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(54) **HEAT RESISTANT STEEL FOR EXHAUST VALVE**

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(57) **ABSTRACT**

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The present invention provides a heat resistant steel for an exhaust valve, containing: more than 0.50% by mass but less than 0.80% by mass of C, more than 0.30% by mass but less than 0.60% by mass of N, 17.0% by mass or more but less than 25.0% by mass of Cr, 4.0% by mass or more but less than 12.0% by mass of Ni, 7.0% by mass or more but less than 14.0% by mass of Mn, 2.0% by mass or more but less than 6.0% by mass of Mo, more than 0.5% by mass but less than 1.5% by mass of Si, and 0.025% by mass or more but less than 1.0% by mass of Nb, with the balance consisting of Fe and unavoidable impurities, in which a content of P contained in the unavoidable impurities is regulated to less than 0.03% by mass, a total content of C and N is from 0.85% by mass to 1.3% by mass, and a ratio of the content of Nb to the content of C is 0.05 or more but less than 1.8.

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## HEAT RESISTANT STEEL FOR EXHAUST VALVE

### FIELD OF THE INVENTION

[0001] The present invention relates to a heat resistant steel for an exhaust valve.

### BACKGROUND OF THE INVENTION

[0002] An inlet valve for introducing a mixed gas of fuel and air into a cylinder and an exhaust valve for discharging combustion gas to the outside of the cylinder have been used in an engine. Of these, the exhaust valve is exposed to high-temperature combustion gas, so that a material having excellent high-temperature properties (for example, high-temperature hardness, fatigue properties, wear resistance and oxidation resistance) has been used in the exhaust valve. As the material for the exhaust valve, there has been known a Ni base superalloy (for example, NCF751), an austenitic heat resistant steel (for example, SUH35) or the like.

[0003] Ni base superalloys are a material in which a  $\gamma'$  phase is allowed to be precipitated by aging treatment, thereby enhancing strength and wear resistance thereof at high temperature. Ni base superalloys are expensive, but have extremely high heat resistance. Accordingly, a valve using the same has been mainly used in a high-power engine exposed to a temperature of 800° C. or more.

[0004] On the other hand, austenitic heat resistant steels are a material in which  $M_{23}C_6$  type carbides are allowed to be precipitated, thereby enhancing strength and wear resistance thereof at high temperature. The austenitic heat resistant steels are inferior to the Ni base superalloys in high-temperature properties, but are inexpensive. Accordingly, a valve using the same has been mainly used in an engine for which high heat resistance is not required.

[0005] With respect to such materials suitable for the exhaust valve, various proposals have hitherto been made. For example, JP-A-2004-277860 discloses a heat resistant alloy for an exhaust valve comprising, by weight %, C: 0.01% to 0.2%, Si: 1% or less, Mn: 1% or less, Ni: 30% to 62%, Cr: 13% to 20%, W: 0.01% to 3.0%, Al: 0.7% to less than 1.6%, Ti: 1.5% to 3.0%, B: 0.001% to 0.01%, P: 0.02% or less and S: 0.01% or less, with the balance consisting of Fe and unavoidable impurities.

[0006] Further, JP-A-9-279309 discloses a Fe—Cr—Ni heat resistant alloy comprising, by weight %, C: 0.01% to 0.10%, Si: 2% or less, Mn: 2% or less, Cr: 14% to 18%, Nb+Ta: 0.5% to 1.5%, Ti: 2.0% to 3.0%, Al: 0.8% to 1.5%, Ni: 30% to 35%, B: 0.001% to 0.01%, Cu: 0.5% or less, P: 0.02% or less, S: 0.01% or less, O: 0.01% or less and N: 0.01% or less, with the balance consisting of Fe and unavoidable impurities and having a predetermined component balance.

[0007] Furthermore, JP-A-2001-323323 discloses a method for manufacturing an automotive engine valve comprising subjecting a Fe base heat resistant steel having a Fe-0.53% C-0.2% Si-9.2% Mn-3.9% Ni-21.5% Cr-0.43% N composition to solution treatment at 1,100° C. to 1,180° C., and forging a bevel portion of the valve at 700° C. to 1,000° C., followed by aging treatment.

[0008] This document describes that when the Fe base heat resistant steel having the predetermined composition is subjected to the solution treatment, the forging and the aging

treatment under the predetermined conditions, the hardness of a valve face portion can be adjusted to HV 400 or more.

[0009] Due to the recent rising cost of raw materials, the production cost of exhaust valves is significantly affected by fluctuations of the raw material cost. In particular, the Ni base superalloy has a large Ni content, so that the raw material cost and production cost of the exhaust valves made of Ni base superalloy are largely affected by the price of Ni. Accordingly, materials in which the amount of Ni is decreased to decrease the fluctuation band of the raw material cost have been desired. However, in the Ni base superalloy, Ni is an element for forming a  $\gamma'$  phase as a reinforcing phase, so that a further decrease in the amount of Ni results in a difficulty of achieving high strength utilizing the  $\gamma'$  phase.

[0010] On the other hand, the carbide precipitation type austenitic heat resistant steel is hard to be affected by the price of Ni, but has a problem of being poor in high temperature properties, compared to the  $\gamma'$  precipitation type Ni base superalloy. There has been also known a material obtained by increasing the strength of SUH35 in order to solve this problem (for example, overseas standard LV21-43 steel (SUH 35+1W, 2Nb)). However, regarding the LV21-43 steel, problems of difficult texture control and poor hot workability still remain.

### SUMMARY OF THE INVENTION

[0011] A problem that the invention is to solve is to provide a heat resistant steel for an exhaust valve, which has a relatively small Ni content, has high mechanical properties (for example, tensile strength, fatigue strength, wear resistance, hardness and the like), and moreover, has an excellent corrosion resistance.

[0012] Namely, the present invention provides the following items 1 to 4.

[0013] 1. A heat resistant steel for an exhaust valve, comprising:

[0014] more than 0.50% by mass but less than 0.80% by mass of C,

[0015] more than 0.30% by mass but less than 0.60% by mass of N,

[0016] 17.0% by mass or more but less than 25.0% by mass of Cr,

[0017] 4.0% by mass or more but less than 12.0% by mass of Ni,

[0018] 7.0% by mass or more but less than 14.0% by mass of Mn,

[0019] 2.0% by mass or more but less than 6.0% by mass of Mo,

[0020] more than 0.5% by mass but less than 1.5% by mass of Si, and

[0021] 0.025% by mass or more but less than 1.0% by mass of Nb,

[0022] with the balance consisting of Fe and unavoidable impurities,

[0023] wherein a content of P contained in the unavoidable impurities is regulated to less than 0.03% by mass,

[0024] wherein a total content of C and N is from 0.85% by mass to 1.3% by mass, and

[0025] wherein a ratio of the content of Nb to the content of C is 0.05 or more but less than 1.8.

[0026] 2. The heat resistant steel for an exhaust valve according to item 1 above, which further comprises 0.001% by mass or more but less than 0.01% by mass of Mg and Ca in total.



**[0027]** 3. The heat resistant steel for an exhaust valve according to item 1 or 2 above, which further comprises at least one selected from the group consisting of

**[0028]** 0.001% by mass or more but less than 0.03% by mass of B, and

**[0029]** 0.001% by mass or more but less than 0.1% by mass of Zr.

**[0030]** 4. The heat resistant steel for an exhaust valve according to any one of items 1 to 3 above, which further comprises 0.01% by mass or more but less than 5.0% by mass of Co.

**[0031]** Both of C and N are austenite-stabilizing elements, and at the same time, also elements for forming an MX type carbonitride (including an MC type carbide). In the invention, the (C+N) amount (total content of C and N) and the Nb/C ratio (ratio of the content of Nb to the content of C) are regulated in specific ranges, so that the MX type carbonitrides (including the MC type carbides) having a proper size are formed in proper amounts in the material after solution treatment. Accordingly, grains are not coarsened after the solution treatment, and coarse primary crystal MX type carbonitrides also do not remain. Further, since  $M_{23}C_6$  type carbides are precipitated in proper amounts in the material by aging treatment, high-temperature properties are improved. Furthermore, since a solid-solution hardening element is limited to Mo, the high-temperature properties are improved.

#### BEST MODE FOR CARRYING OUT THE INVENTION

**[0032]** Some embodiments of the invention will be described in detail below. Herein, in the present specification, all the percentages defined by mass are the same as those defined by weight, respectively.

##### [1. Heat Resistant Steel for Exhaust Valve]

**[0033]** The heat resistant steel for an exhaust valve according to the invention comprises the following elements with the balance consisting of Fe and unavoidable impurities. The kind of additive elements, the component range thereof and the reason for limitation thereof are as follows. In an embodiment, the heat resistant steel according to the invention comprises the following main constituent elements and optional secondary constituent element(s), with the balance consisting of Fe and unavoidable impurities. In another embodiment, the heat resistant steel according to the invention consists essentially of the following main constituent elements and optional secondary constituent element(s), with the balance consisting of Fe and unavoidable impurities. In still another embodiment, the heat resistant steel according to the invention consists of the following main constituent elements and optional secondary constituent element(s), with the balance consisting of Fe and unavoidable impurities.

##### [1.1. Main Constituent Elements]

**[0034]** (1)  $0.50 < C < 0.80$  mass %

**[0035]** C is an austenite-stabilizing element, and inhibits the formation of a sigma phase or a Laves phase as a harmful phase. Further, C is preferentially bound to Nb to produce an MC type carbide. A proper amount of the MC type carbide having a proper size inhibits grains from being coarsened during solution treatment and improves strength properties. Further, a proper amount of the MC type carbide having a proper size acts as a hard phase to improve wear resistance.

Furthermore, C is bound to Cr to produce  $M_{23}C_6$  type carbides, thereby improving the wear resistance and the strength properties. In order to obtain such effects, it is necessary that the C content exceeds 0.50 mass %. The C content preferably exceeds 0.52 mass %.

**[0036]** On the other hand, an excessive C content results in an excessive carbide amount that causes deterioration of processability. It is therefore necessary that the C content is less than 0.80 mass %. The C content is more preferably less than 0.70 mass %, and furthermore preferably less than 0.67 mass %.

(2)  $0.30 < N < 0.60$  mass %

**[0037]** N is an austenite-stabilizing element, and acts as an alternative element for austenite-forming elements such as Ni and Mn. Further, N acts for reinforcement of a matrix as an interstitial solid-solution hardening element, because of its small atomic radius. Furthermore, N acts in complex with substitutional solid-solution hardening elements such as Mo and W to contribute to improvement on strength. In addition, N is substituted for a C site of the MC type carbide to form an MX type carbonitride. In order to obtain such effects, it is necessary that the N content exceeds 0.30 mass %. It is more preferable that the N content exceeds 0.35 mass %.

**[0038]** On the other hand, an excessive N content results in a difficulty of allowing N to be dissolved in the matrix. It is therefore necessary that the N content is less than 0.60 mass %. The N content is more preferably less than 0.50 mass %, and furthermore preferably less than 0.47 mass %.

(3)  $17.0 \leq Cr < 25.0$  mass %

**[0039]** Cr has a function of forming a protective oxide coating of  $Cr_2O_3$  in an operating temperature range of the exhaust valve. Cr is therefore an element indispensable for improving corrosion resistance and oxidation resistance. Further, Cr binds to C to form the  $Cr_{23}C_6$  carbide, thereby contributing to improvement of the strength properties. In order to obtain such effects, it is necessary that the Cr content is 17.0 mass % or more. The Cr content is more preferably 18.0 mass % or more, and furthermore preferably 19.5 mass % or more.

**[0040]** On the other hand, an excessive Cr content causes destabilization of austenite, because Cr is a ferrite-stabilizing element. Further, the excessive addition of Cr promotes the formation of the sigma phase or the Laves phase that are an embrittlement phase, thereby causing deterioration of hot workability and strength property. It is therefore necessary that the Cr content is less than 25.0 mass %. The Cr content is more preferably less than 23.5 mass %, and furthermore preferably 22.5 mass % or less.

(4)  $4.0 \leq Ni < 12.0$  mass %

**[0041]** Ni is added as an austenite-stabilizing element. In order to stabilize austenite, it is necessary that the Ni content is 4.0 mass % or more. The Ni content is more preferably 4.5 mass % or more, and furthermore preferably 5.1 mass % or more.

**[0042]** On the other hand, an excessive Ni content causes an increase in cost. It is therefore necessary that the Ni content is less than 12.0 mass %. The Ni content is more preferably less than 11.5 mass %, and furthermore preferably 10.5 mass % or less.

(5)  $7.0 \leq Mn < 14.0$  mass %

**[0043]** Mn is added as an austenite-stabilizing element. Mn not only acts as an alternative element for expensive Ni, but also has an effect of enhancing solubility of N. In order to obtain such effects, it is necessary that the Mn content is 7.0



mass % or more. The Mn content is more preferably 7.5 mass % or more, and furthermore preferably 8.0 mass % or more.

**[0044]** On the other hand, an excessive Mn content causes deterioration of high-temperature properties due to a decrease in melting point. It is therefore necessary that the Mn content is less than 14.0 mass %. The Mn content is more preferably 12.5 mass % or less, and furthermore preferably less than 11.0 mass %.

(6)  $2.0 \leq \text{Mo} < 6.0$  mass %

**[0045]** Mo acts as a solid-solution hardening element for a  $\gamma$  phase of the matrix, and is an element effective for improvement of high-temperature strength. In order to obtain such an effect, it is necessary that the Mo content is 2.0 mass % or more. The Mo content is more preferably 2.9 mass % or more, and furthermore preferably 3.3 mass % or more.

**[0046]** On the other hand, an excessive Mo amount causes an increase in deformation resistance. Further, the formation of the sigma phase or the Laves phase, that are an embrittlement phase, is promoted and thus the hot workability and fatigue properties are deteriorated. It is therefore necessary that the Mo content is less than 6.0 mass %. The Mo content is more preferably less than 5.1 mass %, and furthermore preferably 4.5 mass % or less.

**[0047]** Incidentally, there is also a technique of adding W besides Mo as the solid-solution hardening element. However, in the invention, the technique is limited to the addition of Mo. The amount of solid-solution hardening due to the solid-solution hardening element such as Mo or W largely depends on the atomic weight of the element. Mo is smaller in the atomic weight than W, and larger in the number of atoms per unit mass %. Accordingly, Mo provides a larger amount of solid-solution hardening. For this reason, when it is intended to obtain the equivalent amount of solid-solution hardening by the addition of W, precipitation of the Laves phase becomes dominant, resulting in a failure to obtain an effect equivalent to that due to Mo. Accordingly, in order to maximally obtain the effect of solid-solution hardening, in the invention, the technique is limited to the addition of Mo.

(7)  $0.5 < \text{Si} < 1.5$  mass %

**[0048]** Si is an effective element as a deoxidizing agent at the time of dissolution and for imparting the oxidation resistance in a high-temperature region. Further, Si has an effect of improving strength as a solid-solution hardening element. In order to obtain such effects, it is necessary that the Si content exceeds 0.5 mass %. The Si content is more preferably 0.55 mass % or more. Furthermore preferably, the Si content exceeds 0.60 mass %.

**[0049]** On the other hand, an excessive Si amount conversely results in a decrease in the strength properties. Further, an oxide of Si is liable to delaminate. When Si oxides are produced in large amounts, oxide layers delaminate, thereby deteriorating the oxidation resistance. It is therefore necessary that the Si content is less than 1.5 mass %. The Si content is more preferably less than 1.1 mass %, and furthermore preferably less than 0.9 mass %.

**[0050]** Incidentally, there is a problem that a Si-containing Fe base alloy is generally liable to corrode in high-temperature environments where Pb coexists. Accordingly, Si-free materials have hitherto been used in steels for exhaust valves. However, according to the present fuel circumstances (production of lead-free gasoline), lead corrosion resistance has become out of the question. In the invention, therefore, Si is positively added to make efficient use of it for improvement of

the oxidation resistance and the strength properties. This point is one of major characteristics of the invention.

(8)  $0.025 \leq \text{Nb} < 1.0$  mass %

**[0051]** Nb binds to C and N to cause precipitation of MX type carbonitrides (including MC type carbides, hereinafter the same). A proper amount of the MX type carbonitride having a proper size inhibits grains from being coarsened after the solution treatment, which is effective for improvement of the high-temperature strength properties. In order to obtain such an effect, it is necessary that the Nb content is 0.025 mass % or more.

**[0052]** On the other hand, the addition of excessive Nb promotes the production of ferrite and generates coarse MX type carbonitrides in large amounts. The coarse carbonitrides partially remain even after the solution treatment, which causes deterioration of the hot workability. Further, the fatigue properties also deteriorate. It is therefore necessary that the Nb content is less than 1.0 mass %. The Nb content is more preferably less than 0.9 mass %, and furthermore preferably less than 0.8 mass %.

**[0053]** Incidentally, elements for forming the MX type carbides include Ti, V and the like, as well as Nb. However, in the invention, the forming element is limited to Nb. The reason for this is as follows.

**[0054]** Ti has a strong bonding force to C and N, and relatively coarse primary crystal MX type carbonitrides (primary carbides) are precipitated in large amounts. The primary carbides are not dissolved even by the solution treatment, so that the coarse carbonitrides exert a significant influence on deterioration of the fatigue properties and impact properties.

**[0055]** Further, V is effective for improvement of the strength properties. However, V has a strong bonding force to O, so that a V oxide is formed to significantly deteriorate the oxidation resistance of the material.

**[0056]** Accordingly, from the balance of the strength properties and the oxidation resistance, the forming element of the MX type carbonitrides is limited to Nb.

(9)  $\text{P} < 0.03$  mass %

**[0057]** The addition of P stimulates a refinement effect of the carbide, and is effective for improvement of the high-temperature strength properties. However, the addition of excessive P significantly decreases the melting point to deteriorate the high temperature strength and the hot workability. Further, the precipitated carbide is coarsened depending on aging treatment conditions. Regarding the fatigue properties, the coarse carbide becomes a starting point of breakage to cause deterioration of properties. It is therefore necessary that the P content is regulated to less than 0.03 mass %. The present application aims at improvement of the high-temperature strength properties by the increases in the solid-solution hardening element amount and the carbide amount, so that a smaller P content is preferred in order to inhibit deterioration of processability as much as possible.

## [1.2. Secondary Constituent Elements]

**[0058]** The heat resistant steel for an exhaust valve according to the invention may further contain any one or two or more of the following elements, in addition to the above-mentioned elements.

(1)  $0.001 \leq (\text{Mg}, \text{Ca}) < 0.01$  mass %

**[0059]** Both of Mg and Ca can be added as a deoxidizing/desulfurizing agent at the time of melting of the alloy. Mg and/or Ca contribute to improvement of the hot workability of



the alloy. In order to obtain such effects, it is necessary that the total content of Mg and Ca is 0.001 mass % or more.

**[0060]** On the other hand, an excessive content of Mg and/or Ca tends to deteriorate the processability rather than to improve it. It is therefore necessary that the total content of Mg and Ca is less than 0.01 mass %.

(2)  $0.001 \leq R < 0.03$  mass %

(3)  $0.001 \leq Zr < 0.1$  mass %

**[0061]** Both of B and Zr segregate in grain boundaries to reinforce the boundaries. In order to obtain such an effect, it is necessary that the contents of B and Zr are each 0.001 mass % or more.

**[0062]** On the other hand, excessive contents of B and Zr results in impairing the hot workability. It is therefore necessary that the B content is less than 0.03 mass %. Further, it is necessary that the Zr content is less than 0.1 mass %. Any one or both of B and Zr may be added.

(4)  $0.01 \leq Co < 5.0$  mass %

**[0063]** Co acts as an austenite-stabilizing element, and is used as an alternative element for Ni. Further, Co contributes to improvement of the strength properties. In order to obtain such effects, it is necessary that the Co content is 0.01 mass % or more.

**[0064]** On the other hand, an excessive Co amount results in high cost. It is therefore necessary that the Co content is less than 5.0 mass %.

**[0065]** In this regard, with regard to each element contained in the steel of the invention, according to an embodiment, the minimal amount thereof present in the steel is the smallest non-zero amount used in the Examples of the developed steels as summarized in Table 1. According to a further embodiment, the maximum amount thereof present in the steel is the maximum amount used in the Examples of the developed steels as summarized in Table 1.

### [1.3. Component Balance]

**[0066]** The heat resistant steel for an exhaust valve according to the invention satisfies the following conditions, in addition to that the component elements are within the above-mentioned ranges.

(1)  $0.85 \leq C+N \leq 1.3$  mass %

**[0067]** As described above, each of C and N is a strong austenite-stabilizing element, and effectively acts as an alternative element for expensive Ni on cost reduction. Further, both of C and N have a function of forming the MX type carbonitrides.

**[0068]** A proper amount of the MX type carbonitride having a proper size inhibits grains from being coarsened after the solution treatment, which is effective for improvement of the high-temperature strength properties. In order to obtain such effects, it is necessary that the (C+N) content (total content of C and N) is 0.85 mass % or more. The (C+N) content is more preferably 0.87 mass % or more, and furthermore preferably 0.9 mass % or more.

**[0069]** On the other hand, an excessive (C+N) content results in forming coarse MX type carbonitrides in large amounts. The coarse carbonitrides partially remain even after the solution treatment, which causes deterioration of the hot workability. It is therefore necessary that the (C+N) content is

1.3 mass % or less. The (C+N) content is more preferably 1.20 mass % or less, and furthermore preferably 1.15 mass % or less.

(2)  $0.05 \leq Nb/C < 1.8$

**[0070]** A proper amount of the MX type carbonitride having a proper size has a role of preventing grains from being coarsened due to a pinning effect. In order to obtain such an effect, it is necessary that the ratio (Nb/C) of the Nb content (mass %) to the C content (mass %) is 0.05 or more. The Nb/C ratio is more preferably 0.07 or more, and furthermore preferably 0.1 or more.

**[0071]** On the other hand, when Nb becomes relatively excessive to C, Nb preferentially binds to C, and the coarse primary crystal MX type carbonitrides are precipitated in a large amount. The coarse primary crystal MX type carbonitrides do not disappear completely even after the solution treatment, which causes deterioration of the fatigue properties. Further, C is depleted to decrease the amount of the  $M_{23}C_6$  type carbides precipitated, which are effective for improvement of the wear resistance and the strength properties. It is therefore necessary that the Nb/C ratio is less than 1.8. The Nb/C ratio is more preferably less than 1.5, and furthermore preferably 1.3 or less.

## [2. Manufacturing Method of Heat Resistant Steel for Exhaust Valve]

**[0072]** A manufacturing method of the heat resistant steel for an exhaust valve according to the invention comprises a melting/casting step, a homogenized heat treatment step, a forging step, a solution treatment step and an aging step.

### [2.1. Melting/Casting Step]

**[0073]** The melting/casting step is a step of melting and casting the raw materials blended to a predetermined composition. A melting method of the raw materials and a casting method of molten metal are not particularly limited, and various methods can be used. Any melting conditions may be used as long as they are conditions under which the molten metal which has homogeneous components and is possible to be casted is obtained.

### [2.2. Homogenized Heat Treatment Step]

**[0074]** The homogenized heat treatment step is a step of subjecting an ingot obtained in the melting/casting step to homogenized heat treatment. The homogenized heat treatment is performed in order to homogenize components of the ingot.

**[0075]** As the conditions for the homogenized heat treatment, optimum conditions are selected depending on the components. Usually, the heat treatment temperature is from 1,100° C. to 1,250° C. Further, the heat treatment time is from 5 hours to 25 hours.

### [2.3. Forging Step]

**[0076]** The forging step is a step of plastically deforming the ingot subjected to the homogenized heat treatment to a predetermined shape. A forging method and forging conditions are not particularly limited, and any method and conditions may be used as long as a desired shape can be efficiently produced.



## [2.4. Solution treatment Step]

**[0077]** The solution treatment step is a step of subjecting the material obtained in the forging step to solution treatment. The solution treatment is performed in order to allow the coarse primary crystal MX type carbonitrides to disappear.

**[0078]** As the solution treatment conditions, optimum conditions are selected depending on the components. In general, with an increase in the solution treatment temperature, the remaining amount of primary carbides decreases and the amount of fine intragranular carbides precipitated in the aging treatment increases. This is therefore effective for improvement of the fatigue properties. However, when the treatment is performed at a temperature higher than 1,200° C., precipitation of grain boundary reaction carbides is promoted, leading to deterioration of properties. Accordingly, the solution treatment is preferably performed at 1,000° C. to 1,200° C. for 20 minutes or more, followed by oil cooling treatment.

## [2.5. Aging Step]

**[0079]** The aging step is a step of subjecting the material after the solution treatment to aging treatment. The aging treatment is performed in order to allow the  $M_{23}C_6$  type carbides to be precipitated.

**[0080]** As the aging treatment conditions, optimum conditions are selected depending on the components. The aging treatment is preferably performed at 700° C. to 850° C. for 2 hours or more, followed by air cooling treatment, although depending on the components.

## [3. Operation of Heat Resistant Steel for Exhaust Valve]

**[0081]** Both of C and N are the austenite-stabilizing elements, and at the same time, also the elements for forming the MX type carbonitride. In the invention, the (C+N) amount and the Nb/C ratio are respectively controlled in specific

ranges, so that the MX type carbonitrides having a proper size are formed in proper amounts in the material after the solution treatment. Accordingly, the grains are not coarsened after the solution treatment, and the coarse primary crystal MX type carbonitrides also do not remain. Further, since the  $M_{23}C_6$  type carbides are precipitated in proper amounts in the material by the aging treatment, the high-temperature properties are improved. Furthermore, since the solid-solution hardening element is limited to Mo, the high-temperature properties are improved.

**[0082]** Further, the amount of Si added is controlled in a specific range, so that the oxidation resistance is improved, and the solid-solution hardening is also achieved.

**[0083]** Furthermore, the amount of Ni is increased compared to conventional austenitic heat resistant steels, so that the  $\gamma$  phase is stabilized to improve toughness.

## EXAMPLES

Examples 1 to 24 and Comparative Examples 1 to 16

## [1. Preparation of Specimens]

**[0084]** Alloys having compositions shown in Tables 1 and 2 were each melted in a high-frequency induction furnace to obtain 50 kg of an ingot. To each ingot prepared by melting, homogenized heat treatment was performed at 1,180° C. for 16 hours. Then, the ingot was forged to a rod stock having a diameter of 18 mm. To the material forged, solution treatment (ST) was further performed. Solution treatment was conducted under conditions at 1,150° C. for 30 minutes, followed by oil cooling (Examples 1 to 24) or conditions at 1,050° C. for 30 minutes, followed by oil cooling (Comparative Examples 1 to 16). Further, to the material after the solution treatment (ST), aging treatment (AG) was performed under conditions of 750° C. for 4 hours, followed by air cooling.

TABLE 1

|            | Component (mass %) |      |      |      |      |      |     |      |       |           |      |       |
|------------|--------------------|------|------|------|------|------|-----|------|-------|-----------|------|-------|
|            | C                  | N    | Si   | Mn   | Cr   | Ni   | Mo  | Nb   | P     | Others    | Nb/C | C + N |
| Example 1  | 0.62               | 0.46 | 0.75 | 9.3  | 20.6 | 6.5  | 4.1 | 0.71 | 0.010 |           | 1.15 | 1.08  |
| Example 2  | 0.53               | 0.42 | 0.62 | 8.5  | 20.3 | 5.8  | 5.7 | 0.72 | 0.009 |           | 1.36 | 0.95  |
| Example 3  | 0.58               | 0.38 | 0.71 | 7.2  | 19.3 | 6.9  | 2.3 | 0.44 | 0.008 |           | 0.76 | 0.96  |
| Example 4  | 0.62               | 0.51 | 0.67 | 8.7  | 24.1 | 5.5  | 4.8 | 0.84 | 0.014 |           | 1.35 | 1.17  |
| Example 5  | 0.63               | 0.44 | 0.73 | 11.5 | 21.3 | 5.4  | 2.5 | 0.72 | 0.008 |           | 1.14 | 1.07  |
| Example 6  | 0.62               | 0.40 | 0.72 | 7.2  | 20.9 | 10.4 | 3.8 | 0.69 | 0.010 |           | 1.11 | 1.02  |
| Example 7  | 0.60               | 0.39 | 0.59 | 8.7  | 23.6 | 4.3  | 4.6 | 0.62 | 0.009 |           | 1.03 | 0.99  |
| Example 8  | 0.61               | 0.44 | 0.63 | 8.9  | 20.9 | 5.9  | 4.1 | 0.71 | 0.007 | Mg: 0.005 | 1.16 | 1.05  |
| Example 9  | 0.55               | 0.43 | 0.73 | 9.2  | 20.1 | 5.8  | 3.9 | 0.73 | 0.007 | Ca: 0.005 | 1.33 | 0.98  |
| Example 10 | 0.55               | 0.47 | 0.67 | 9.7  | 21.4 | 6.2  | 4.2 | 0.66 | 0.012 | B: 0.015  | 1.20 | 1.02  |
| Example 11 | 0.57               | 0.42 | 0.68 | 9.3  | 21.3 | 5.9  | 4.3 | 0.68 | 0.011 | Zr: 0.05  | 1.19 | 0.99  |
| Example 12 | 0.62               | 0.44 | 0.65 | 9.3  | 21.4 | 5.2  | 3.8 | 0.71 | 0.010 | Co: 2.5   | 1.15 | 1.06  |
| Example 13 | 0.59               | 0.42 | 0.71 | 9.2  | 19.8 | 11.7 | 4.2 | 0.70 | 0.009 |           | 1.19 | 1.01  |
| Example 14 | 0.51               | 0.40 | 0.68 | 8.6  | 20.8 | 6.2  | 5.4 | 0.71 | 0.009 |           | 1.39 | 0.91  |
| Example 15 | 0.59               | 0.38 | 1.31 | 8.9  | 19.3 | 6.3  | 3.4 | 0.72 | 0.008 |           | 1.22 | 0.97  |
| Example 16 | 0.73               | 0.32 | 0.71 | 9.1  | 20.1 | 5.9  | 3.8 | 0.68 | 0.010 |           | 0.93 | 1.06  |
| Example 17 | 0.61               | 0.43 | 0.63 | 9.3  | 20.9 | 4.6  | 4.1 | 0.71 | 0.013 |           | 1.16 | 1.04  |
| Example 18 | 0.55               | 0.48 | 0.53 | 8.3  | 21.8 | 5.8  | 4.2 | 0.68 | 0.007 |           | 1.24 | 1.03  |
| Example 19 | 0.56               | 0.45 | 0.61 | 9.5  | 17.2 | 5.9  | 3.9 | 0.70 | 0.009 |           | 1.25 | 1.01  |
| Example 20 | 0.57               | 0.54 | 0.73 | 8.1  | 17.8 | 6.0  | 4.1 | 0.71 | 0.013 |           | 1.25 | 1.11  |
| Example 21 | 0.61               | 0.44 | 0.74 | 8.3  | 21.4 | 5.9  | 4.0 | 0.94 | 0.009 |           | 1.54 | 1.05  |
| Example 22 | 0.53               | 0.41 | 0.69 | 9.3  | 20.1 | 5.9  | 3.8 | 0.08 | 0.010 |           | 0.15 | 0.94  |
| Example 23 | 0.62               | 0.38 | 0.60 | 9.2  | 20.9 | 6.2  | 3.9 | 0.31 | 0.011 |           | 0.50 | 1.00  |
| Example 24 | 0.53               | 0.42 | 0.68 | 9.3  | 21.1 | 9.8  | 4.0 | 0.69 | 0.009 |           | 1.30 | 0.95  |



TABLE 2

|                        | Component (mass %) |      |      |      |      |     |     |      |       |          |      |       |
|------------------------|--------------------|------|------|------|------|-----|-----|------|-------|----------|------|-------|
|                        | C                  | N    | Si   | Mn   | Cr   | Ni  | Mo  | Nb   | P     | Others   | Nb/C | C + N |
| Comparative Example 1  | 0.49               | 0.40 | 0.09 | 8.9  | 21.2 | 3.9 | —   | —    | 0.009 |          | 0.00 | 0.89  |
| Comparative Example 2  | 0.50               | 0.45 | 0.08 | 9.0  | 21.0 | 4.0 | —   | 2.03 | 0.010 | W: 1.0   | 4.06 | 0.95  |
| Comparative Example 3  | 0.61               | 0.45 | 0.72 | 9.2  | 21.6 | 5.2 | 1.5 | 0.69 | 0.009 |          | 1.13 | 1.06  |
| Comparative Example 4  | 0.63               | 0.42 | 0.69 | 8.6  | 20.4 | 6.3 | 3.9 | 1.45 | 0.011 |          | 2.30 | 1.05  |
| Comparative Example 5  | 0.59               | 0.43 | 0.72 | 9.5  | 21.6 | 6.1 | 1.9 | 0.67 | 0.014 | W: 1.1   | 1.14 | 1.02  |
| Comparative Example 6  | 0.61               | 0.40 | 0.82 | 9.0  | 21.0 | 6.0 | —   | 0.69 | 0.008 | W: 3.5   | 1.13 | 1.01  |
| Comparative Example 7  | 0.63               | 0.51 | 0.78 | 9.1  | 19.2 | 6.3 | 4.0 | —    | 0.009 | V: 0.82  | 1.30 | 1.14  |
| Comparative Example 8  | 0.59               | 0.42 | 0.66 | 9.0  | 21.2 | 6.1 | 4.0 | —    | 0.010 | Ti: 0.78 | 1.32 | 1.01  |
| Comparative Example 9  | 0.61               | 0.40 | 0.71 | 9.2  | 21.1 | 5.9 | 4.2 | 0.69 | 0.120 |          | 1.13 | 1.01  |
| Comparative Example 10 | 0.62               | 0.42 | 0.32 | 9.9  | 21.2 | 6.2 | 4.1 | 0.66 | 0.007 |          | 1.06 | 1.04  |
| Comparative Example 11 | 0.60               | 0.38 | 1.67 | 9.1  | 21.0 | 6.0 | 3.9 | 0.68 | 0.014 |          | 1.13 | 0.98  |
| Comparative Example 12 | 0.72               | 0.41 | 0.70 | 9.2  | 20.9 | 6.1 | 4.0 | 0.03 | 0.008 |          | 0.04 | 1.13  |
| Comparative Example 13 | 0.51               | 0.53 | 0.70 | 10.2 | 22.3 | 6.0 | 4.1 | 0.98 | 0.008 |          | 1.92 | 1.04  |
| Comparative Example 14 | 0.51               | 0.31 | 0.70 | 9.0  | 20.9 | 6.1 | 3.9 | 0.73 | 0.008 |          | 1.43 | 0.82  |
| Comparative Example 15 | 0.73               | 0.59 | 0.70 | 10.5 | 22.1 | 5.9 | 4.0 | 0.88 | 0.008 |          | 1.21 | 1.32  |
| Comparative Example 16 | 0.55               | 0.38 | 0.71 | 9.0  | 21.2 | 6.1 | 6.5 | 0.71 | 0.010 |          | 1.29 | 0.93  |

## [2. Test Methods]

## [2.1. Hardness]

[0085] The hardness at ordinary temperature was measured using the C scale of a Rockwell hardness tester. Further, the hardness at 800° C. was measured at a measuring load of 5 kg using a high-temperature Vickers hardness tester.

## [2.2. Tensile Test]

[0086] A test piece having a test portion diameter of 8 mm and a test piece length of 90 mm was cut out of each material. The tensile test was performed at 800° C. using this test piece to measure the tensile strength.

## [2.3. Fatigue Test]

[0087] A test piece having a parallel portion diameter of 8 mm and a test piece length of 90 mm was cut out of each material. The Ono-type rotary bending fatigue test was performed at 800° C. using this test piece to measure 10<sup>7</sup>-cycle fatigue strength.

## [2.4. Oxidation Test]

[0088] A cylindrical test piece having a diameter of 8 mm and a length of 17 mm was prepared from each material. This test piece was continuously heated for 400 hours in an atmospheric atmosphere of 850° C., and air-cooled. The weight increase by oxidation was calculated from the difference in weight between before and after the test, and taken as the index of oxidation resistance.

## [Results]

[0089] The results thereof are shown in Tables 3 and 4. The following are known from Tables 3 and 4.

[0090] (1) In all of Examples 1 to 24, a high-temperature hardness at 800° C. of about 200 HV or more is obtained, and the specimens have sufficient high-temperature wear resistance required at the time of use in an exhaust valve application. Further, in all of Examples 1 to 24, the specimens have a tensile strength of 370 MPa or more at 800° C. These are affected by solid-solution hardening due to Mo and hardening due to the carbides (particularly, the M<sub>23</sub>C<sub>6</sub> type carbides).

[0091] (2) In all of Examples 1 to 24, the specimens have a 10<sup>7</sup>-cycle fatigue strength of 240 MPa or more, and are also

excellent in the high-temperature fatigue properties as carbide precipitation type austenitic heat resistant steels used for exhaust valve materials. The reason for this is considered to be that the grains are prevented from being coarsened due to the pinning effect of the Nb-based MX type carbonitrides, and that the size and amount of the coarse carbides (initial crystal carbides) contributing to early breakage are optimized by the Nb/C standard.

[0092] (3) Comparative Examples 1 and 2 are conventional steels. Comparative Example 1 is SUH35 and Comparative Example 2 is LV21-43. Both of them have low mechanical properties, fatigue properties and oxidation resistance at high temperature.

[0093] In both of Comparative Examples 3 and 4, the mechanical properties and fatigue strength at high temperature are low, because the Mo content is small in Comparative Example 3, and because the Nb content is excessive in Comparative Example 4.

[0094] In Comparative Examples 5 and 6 in which a part or all of Mo is substituted by W, the mechanical properties at high temperature are low, and particularly, the fatigue strength is low.

[0095] Ti and V are MX type carbonitride-forming elements similarly to Nb, and have been considered to have an effect equal to that of Nb. However, in Comparative Examples 7 and 8 in which these elements are added, the weight increase by oxidation is large, compared to Examples 1 to 24. The reason for this is considered to be that Ti and V have a strong bonding force to O compared to Nb, resulting in easy occurrence of the production of oxides. Further, in Comparative Example 8, the 10<sup>7</sup>-cycle fatigue strength is low. The reason for this is considered to be that stable and coarse carbonitrides are produced because the bonding force of Ti to C and N is strong, which causes early breakage under repeated stress. Accordingly, Ti and V cannot be alternative elements for Nb.

[0096] In Comparative Example 9, the fatigue strength is low, because the P content is excessive.

[0097] In both of Comparative Examples 10 and 11, the oxidation resistance is low, because the Si content is small in Comparative Example 10, and because the Si content is excessive in Comparative Example 11.

[0098] In both of Comparative Examples 12 and 13, the fatigue strength is low, because the Nb/C ratio is low in Comparative Example 12, and because the Nb/C ratio is excessively high in Comparative Example 13.



[0099] In Comparative Example 14, the mechanical properties and fatigue strength at high temperature are low, because the (C+N) content is small.

[0100] In Comparative Example 15, the fatigue strength is low, because the (C+N) content is excessively large.

[0101] Further, in Comparative Example 16, the fatigue strength is low, because the Mo content is excessively large.

[0102] In contrast, from the oxidation resistance test at 850° C. for 400 hours in an atmospheric atmosphere, it has been shown that the specimens in Examples 1 to 24 have good oxidation resistance in comparison with Comparative Examples 1 to 16.

[0103] Further, as shown in Tables 3 and 4, the high-temperature hardness, the fatigue properties and the oxidation resistance which are desired for exhaust valves are optimized in good levels, when the components are in the more preferred ranges thereof. Specifically, the high-temperature hardness at 800° C. is 210 or more, the 10<sup>7</sup>-cycle fatigue strength at 800° C. is 260 MPa or more, and the weight increase by oxidation after the oxidation test at 800° C. for 400 hours is 1.3 mg/cm<sup>2</sup> or less.

[0104] From the above results, it has been shown that the heat resistant steels according to the invention are excellent in the high-temperature properties and useful as materials for exhaust valves.

TABLE 3

|            | Aging<br>Hardness<br>(HRC) | High-<br>Temperature<br>Hardness<br>800° C.<br>(Hv) | Tensile<br>Strength<br>800° C.<br>(MPa) | 10 <sup>7</sup> -Cycle<br>Fatigue<br>Strength<br>800° C.<br>(MPa) | Oxidation<br>Resistance<br>800° C. ×<br>400 h<br>(mg/cm <sup>2</sup> ) |
|------------|----------------------------|---|---|---|--|
| Example 1  | 36.9                       | 215   | 416                                     | 265   | 1.29   |
| Example 2  | 37.2                       | 218   | 420                                     | 258   | 1.31   |
| Example 3  | 35.3                       | 201   | 406                                     | 250   | 1.30   |
| Example 4  | 35.4                       | 200   | 403                                     | 248   | 1.18   |
| Example 5  | 35.6                       | 201   | 404                                     | 252   | 1.38   |
| Example 6  | 36.1                       | 207   | 411                                     | 256   | 1.26   |
| Example 7  | 36.2                       | 210   | 408                                     | 251   | 1.20   |
| Example 8  | 36.4                       | 208   | 404                                     | 256   | 1.31   |
| Example 9  | 36.1                       | 208   | 407                                     | 257   | 1.29   |
| Example 10 | 35.9                       | 209   | 405                                     | 255   | 1.32   |
| Example 11 | 36.4                       | 211   | 408                                     | 258   | 1.28   |
| Example 12 | 36.6                       | 209   | 410                                     | 255   | 1.22   |
| Example 13 | 36.2                       | 203   | 404                                     | 256   | 1.24   |
| Example 14 | 37.0                       | 216   | 418                                     | 260   | 1.32   |
| Example 15 | 35.2                       | 199   | 398                                     | 243   | 1.21   |
| Example 16 | 37.1                       | 214   | 411                                     | 254   | 1.31   |
| Example 17 | 35.4                       | 202   | 401                                     | 246   | 1.32   |
| Example 18 | 36.0                       | 205   | 410                                     | 255   | 1.35   |
| Example 19 | 34.9                       | 198   | 389                                     | 243   | 1.40   |
| Example 20 | 35.3                       | 200   | 394                                     | 246   | 1.45   |
| Example 21 | 35.6                       | 203   | 405                                     | 250   | 1.28   |
| Example 22 | 36.8                       | 210   | 412                                     | 261   | 1.28   |
| Example 23 | 36.9                       | 212   | 412                                     | 264   | 1.29   |
| Example 24 | 35.6                       | 202   | 404                                     | 251   | 1.28   |

\*Heat treatment: solution treatment/1050° C. × 0.5 h, oil cooling, aging treatment/750° C. × 4 h, air cooling

\*Fatigue test: Ono-type rotary bending fatigue test (the number of rotations/3,500 rpm)

TABLE 4

|                          | Aging<br>Hardness<br>(HRC) | High-<br>Temperature<br>Hardness<br>800° C.<br>(Hv) | Tensile<br>Strength<br>800° C.<br>(MPa) | 10 <sup>7</sup> -Cycle<br>Fatigue<br>Strength<br>800° C.<br>(MPa) | Oxidation<br>Resistance<br>800° C. ×<br>400 h<br>(mg/cm <sup>2</sup> ) |
|--------------------------|----------------------------|---|---|---|--|
| Comparative<br>Example 1 | 32.0                       | 166   | 310                                     | 169   | 3.44   |

TABLE 4-continued

|                           | Aging<br>Hardness<br>(HRC) | High-<br>Temperature<br>Hardness<br>800° C.<br>(Hv) | Tensile<br>Strength<br>800° C.<br>(MPa) | 10 <sup>7</sup> -Cycle<br>Fatigue<br>Strength<br>800° C.<br>(MPa) | Oxidation<br>Resistance<br>800° C. ×<br>400 h<br>(mg/cm <sup>2</sup> ) |
|---------------------------|----------------------------|---|---|---|--|
| Comparative<br>Example 2  | 33.2                       | 167   | 321                                     | 187   | 2.48   |
| Comparative<br>Example 3  | 33.8                       | 187   | 337                                     | 207   | 1.43   |
| Comparative<br>Example 4  | 33.5                       | 189   | 352                                     | 216   | 1.65   |
| Comparative<br>Example 5  | 33.3                       | 179   | 331                                     | 181   | 1.55   |
| Comparative<br>Example 6  | 33.6                       | 181   | 335                                     | 148   | 1.78   |
| Comparative<br>Example 7  | 31.4                       | 191   | 349                                     | 215   | 2.32   |
| Comparative<br>Example 8  | 32.2                       | 193   | 339                                     | 168   | 1.98   |
| Comparative<br>Example 9  | 35.0                       | 190   | 395                                     | 198   | 1.98   |
| Comparative<br>Example 10 | 34.9                       | 192   | 380                                     | 235   | 2.31   |
| Comparative<br>Example 11 | 34.8                       | 188   | 375                                     | 230   | 2.13   |
| Comparative<br>Example 12 | 34.2                       | 188   | 370                                     | 223   | 1.35   |
| Comparative<br>Example 13 | 36.5                       | 187   | 374                                     | 220   | 1.36   |
| Comparative<br>Example 14 | 31.3                       | 160   | 305                                     | 170   | 1.37   |
| Comparative<br>Example 15 | 36.6                       | 189   | 380                                     | 215   | 1.35   |
| Comparative<br>Example 16 | 37.0                       | 220   | 415                                     | 210   | 1.36   |

\*Heat treatment: solution treatment/1050° C. × 0.5 h, oil cooling, aging treatment/750° C. × 4 h, air cooling

\*Fatigue test: Ono-type rotary bending fatigue test (the number of rotations/3,500 rpm)

[0105] Although embodiments of the invention have been described in detail above, the invention should not be construed as being limited to the embodiments set forth above in any way, and various modifications are possible without departing from the gist of the invention.

[0106] This application is based on Japanese patent application No. 2010-070720 filed Mar. 25, 2010, the entire contents thereof being hereby incorporated by reference.

[0107] The heat resistant steel for an exhaust valve according to the invention can be used in exhaust valves of various engines.

What is claimed is:

1. A heat resistant steel for an exhaust valve, comprising: more than 0.50% by mass but less than 0.80% by mass of C, more than 0.30% by mass but less than 0.60% by mass of N, 17.0% by mass or more but less than 25.0% by mass of Cr, 4.0% by mass or more but less than 12.0% by mass of Ni, 7.0% by mass or more but less than 14.0% by mass of Mn, 2.0% by mass or more but less than 6.0% by mass of Mo, more than 0.5% by mass but less than 1.5% by mass of Si, and 0.025% by mass or more but less than 1.0% by mass of Nb, with the balance consisting of Fe and unavoidable impurities, wherein a content of P contained in the unavoidable impurities is regulated to less than 0.03% by mass,



wherein a total content of C and N is from 0.85% by mass to 1.3% by mass, and

wherein a ratio of the content of Nb to the content of C is 0.05 or more but less than 1.8.

2. The heat resistant steel for an exhaust valve according to claim 1, which further comprises 0.001% by mass or more but less than 0.01% by mass of Mg and Ca in total.

3. The heat resistant steel for an exhaust valve according to claim 1, which further comprises at least one selected from the group consisting of:

0.001% by mass or more but less than 0.03% by mass of B, and

0.001% by mass or more but less than 0.1% by mass of Zr.

4. The heat resistant steel for an exhaust valve according to claim 2, which further comprises at least one selected from the group consisting of:

0.001% by mass or more but less than 0.03% by mass of B, and

0.001% by mass or more but less than 0.1% by mass of Zr.

5. The heat resistant steel for an exhaust valve according to claim 1, which further comprises 0.01% by mass or more but less than 5.0% by mass of Co.

6. The heat resistant steel for an exhaust valve according to claim 2, which further comprises 0.01% by mass or more but less than 5.0% by mass of Co.

7. The heat resistant steel for an exhaust valve according to claim 3, which further comprises 0.01% by mass or more but less than 5.0% by mass of Co.

8. The heat resistant steel for an exhaust valve according to claim 4, which further comprises 0.01% by mass or more but less than 5.0% by mass of Co.

\* \* \* \* \*