example 4), a high-Cr material (Comparative Example 5), a low-Ni material (Comparative Example 6), a high-Ni material (Comparative Example 7), a high-Al material (Comparative Example 8), and a high-Mn material (Comparative Example 9). Production process of Comparative Examples 2 to 9 was the same as that of Examples 1 to 14.

[0078] Table 1 shows alloy composition of the respective materials. Further, Table 2 shows primary hardness (HRC) after the aging treatment, tensile strength (MPa) at 600°C and 700°C, hardness (HRC) after kept at 600°C and 700°C for 400 hours, and the residual stress ratio (%). As demonstrated in Tables 1 and 2, Examples 1 to 14 respectively satisfy requirements for both the primary hardness of not less than 45HRC and the residual stress ratio at 700°C of not less than 25% at the same time, while Comparative Examples 1 to 9 cannot satisfy both the requirements at the same time. In addition, Tables 1 and 2 shows that the high-temperature tensile strength and the hardness after the long-time heat treatment at a high temperature in Examples 1 to 14 are the same as or greater than those in Comparative Examples 1 to 9.

[Table 1]

	C	Si	Mn	P	S	Cu	Ni	Cr	Mo	W	Co	Al	Ti	Nb	V	N	B	Zr	Mg	Ca	PN
Example 1	0.02	0.26	9.76	0.019	0.002	0.11	7.3	24.8	4.7	—	—	0.005	—	—	—	0.71	—	—	—	—	97.1
Example 2	0.03	0.35	7.66	0.018	0.003	0.15	8.1	19.2	4.5	—	—	0.009	—	—	—	0.44	0.003	—	—	—	74.6
Example 3	0.02	0.20	5.98	0.019	0.002	0.05	10.1	23.2	1.9	—	—	0.003	—	—	0.09	0.50	—	—	—	—	79.3
Example 4	0.02	0.31	6.20	0.019	0.003	0.10	11.0	23.5	2.1	0.82	—	0.018	—	0.15	—	0.52	—	0.07	—	—	80.4
Example 5	0.08	0.10	5.09	0.020	0.006	2.12	7.9	22.2	2.5	—	2.01	0.009	—	0.06	0.08	0.45	—	—	0.003	—	74.0
Example 6	0.04	0.89	5.02	0.019	0.004	0.18	12.1	22.1	3.1	0.48	1.11	0.007	0.05	—	0.14	0.43	—	—	—	—	73.4
Example 7	0.05	0.19	7.11	0.022	0.005	1.00	9.0	24.4	3.2	0.12	—	0.026	0.06	—	—	0.58	—	—	0.001	0.002	86.4
Example 8	0.01	0.56	3.99	0.022	0.005	0.27	11.5	21.6	2.1	—	—	0.013	0.35	—	—	0.41	—	—	—	—	68.9
Example 9	0.03	0.35	6.07	0.019	0.003	0.14	9.8	22.9	2.2	0.22	—	0.017	—	—	0.71	0.58	—	—	—	—	79.0
Example10	0.03	0.37	4.96	0.021	0.008	0.14	7.4	23.3	2.0	—	3.62	0.011	0.09	0.05	0.05	0.46	—	—	—	0.003	78.8
Example11	0.02	0.14	6.03	0.019	0.007	0.11	10.2	22.5	1.5	—	0.52	0.012	—	0.36	—	0.50	0.002	0.07	0.003	—	76.9
Example12	0.02	0.20	5.92	0.021	0.002	0.09	8.1	22.0	1.9	—	0.18	0.009	—	—	—	0.47	—	—	—	—	76.8
Example13	0.06	0.38	6.00	0.023	0.004	0.15	10.2	23.1	2.0	—	—	0.003	0.04	—	0.19	0.51	0.003	0.08	—	0.001	79.0
Example14	0.03	0.24	6.99	0.020	0.001	0.12	14.1	22.7	0.9	0.53	—	0.020	0.14	0.05	—	0.47	0.002	0.05	0.002	0.001	77.0
Comparative Example 1	0.06	0.43	0.62	0.020	0.001	0.03	24.9	14.3	1.1	—	—	0.180	2.11	0.01	0.25	0.03	0.002	—	—	—	30.3
Comparative Example 2	0.02	0.15	5.90	0.018	0.002	0.21	9.9	23.0	0.1	—	—	0.009	—	—	—	0.48	—	—	—	—	77.1
Comparative Example 3	0.04	0.15	6.02	0.028	0.008	0.17	10.0	22.1	6.0	—	—	0.008	—	—	—	0.51	—	—	—	—	79.4
Comparative Example 4	0.03	0.25	8.94	0.017	0.008	0.16	10.2	13.1	1.9	—	—	0.009	—	—	—	0.30	—	—	—	—	56.0
Comparative Example 5	0.02	0.19	5.99	0.018	0.008	0.20	9.9	27.9	1.9	—	—	0.009	—	—	—	0.67	—	—	—	—	93.5
Comparative Example 6	0.04	0.15	5.10	0.018	0.008	0.11	5.1	22.9	1.8	—	—	0.011	—	—	—	0.51	—	—	—	—	79.2
Comparative Example 7	0.02	0.21	4.97	0.021	0.003	0.12	17.9	23.3	3.2	—	—	0.009	—	—	—	0.45	—	—	—	—	73.5
Comparative Example 8	0.02	0.16	5.12	0.017	0.005	0.18	10.1	23.0	2.0	—	—	0.059	—	—	—	0.48	—	—	—	—	76.6
Comparative Example 9	0.02	0.22	12.11	0.017	0.005	0.17	9.7	22.9	2.1	—	—	0.008	—	—	—	0.63	—	—	—	—	93.5

[Table 2]

	Primary Hardness After Aging Treatment (HRC)	High-temperature Tensile Strength		Hardness after Heat Treatment		Residual Stress Ratio
		600°C (MPa)	700°C (MPa)	600°C/400h (HRC)	700°C/400h (HRC)	(%)
Example 1	53	1053	853	51	44	36
Example 2	51	987	796	50	42	32
Example 3	51	1001	802	50	42	35
Example 4	52	1027	844	51	43	31
Example 5	51	1003	801	50	42	31
Example 6	51	992	798	50	42	30
Example 7	52	1038	846	51	43	33
Example 8	51	987	797	50	42	30
Example 9	52	1021	849	51	43	31
Example 10	51	1023	842	51	43	31
Example 11	51	996	795	50	42	30
Example 12	51	1004	803	50	42	33
Example 13	51	1005	805	50	42	35
Example 14	51	1009	809	51	43	32
Comparative 1 Example	40	1098	877	43	34	30
Comparative 2 Example	42	816	589	42	38	18
Comparative 3 Example	40	791	593	40	33	22
Comparative 4 Example	40	803	611	38	32	12
Comparative 5 Example	41	800	608	43	38	23
Comparative 6 Example	43	837	626	40	34	17
Comparative 7 Example	52	954	663	45	34	12
Comparative 8 Example	51	931	624	43	32	10
Comparative 9 Example	51	893	614	41	32	15
Comparative Example 1 : SUH660 Comparative Example 2 : Low Mo Comparative Example 3 : High Mo Comparative Example 4 : Low Cr, N, PN Comparative Example 5 : High Cr Comparative Example 6 : Low Ni Comparative Example 7 : High Ni Comparative Example 8 : High Al Comparative Example 9 : High Mn						

[0079] Next, a material having the same composition as Example 3 was subjected to melting, forging, solution treatment, cold working and aging treatment following the same procedure as above except that only the cold working ratio at the time of the cold working after the solution treatment was changed. A test piece was taken from the obtained material, and residual stress ratios (%) thereof under the above-described conditions were obtained. Table 3 shows the result. As demonstrated in Table 3, in cases where the cold working ratios are below 40%, and over 70%, the residual stress ratios decline.

[Table3]

Cold Working Ratio (%)	Residual Stress Ratio (%)
30	18
40	31
50	34
60	35
70	32
80	12

[0080] Next, a material having the same composition as Example 3 was subjected to melting, forging, solution treatment, cold working and aging treatment following the same procedure as above except that only the condition of the aging treatment was changed. A test piece was taken from the obtained material, and the residual stress ratios (%) thereof under the above-described conditions were obtained. Table 4 shows the result. As demonstrated in Table 4, in cases where the temperatures of the aging treatment are below 400°C, and over 650°C, the residual stress ratios decline.

[Table 4]

Aging Heat Treatment Temperature (°C)	Aging Heat Treatment Time (h)	Residual Stress Ratio (%)
300	1.0	18
500	0.1	34
500	1.0	35
500	4.0	35
700	1.0	24

[0081] The heat-resistant austenitic stainless steel consistent with the present invention may be applied extensively to a heat-resistant member for which a low cost, and the high-temperature strength and the sag-resistance are required. Examples of specific applications include: a heat-resistant spring used in exhaust systems of an automobile engine and an aeroengine, an industrial manufacturing facilities and the like; a high-temperature bolt and the like which are typically used in the automobile engine, the aeroengine, a generator turbine and the like; a turbo casing; a boiler part; a part for an industrial furnace, and the like.

[0082] Further, examples of more specific applications include: a nozzle, a vane, a blade, a disk, a casing and a bolt of a gas turbine, a combustor liner, a compressor disk and the like for aviation and generator; intake and exhaust valves for automobile engine, a rotor, a housing, a nozzle and a vane of a turbocharger, an exhaust manifold, a front pipe, a muffler, an exhaust valve spring, an exhaust bolt and the like for an automobile; a boiler, a rotor, a casing, a blade, a bolt and the like for a steam turbine; petrochemical industrial parts such as a heat exchanger, a pressure vessel, an ethylene decomposition tube and a valve; parts for a heat treating furnace such as a fitting, a fixture, a jig for heat treatment, a forging mold or die, a hot reduction roll, a continuous cast roll, a heater sheath and a radiant tube; parts for a garbage incinerator such as a heat exchanger tube; parts for a burner such as a nozzle and a casing; a valve for a ship diesel engine, and the like.

[0083] The foregoing description of the preferred embodiments of the invention has been presented for purposes of illustration and description. It is not intended to be exhaustive or to limit the invention to the precise form disclosed, and modifications and variations are possible in the light of the above teachings or may be acquired from practice of the invention. The embodiments chosen and described in order to explain the principles of the invention and its practical application to enable one skilled in the art to utilize the invention in various embodiments and with various modifications as are suited to the particular use contemplated. It is intended that the scope of the invention be defined by the claims appended hereto.

Claims

1. A heat-resistant austenitic stainless steel comprising:

not more than 0.1wt% C;
less than 1.0wt% Si;
1.0wt% to 10.0wt% Mn;
not more than 0.03wt% P;
not more than 0.01wt% S;
0.01wt% to 3.0wt% Cu;
7.0wt% to 15.0wt% Ni;
15.0wt% to 25.0wt% Cr;
0.5wt% to 5.0wt% Mo;
not more than 0.03wt% Al;
0. 4wt% to 0.8wt% N, and optionally

at least one element selected from the group consisting of:

not more than 1.0wt% W; and
not more than 5.0wt% Co;

at least one element selected from the group consisting of:

0.03wt% to 0.5wt% Ti;
0.03wt% to 0.5wt% Nb; and
0.03wt% to 1.0wt% V;

at least one element selected from the group consisting of:

0.001wt% to 0.010wt% B; and
0.01wt% to 0.10wt% Zr;

at least one element selected from the group consisting of:

0.001wt% to 0.010wt% Ca;
0. 001wt% to 0.010wt% Mg, and

the remainder substantially consisting of Fe and unavoidable impurities.

2. The heat-resistant austenitic stainless steel according to claim 1, wherein PN is not less than 60 when expressed by the following equation:

$$PN=2.4Mn-Cu-0.6Ni+3Cr+0.8Mo \text{ (wt\%)}.$$

3. The heat-resistant austenitic stainless steel according to claim 2, wherein the heat-resistant austenitic stainless steel is subjected to solution treatment, cold working at a cold working ratio of 40% to 70%, and aging treatment at 400°C to 650°C for not less than one minute.

4. The heat-resistant austenitic stainless steel according to claim 3, wherein primary hardness at room temperature is not less than 45HRC.

5. The heat-resistant austenitic stainless steel according to claim 4, wherein
room-temperature hardness after 400-hour heat treatment at 600°C is 45HRC, and
room-temperature hardness after 400-hour heat treatment at 700°C is 40HRC.

6. The heat-resistant austenitic stainless steel according to claim 5, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

7. The heat-resistant austenitic stainless steel according to claim 4, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

8. The heat-resistant austenitic stainless steel according to claim 3, wherein
room-temperature hardness after 400-hour heat treatment at 600°C is 45HRC, and
room-temperature hardness after 400-hour heat treatment at 700°C is 40HRC.

9. The heat-resistant austenitic stainless steel according to claim 8, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

10. The heat-resistant austenitic stainless steel according to claim 3, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

11. The heat-resistant austenitic stainless steel according to claim 2, wherein primary hardness at room temperature is not less than 45HRC.

12. The heat-resistant austenitic stainless steel according to claim 2, wherein
room-temperature hardness after 400-hour heat treatment at 600°C is 45HRC, and
room-temperature hardness after 400-hour heat treatment at 700°C is 40HRC.

13. The heat-resistant austenitic stainless steel according to claim 2, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

14. A production process of a heat-resistant austenitic stainless steel comprising the steps of:

applying solution treatment to the heat-resistant austenitic stainless steel according to claim 2;
providing cold-working at a cold working ratio of 40% to 70% to the heat-resistant austenitic stainless steel subjected to the solution treatment; and
applying aging treatment at temperatures of 400°C to 650°C for not less than one minute to the heat-resistant austenitic stainless steel subjected to the cold working.

15. The heat-resistant austenitic stainless steel according to claim 1, wherein the heat-resistant austenitic stainless steel is subjected to solution treatment, cold working at a cold working ratio of 40% to 70%, and aging treatment at 400°C to 650°C for not less than one minute.

16. The heat-resistant austenitic stainless steel according to claim 15, wherein primary hardness at room temperature is not less than 45HRC.

17. The heat-resistant austenitic stainless steel according to claim 15, wherein
room-temperature hardness after 400-hour heat treatment at 600°C is 45HRC, and
room-temperature hardness after 400-hour heat treatment at 700°C is 40HRC.

18. The heat-resistant austenitic stainless steel according to claim 15, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

19. The heat-resistant austenitic stainless steel according to claim 1, wherein primary hardness at room temperature is not less than 45HRC.

20. The heat-resistant austenitic stainless steel according to claim 1, wherein
room-temperature hardness after 400-hour heat treatment at 600°C is 45HRC, and
room-temperature hardness after 400-hour heat treatment at 700°C is 40HRC.

21. The heat-resistant austenitic stainless steel according to claim 1, wherein a residual stress ratio after a 50-hour relaxation test at 700°C is not less than 25%.

22. A production process of a heat-resistant austenitic stainless steel comprising the steps of:

applying solution treatment to the heat-resistant austenitic stainless steel according to claim 1;
providing cold-working at a cold working ratio of 40% to 70% to the heat-resistant austenitic stainless steel subjected to the solution treatment; and
applying aging treatment at temperatures of 400°C to 650°C for not less than one minute to the heat-resistant austenitic stainless steel subjected to the cold working.