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(54) CARBURIZATION-RESISTANT METAL MATERIAL

(57) There is provided a metal material having excellent workability and metal dusting resistance, which is suitable as a raw material for cracking furnaces, reforming furnaces, heating furnaces, heat exchangers, etc. in petroleum refining, petrochemical plants, and the like.

The metal material is **characterized by** consisting of, by mass%, C: 0.08 to 0.4%, Si: 0.6 to 2.0%, Mn: 0.05 to 2.5%, P: 0.04% or less, S: 0.015% or less, Cr: 18 to 30%, Ni: 20% or higher and less than 30%, Cu: 0.5 to 10.0%, Al: 0.01 to 1%, Ti: 0.01 to 1%, N: 0.15% or less, and O (oxygen): 0.02% or less , the balance being Fe and impurities, and satisfying Expression (1).

$$C \geq 0.062\times Si + 0.033\times Cu - 0.004\times Cr + 0.043 \quad \ldots (1)$$

in which the symbol of element in Expression (1) represents the content of that element in mass%.

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Description

Technical Field

[0001] The present invention relates to a metal material that has excellent high-temperature strength and superior corrosion resistance, and in particular is used in a carburizing gas atmosphere containing hydrocarbon gas and CO gas. More particularly, it relates to a metal material having excellent weldability and metal dusting resistance, which is suitable as a raw material for cracking furnaces, reforming furnaces, heating furnaces, heat exchangers, etc. in petroleum refining, petrochemical plants, and the like.

Background Art

[0002] Demand for clean energy fuels such as hydrogen, methanol, liquid fuels (GTL: Gas to Liquids), and dimethyl ether (DME) is expected to significantly increase in the future. Therefore, a reforming apparatus for producing such a synthetic gas tends to be large in size, and an apparatus that achieves higher thermal efficiency and is suitable for mass production is demanded. Also, heat exchange for recovering exhaust is often used to enhance energy efficiency in reforming apparatuses in the conventional petroleum refining, petrochemical plants, and the like, and ammonia manufacturing apparatuses, hydrogen manufacturing apparatuses, and the like, in which raw materials such as petroleum are used.

[0003] To effectively use the heat of such a high-temperature gas, heat exchange in a temperature range of 400 to 800°C, which is relatively low, has become important, and corrosion caused by carburization of a high Cr - high Ni - Fe alloy based metal material used for reaction tubes, heat exchangers, and the like in this temperature range poses a problem.

[0004] Usually, a synthetic gas reformed in the above-described reactors, that is, a gas containing H_2, CO, CO, H_2O, and hydrocarbon such as methane comes into contact with the metal material of a reaction tube and the like at a temperature of about 1000°C or higher. In this temperature range, on the surface of the metal material, elements such as Cr and Si, which have higher oxidation tendency than Fe or Ni or the like, are oxidized selectively, and a dense film of chromium oxide or silicon oxide or the like is formed, by which corrosion is restrained. In a portion such as a heat exchange part in which the temperature is relatively low, however, the diffusion of element from the inside to the surface of metal material is insufficient. Therefore, the formation of oxide film, which achieves a corrosion restraining effect, delays, and additionally, such a gas having a composition containing hydrocarbon comes to have carburizing properties, so that carbon intrudes into the metal material through the surface thereof, and carburization occurs.

[0005] In an ethylene cracking furnace tube and the like, if carburization proceeds and a carburized layer comprising carbide of Cr or Fe or the like is formed, the volume of that portion increases. As a result, fine cracks are liable to develop, and in the worst case, the tube in use is broken. Also, if the metal surface is exposed, carbon precipitation (coking) in which metal serves as a catalyst occurs on the surface, so that the flow path area of the tube decreases and the heat-transfer characteristics degrade.

[0006] In a heating furnace tube and the like for a catalytic cracking furnace for increasing the octane value of naphtha obtained by distillation of crude oil as well, a heavily carburizing environment consisting of hydrocarbon and hydrogen is created, so that carburization and metal dusting occur.

[0007] On the other hand, in an environment in which the carburizing properties of gas in the reforming furnace tube, heat exchanger, and the like are severer, the carbide is supersaturated, and thereafter graphite precipitates directly. Therefore, a base material metal is exfoliated away and the thickness of base material decreases, that is, corrosion loss called metal dusting proceeds. Further, coking occurs with the exfoliated metal powder serving as a catalyst.

[0008] If the cracks, loss, and in-tube closure increase, an apparatus failure or the like occurs. As a result, operation may be suspended. Therefore, careful consideration must be given to the selection of material used for an apparatus member.

[0009] To prevent the aforementioned carburization and the corrosion caused by metal dusting, various countermeasures have conventionally been studied.

[0010] For example, Patent Document 1 proposes an Fe-based alloy or a Ni-based alloy containing 11 to 60% (mass%, the same shall apply hereinafter) of Cr concerning the metal dusting resistance in an atmospheric gas of 400 to 700°C containing H_2, CO, CO_2 and H_2O. Specifically, it is shown that the invention of an Fe-based alloy containing 24% or more of Cr and 35% or more of Ni, a Ni-based alloy containing 20% or more of Cr and 60% or more of Ni, and an alloy material in which Nb is further added to these alloys is excellent. However, even if a Cr or Ni content in the Fe-based alloy or the Ni-based alloy is merely increased, a sufficient carburization restraining effect cannot be achieved, so that a metal material having higher metal dusting resistance has been demanded.

[0011] Also, in a method disclosed in Patent Document 2, to prevent corrosion caused by metal dusting of a high-temperature alloy containing iron, nickel, and chromium, one or more kinds of metals of the VIII group, the IB group, the

IV group, and the V group of the element periodic table and a mixture thereof are adhered to the surface by the ordinary physical or chemical means, and the alloy is annealed in an inert atmosphere to form a thin layer having a thickness of 0.01 to 10 μm, by which the alloy surface is protected. In this case, Sn, Pb, Bi, and the like are especially effective. Although effective at the early stage, this method may lose effectiveness in that the thin layer is exfoliated in long-term use.

[0012] Patent Document 3 relates to the metal dusting resistance of a metal material in an atmospheric gas of 400 to 700°C containing H_2, CO, CO_2 and H_2O. As the result of an investigation of the interaction with carbon made from the viewpoint of solute element in iron, Patent Document 3 discloses that the addition of an element producing stable carbide in the metal material, such as Ti, Nb, V and Mo, or the alloying element in which the interaction co-factor Ω represents a positive value, such as Si, Al, Ni, Cu and Co is effective in restraining metal dusting in addition to enhancing the protecting properties of oxide film. However, the increase of Si, Al and the like sometimes leads to the decrease in hot workability and weldability. Therefore, considering the manufacturing stability and plant working, this metal material leaves room for improvement.

[0013] Next, to break off the contact of carburizing gas with the metal surface, there have been disclosed a method for oxidizing a metal material in advance and a method for performing surface treatment.

[0014] For example, Patent Document 4 and Patent Document 5 disclose a method for pre-oxidizing a low Si-based 25Cr-20Ni (HK40) heat resistant steel or a low Si-based 25Cr-35Ni heat-resisting steel at a temperature near 1000°C for 100 hours or longer in the air. Also, Patent Document 6 discloses a method for pre-oxidizing an austenitic heat-resisting steel containing 20 to 35% of Cr in the air. Further, Patent Document 7 proposes a method for improving the carburization resistance by heating a high Ni-Cr alloy in a vacuum and by forming a scale film.

[0015] Patent Document 8 proposes an austenitic alloy whose contents of Si, Cr and Ni satisfy the formula of $Si < (Cr + 0.15Ni - 18)/10$; thereby a Cr-based oxide film having high adhesiveness even in an environment, in which the alloy is subjected to a heating/cooling cycle, is formed to provide the alloy with excellent carburization resistance even in an environment in which the alloy is exposed to a corrosive gas at high temperatures. Patent Document 9 proposes an austenitic stainless steel having excellent scale exfoliation resistance even in an environment in which the steel is subjected to a heating/cooling cycle, which is produced by containing Cu and a rare earth element (Y and Ln group) therein and thereby forming a uniform oxide film having high Cr concentration in the film. Also, Patent Document 10 proposes a method for improving the carburization resistance by forming a concentrated layer of Si or Cr by performing surface treatment. Unfortunately, all of these prior arts require special heat treatment or surface treatment, and therefore they are inferior in economy. Also, since scale restoration (scale recycling) after the pre-oxidized scale or the surface treatment layer has exfoliated away is not considered, if the material surface is damaged once, the subsequent effect cannot be anticipated.

[0016] Patent Document 11 proposes a stainless steel pipe having excellent carburization resistance and containing 20 to 55% of Cr, which is produced by forming a Cr-deficient layer, which has a Cr concentration of 10% or higher and lower than the Cr concentration of the base material, on the surface of steel pipe. In this patent document, however, the improvement of weldability, which is an issue of the Cu-containing steel, has not been studied.

[0017] Besides, a method for adding H_2S into the atmospheric gas has been thought of. However, the application of this method is restricted because H_2S may remarkably decrease the activity of a catalyst used for reforming.

[0018] Patent Document 12 and Patent Document 13 propose a metal material in which the gas dissociative adsorption (gas/metal surface reaction) is restrained by containing a proper amount of one kind or two or more kinds of P, S, Sb and Bi. Since these elements segregate on the metal surface, even if the elements are not added excessively, the elements can restrain carburization and metal dusting corrosion significantly. However, since these elements segregate not only on the metal surface but also at the grain boundary of metal grainy, a problem associated with hot workability and weldability remains to be solved.

[0019] Techniques for enhancing corrosion resistance and crevice corrosion resistance by adding Cu have also been proposed. Patent Document 14 describes a technique for enhancing corrosion resistance by containing Cu, and on the other hand, for increasing the hot workability improving effect due to B by reducing S and O as far as possible. Patent Document 15 describes a technique for improving corrosion resistance and crevice corrosion resistance excellent in sulfuric acid and sulfate environments by setting the G.I. value (General Corrosion Index) represented by "$-Cr + 3.6Ni + 4.7Mo + 11.5Cu$," at 60 to 90 and by setting the C.I. value (Crevice Corrosion Index) represented by "$Cr + 0.4Ni + 2.7Mo + Cu + 18.7N$" at 35 to 50. Patent Document 16 describes a technique for improving hot workability by adding B exceeding 0.0015% while increasing a Cu content and by keeping an oxygen content low. In all of these techniques, the upper limit of a C content is restricted to a low level to avoid the decrease in corrosion resistance. Therefore, the solid-solution strengthening of C cannot be anticipated, and a sufficient high-temperature strength cannot be obtained. For this reason, these techniques are unsuitable for a metal material used at high temperatures.

[0020]

[Patent Document 1] JP9-78204A
[Patent Document 2] JP11-172473A

[Patent Document 3] JP2003-73763A
[Patent Document 4] JP53-66832A
[Patent Document 5] JP53-66835A
[Patent Document 6] JP57-43989A
[Patent Document 7] JP11-29776A
[Patent Document 8] JP2002-256398A
[Patent Document 9] JP2006-291290A
[Patent Document 10] JP2000-509105A
[Patent Document 11] JP2005-48284A
[Patent Document 12] JP2007-186727A
[Patent Document 13] JP2007-186728A
[Patent Document 14] JP1-21038A
[Patent Document 15] JP2-170946A
[Patent Document 16] JP4-346638A

Disclosure of the Invention

Problems to be Solved by the Invention

[0021] As described above, various techniques for enhancing the metal dusting resistance, the carburization resistance, and the coking resistance of metal material have been proposed conventionally. However, all of these techniques require special heat treatment and surface treatment, so that cost and labor are needed. Also, these techniques have no function of scale restoration (scale recycling) after the pre-oxidized scale or the surface treatment layer has exfoliated away. Therefore, if the material surface is damaged once, the subsequent metal dusting cannot be restrained. Also, these techniques have a problem associated with weldability of metal material.

[0022] Also, there is a method for restraining metal dusting by adding H_2S into the atmospheric gas in the tube of a reforming apparatus and manufacturing apparatus for synthetic gas as described above, not by improving the metal material itself. However, since H_2S may remarkably decrease the activity of a catalyst used for reforming hydrocarbon, the technique for restraining metal dusting by adjusting the components of atmospheric gas is merely applied limitedly.

[0023] The present invention has been made in view of the present situation, and accordingly an object thereof is to provide a metal material that has metal dusting resistance, carburization resistance, and coking resistance, and further has improved weldability due to the restraint of reaction between carburizing gas and the metal surface in an ethylene plant cracking furnace tube, a heating furnace tube of catalytic reforming furnace, a synthetic gas reforming furnace tube, and the like.

Means for Solving the Problems

[0024] The inventors analyzed a phenomenon that carbon intrudes into a metal in a molecular state, and revealed that this phenomenon progresses in an elementary process consisting of the following items (a) to (c).

[0025] (a) Gas molecules consisting of C compounds such as hydrocarbon and CO approach the metal surface.

[0026] (b) The approaching gas molecules are dissociatively adsorbed onto the metal surface.

[0027] (c) The dissociated atomic carbon intrudes into the metal and diffuses.

[0028] As the result of various studies on methods for restraining the aforementioned phenomenon, it was found that the following methods (d) and (e) are effective.

[0029] (d) Oxide scale is formed positively on the metal surface during the use of metal material, by which the contact with the metal of the gas molecules consisting of C compounds is broken off.

[0030] (e) The dissociative adsorption of the gas molecules consisting of C compounds is restrained on the metal surface.

[0031] As the result that the study on oxide scale having a breaking-off effect as in the item (d) was conducted, it was revealed that oxide scale consisting of Cr and Si acts effectively. In particular, in a carburizing gas environment such as an ethylene plant cracking furnace tube, a heating furnace tube of catalytic reforming furnace, and a synthetic gas reforming furnace tube, the partial pressure of oxygen in gas is low. Therefore, it was revealed that oxide scale consisting mainly of Cr can be formed on the gas side and oxide scale consisting mainly of Si can be formed on the metal side by containing proper amounts of Cr and Si.

[0032] On the other hand, as the result that the study was conducted from the viewpoint of dissociative adsorption as in the item (e), it was revealed that if proper amounts of noble metal elements such as Cu, Ag and Pt and elements of the VA group and the VIA group in the periodic table are added, an effect of restraining the dissociative adsorption of gas molecules consisting of C compounds is achieved. In particular, Cu is low in cost among the noble metal elements, and additionally less problems occur in melting and solidification when Cu is contained in an Fe-Ni-Cr based metal material. Therefore, the use of Cu is preferable.

[0033] It was revealed that according to the methods (d) and (e), the intrusion of carbon into the metal in the above-described elementary process of items (a) to (c) can be restrained effectively, and by applying the methods (d) and (e) simultaneously, the metal dusting resistance, the carburization resistance, and the coking resistance can be improved dramatically.

[0034] However, if an element such as Si and Cu is added, the corrosion resistance can be improved; on the other hand, the weldability is deteriorated. In particular, in a region subjected to an influence of heat cycle of rapid heating/rapid cooling caused by welding, that is in a welding heat affected zone (hereinafter, referred to as "HAZ"), cracks caused by grain boundary melting are liable to develop. Specifically, if Si, Cu or the like element segregates at the crystal grain boundary of the base material, the melting point of grain boundary lowers. At this time, when the grain boundary is subjected to welding heat cycle and is heated to a temperature just below the melting point, the grain boundary melts and is torn off by the thermal stress at the time of welding, which develops a crack. This is a HAZ crack. Therefore, in the case where the metal material is used for a welded structure, weld cracks of this kind must be restrained.

[0035] The inventors studied various methods capable of restraining HAZ cracks at the time of welding while improving the corrosion resistance by adding a considerable amount of Si or Cu. As a result, the inventors came to obtain a knowledge that the HAZ cracks can be restrained by the following methods (f) and (g).

[0036] (f) Cr-based carbides are precipitated at the crystal grain boundary of the base material by increasing the C content, by which the melting point of grain boundary is raised.

[0037] (g) The grain coarsening in the HAZ at the time when the welding heat cycle occurs is restrained by the precipitation of Cr carbides of high melting point, by which the surface area of grain boundary is increased, and thereby the segregation of Si, Cu or the like at the grain boundary is decreased.

[0038] Based on this knowledge, in a metal material containing 18 to 30% of Cr or 22 to 30% of Cr, the contents, i.e. C, Si and Cu, were changed variously, by which the HAZ crack susceptibility was studied. As a result, it was revealed that the lower limit of C content capable of preventing HAZ cracks changes according to the Si, Cu and Cr contents. Specifically, it was revealed that as the Si and Cu contents lowering the melting point of grain boundary increase, the allowable lower limit of C content is raised, and as the Cr content constituting the carbides raising the melting point of grain boundary increases, the allowable lower limit of C content is lowered.

[0039] From the results of systematical experiments in which components were changed variously, a relational expression between the C content capable of preventing HAZ cracks and the Si, Cu and Cr contents was estimated experimentally. As a result, the inventors obtained a knowledge that by satisfying Expression (1), both of excellent metal dusting resistance and excellent HAZ crack susceptibility resistance can be obtained.

[0040]

$$\mathrm{C} \geq 0.062\times\mathrm{Si} + 0.033\times\mathrm{Cu} - 0.004\times\mathrm{Cr} + 0.043 \quad \ldots (1)$$

in which the symbol of element in Expression (1) represents the content of that element in mass%.

[0041] The present invention has been completed based on the above-described knowledge, and the gists of the present invention are as described in the following items (1) to (3). Hereunder, the gists are called invention (1) to invention (3), and are sometimes generally named the present invention.

[0042] (1) A carburization resistant metal material characterized by consisting of, by mass%, C: 0.08 to 0.4%, Si: 0.6 to 2.0%, Mn: 0.05 to 2.5%, P: 0.04% or less, S: 0.015% or less, Cr: 22 to 30%, Ni: 20% or higher and less than 30%, Cu: 0.5 to 10.0%, Al: 0.01 to 1%, Ti: 0.01 to 1%, N: 0.15% or less, and O (oxygen): 0.02% or less , the balance being Fe and impurities, and satisfying Expression (1).

[0043]

$$\mathrm{C} \geq 0.062\times\mathrm{Si} + 0.033\times\mathrm{Cu} - 0.004\times\mathrm{Cr} + 0.043 \quad \ldots (1)$$

in which the symbol of element in Expression (1) represents the content of that element in mass%.

[0044] (2) A carburization resistant metal material characterized by consisting of, by mass%, C: 0.08 to 0.4%, Si: 0.6 to 2.0%, Mn: 0.05 to 2.5%, P: 0.04% or less, S: 0.015% or less, Cr: 18 to 30%, Ni: 20% or higher and less than 30%, Cu: 0.5 to 10.0%, Al: 0.01 to 1%, Ti: 0.01 to 1%, N: 0.15% or less, and O (oxygen): 0.02% or less , the balance being Fe and impurities, and satisfying Expression (1).

[0045]

$$C \geq 0.062\times Si + 0.033\times Cu - 0.004\times Cr + 0.043 \quad ... (1)$$

in which the symbol of element in Expression (1) represents the content of that element in mass%.

[0046] (3) The carburization resistant metal material described in item (1) or (2) above, characterized by further containing, by mass%, at least one kind of a component selected from at least one group of the first group to the fifth group described below:

first group: Co: 10% or less,
second group: Mo: 2.5% or less and W: 5% or less,
third group: B: 0.1% or less, V: 0.5% or less, Zr: 0.1% or less, Nb: 2% or less, and Hf: 0.5% or less,
fourth group: Mg: 0.1 % or less and Ca: 0.1% or less,
fifth group: Y: 0.15% or less, La: 0.15% or less, Ce: 0.15% or less, and Nd: 0.15% or less.

Advantages of the Invention

[0047] The metal material in accordance with the present invention has an effect of restraining reaction between carburizing gas and the metal surface, and has excellent metal dusting resistance, carburization resistance, and coking resistance. Further, since the weldability is improved, the metal material can be used for welded structure members of cracking furnaces, reforming furnaces, heating furnaces, heat exchangers, etc. in petroleum refining, petrochemical plants, and the like, and can significantly improve the durability and operation efficiency of apparatus.

[0048] In particular, the metal material in accordance with the present invention is suitable as a metal material used for reaction tubes and heat exchangers used for heat exchange in a temperature range (400 to 800°C) lower than the conventional temperature range, so that metal dusting, which poses a problem in this temperature range, can be restrained effectively.

Best Mode for Carrying Out the Invention

[0049] The reason why the composition range of metal material is restricted according to the invention is as described below. In the explanation below, the "%" representation of the content of each element means "mass%".

C: 0.08 to 0.4%

[0050] C (carbon) is one of important elements in the present invention. Carbon not only enhances the strength at high temperatures but also achieves an effect of improving the weldability in combination with chromium to form carbides. In particular, the effect is remarkable in the metal material in accordance with the present invention that has high Si and Cu contents. To sufficiently achieve this effect, 0.08% or more of C must be contained. However, if C content exceeds 0.4%, the toughness of alloy lowers extremely, so that the upper limit of C content is set at 0.4%. The C content is preferably in the range of higher than 0.1% and 0.35% or less, further preferably in the range of higher than 0.15% and 0.25% or less.

Si: 0.6 to 2.0%

[0051] Si (silicon) is one of important elements in the present invention. Since silicon has a strong affinity with oxygen, it forms Si-based oxide scale in the lower layer of a protective oxide scale layer such as Cr_2O_3, and isolates carburizing gas. This action is brought about when the Si content is 0.6% or higher. However, if the Si content exceeds 2.0%, the weldability decreases remarkably, so that the upper limit of Si content is set at 2.0%. The Si content is preferably in the range of 0.7 to 2.0%, further preferably in the range of 0.8 to 1.5%.

Mn: 0.05 to 2.5%

[0052] Mn (manganese) has deoxidizing ability and also improves the workability and weldability, so that 0.05% or more of Mn is added. Also, since manganese is an austenite-generating element, some of Ni can be replaced with Mn. However, excessive addition of Mn harms the carburizing gas isolating properties of protective oxide scale layer, so that the upper limit of Mn content is set at 2.5%. The Mn content is preferably in the range of 0.1 to 2.0%, further preferably in the range of 0.7 to 1.6%.

P: 0.04% or less

[0053] P (phosphorus) decreases the hot workability and weldability, so that the upper limit of P content is set at 0.04%. In particular, when the Si and Cu contents are high, this effect is important. The upper limit of P content is preferably 0.03%, further preferably 0.025%. However, since phosphorus acts to restrain the dissociative adsorption reaction on the metal surface of carburizing gas, it may be contained when the decrease in weldability can be permitted.

S: 0.015% or less

[0054] S (sulfur) decreases the hot workability and weldability like phosphorus, so that the upper limit of S content is set at 0.015%. In particular, when the Si and Cu contents are high, this effect is important. The upper limit of S content is preferably 0.01 %, further preferably 0.003%. However, like phosphorus, since sulfur acts to restrain the dissociative adsorption reaction on the metal surface of carburizing gas, it may be contained when the decrease in weldability can be permitted.

Cr: 18 to 30% or 22 to 30%

[0055] Cr (chromium) forms oxide scale such as Cr_2O_3 stably, and has an effect of isolating carburizing gas. Therefore, even in a severe carburizing gas environment, chromium provides sufficient carburization resistance, metal dusting resistance, and coking resistance. Also, chromium improves the weldability because it combines with carbon to form carbides. In particular, when the Si and Cu contents are high, this effect is important. To sufficiently achieve this effect, 18% or more of Cr must be contained. However, since excessive addition decreases not only the workability but also the structural stability, the upper limit of Cr is set at 30%. The lower limit of Cr content is preferably 19%, further preferably 22%, and still further preferably 23%. Also, the upper limit of Cr content is preferably 28%, further preferably 27%.

Ni: 20% or higher and less than 30%

[0056] Ni (nickel) is an element necessary for obtaining a stable austenitic micro-structure according to the Cr content, and therefore 20% or more of Ni must be contained. Also, when carbon intrudes into the metal material, nickel has a function of reducing the intrusion rate. Further, nickel acts to secure the high-temperature strength of the metal micro-structure. However, the nickel content higher than necessary may lead to cost increase and manufacturing difficulties, and may also accelerate coking and metal dusting especially in a gas environment that contains hydrocarbon. Therefore, the upper limit of Ni content is restricted to less than 30%. Preferably, the content of Ni is 22.5% or higher and less than 30%. Further preferably, the content of Ni is higher than 25% and 29.5% or less.

Cu: 0.5 to 10.0%

[0057] Cu (copper) is one of important elements in the present invention. Copper restrains reaction between carburizing gas and the metal surface, and greatly improves the metal dusting resistance and the like. Also, since copper is an austenite-generating element, some of Ni can be replaced with Cu. To achieve the metal dusting resistance improving effect, 0.5% or more of Cu must be contained. However, if Cu exceeding 10.0% is contained, the weldability decreases, so that the upper limit of Cu content is set at 10.0%. The Cu content is preferably 1.0 to 6.0%, further preferably 2.1 to 4.0%.

Al: 0.01 to 1%

[0058] Al (aluminum) is an element effective in improving the high-temperature strength. Also, aluminum has an effect as a deoxidizer because it has a high affinity with oxygen. In addition, aluminum serves as one of the constituent elements of oxide scale, and enhances the gas isolating properties. This effect can be anticipated especially in an environment in which the carburizing properties are strong. To achieve this effect, it is effective to contain 0.01% or more of Al. On the other hand, if the Al content exceeds 1%, the weldability is impaired. Therefore, the Al content is set in the range of 0.01 to 1%. The Al content is preferably in the range of 0.12 to 0.8%, further preferably in the range of 0.2 to 0.6%.

Ti: 0.01 to 1%

[0059] Ti (titanium) is an element effective in improving the high-temperature strength. Also, since titanium has an affinity with oxygen, it serves as one of the constituent elements of oxide scale, and enhances the gas isolating properties. This effect can be anticipated especially in an environment in which the carburizing properties are strong. Therefore, titanium is contained positively. To achieve this effect, it is effective to contain 0.01% or more of Ti. However, if titanium is contained excessively, the workability and weldability decrease, so that the upper limit of Ti content is set at 1%. The Ti content is preferably in the range of 0.12 to 0.8%, further preferably in the range of 0.2 to 0.6%.

N: 0.15% or less

[0060] N (nitrogen) need not necessarily be contained. If nitrogen is contained, it acts to enhance the high-temperature strength of metal material. However, if the N content exceeds 0.15%, the workability is impaired. Therefore, the upper limit of N content is set at 0.15%. The preferred upper limit thereof is 0.05%. To achieve the effect of enhancing the high-temperature strength of metal material, preferably 0.0005% or more, further preferably 0.001 % or more, of N is contained.

O: 0.02% or less

[0061] O (oxygen) is an impurity element mingled from a raw material or the like when the metal material is melted . If the O content exceeds 0.02%, large amounts of oxide inclusions exist in the metal material, so that the workability decreases, and also a flaw may occur on the surface of metal material. Therefore, the upper limit of O content is set at 0.02%.

[0062] Next, in addition to the method of invention (1) or invention (2), invention (3) relating to a metal material whose strength, ductility, and toughness are improved is explained.

[0063] Invention (3) relates to a carburization resistant metal material characterized by further containing, by mass%, at least one kind of a component selected from at least one group of the first group to the fifth group described below in a metal material specified in invention (1) or (2):

first group: Co: 10% or less,
second group: Mo: 2.5% or less and W: 5% or less,
third group: B: 0.1% or less, V: 0.5% or less, Zr: 0.1% or less, Nb: 2% or less, and Hf: 0.5% or less,
fourth group: Mg: 0.1 % or less and Ca: 0.1 % or less,
fifth group: Y: 0.15% or less, La: 0.15% or less, Ce: 0.15% or less, and Nd: 0.15% or less.

[0064] Next, these optionally added elements are explained.

First group (Co: 10% or less, by mass%)

[0065] Co (cobalt) acts to stabilize the austenite phase, so that it can replace some of Ni component. Therefore, cobalt may be contained as necessary. However, if the Co content exceeds 10%, cobalt deteriorates the hot workability. Therefore, when cobalt is contained, the content is 10% or less. From the viewpoint of hot workability, the Co content is preferably in the range of 0.01 to 5%, further preferably in the range of 0.01 to 3%.

Second group (Mo: 2.5% or less and W: 5% or less, by mass%)

[0066] Mo (molybdenum) and W (tungsten) are solid-solution strengthening elements, so that either one or both of them may be contained as necessary. However, when molybdenum is contained, molybdenum deteriorates the workability and impairs the structural stability if the content exceeds 2.5%. Therefore, when molybdenum is contained, the content is 2.5% or less. The Mo content is preferably 0.01 to 2.3%. Also, when tungsten is contained, tungsten deteriorates the workability and impairs the structural stability if the content exceeds 5%. Therefore, when tungsten is contained, the content is 5% or less. The W content is preferably 0.01 to 2.3%.

Third group (B: 0.1% or less, V: 0.5% or less, Zr: 0.1% or less, Nb: 2% or less, and Hf: 0.5% or less, by mass%)

[0067] B (boron), V (vanadium), Zr (zirconium), Nb (niobium) and Hf (hafnium) are elements effective in improving the high-temperature strength characteristics, so that one kind or two or more kinds of these elements may be contained. However, when boron is contained, boron deteriorates the weldability if the content exceeds 0.1 %. Therefore, when boron is contained, the content is 0.1% or less. The B content is preferably 0.001 to 0.05%. When vanadium is contained, vanadium deteriorates the weldability if the content exceeds 0.5%. Therefore, when vanadium is contained, the content is 0.5% or less. The V content is preferably 0.001 to 0.1%. When zirconium is contained, zirconium deteriorates the weldability if the content exceeds 0.1%. Therefore, when zirconium is contained, the content is 0.1% or less. The Zr content is preferably 0.001 to 0.05%. When niobium is contained, niobium deteriorates the weldability if the content exceeds 2%. Therefore, when niobium is contained, the content is 2% or less. The Nb content is preferably 0.001 to

0.1%. Also, when hafnium is contained, hafnium deteriorates the weldability if the content exceeds 0.5%. Therefore, when hafnium is contained, the content is 0.5% or less. The Hf content is preferably 0.001 to 0.1%.

Fourth group (Mg: 0.1 % or less and Ca: 0.1 % or less, by mass%)

[0068] Mg (magnesium) and Ca (calcium) have an effect of improving the hot workability, so that one kind or two or more kinds of these elements may be contained as necessary. However, when magnesium is contained, magnesium deteriorates the weldability if the content exceeds 0.1%. Therefore, when magnesium is contained, the content is 0.1% or less. The Mg content is preferably 0.0005 to 0.1%. Also, when calcium is contained, calcium deteriorates the weldability if the content exceeds 0.1%. Therefore, when calcium is contained, the content is 0.1 % or less. The Ca content is preferably 0.0005 to 0.1 %.

Fifth group (Y: 0.15% or less, La: 0.15% or less, Ce: 0.15% or less, and Nd: 0.15% or less, by mass%)

[0069] Y (yttrium), La (lanthanum), Ce (cerium) and Nd (neodymium) have an effect of improving the oxidation resistance, so that one kind or two or more kinds of these elements may be contained as necessary. However, when these elements are contained, these elements deteriorate the workability if the content of any one element thereof exceeds 0.15%. Therefore, when these elements are contained, the content of any one element thereof is 0.15% or less. The content is preferably 0.0005 to 0.15%.

[0070] The metal material in accordance with the present invention having a function of restraining the reaction between carburizing gas and the metal surface has only to satisfy the requirements specified in the above-described items (f) and (g) because the metal material has problems of metal dusting, carburization, and coking.

[0071] The metal material in accordance with the present invention may be formed into a required shape such as a thick plate, sheet, seamless tube, welded tube, forged product, and wire rod by means of melting, casting, hot working, cold rolling, welding, and the like. Also, the metal material may be formed into a required shape by means of powder metallurgy, centrifugal casting, and the like. The surface of the metal material having been subjected to final heat treatment may be subjected to surface treatment such as pickling, shotblasting, shotpeening, mechanical cutting, grinding, and electropolishing. Also, on the surface of the metal material in accordance with the present invention, one or two or more irregular shapes such as protruding shapes may be formed. Also, the metal material in accordance with the present invention may be combined with various kinds of carbon steels, stainless steels, Ni-based alloys, Co-based alloys, Cu-based alloys, and the like to be formed into a required shape. In this case, the joining method of the metal material in accordance with the present invention to the various kinds of steels and alloys is not subject to any restriction. For example, mechanical joining such as pressure welding and "staking" and thermal joining such as welding and diffusion treatment can be performed.

[0072] Next, the present invention is explained in more detail with reference to examples. The present invention is not limited to these examples.

[Example 1]

[0073] A metal material having a chemical composition given in Table 1 was melted by using a high-frequency heating vacuum furnace, and a metal plate having a plate thickness of 6 mm was manufactured by hot forging and hot rolling. The metal plate was subjected to solid-solution heat treatment at 1160 to 1230°C for 5 minutes, a part of which was cut to produce a test piece .

[0074] From the metal material described in Table 1, a test piece measuring 15 mm wide and 20 mm long was cut. This test piece was isothermally maintained at 650°C in a 45%CO-42.5%H_2-6.5%CO_2-6%H_2O (percent by volume) gas atmosphere. The test piece was taken out after 200 hours had elapsed, and the presence of a pit formed on the surface of test piece was examined by visual observation and by optical microscope observation. The results are summarized in Table 2.

[0075] [Table 1]

Table 1

No.	Chemical composition (mass%, balance being Fe and impurities)													Right-hand side of Expression (1)
	C	Si	Mn	P	S	Cr	Ni	Cu	Al	Ti	N	O	Others	
1	0.18	1.16	1.23	0.021	0.0010	25.4	25.2	2.91	0.49	0.57	0.01	<0.01	0.005Ca, 0.002B	0.109
2	0.18	1.16	1.21	0.021	0.0010	25.2	29.9	2.92	0.48	0.54	0.01	<0.01	0.004Ca	0.110
3	0.11	0.98	1.18	0.024	0.0012	23.8	25.3	2.75	0.36	0.47	0.01	<0.01	-	.099
4	0.16	1.07	0.15	0.019	0.0016	24.8	25.6	3.05	0.35	0.40	0.01	<0.01	-	0.111
5	0.14	0.95	1.81	0.014	0.0011	23.2	28.7	2.18	0.47	0.46	0.02	<0.01	1.9Mo	0.081
6	0.23	0.62	1.14	0.012	0.0002	27.5	24.4	4.61	0.03	0.12	0.01	<0.01	1.1W	0.117
7	0.09	0.65	0.75	0.022	0.0004	23.7	21.6	1.46	0.02	0.03	0.12	<0.01	0.11V, 1.4Co	0.030
8	0.18	1.15	0.98	0.022	0.0015	24.9	25.6	2.51	0.16	0.25	0.01	0.02 -	-	0.098
9	0.18	1.04	0.97	0.017	0.0013	23.8	26.7	1.97	0.40	0.37	0.01	<0.01	0.003Mg, 1.1Mo	0.077
10	0.16	1.13	1.04	0.005	0.0010	25.3	25.7	2.88	0.41	0.46	0.01	<0.01	0.032Nd, 0.003Ca	0.107
11	0.21	1.16	1.34	0.013	0.0010	24.9	29.3	1.44	0.32	0.33	0.02	<0.01	0.4Nb, 0.027Ce	0.063
12	0.15	0.89	1.28	0.026	0.0012	26.5	26.0	1.25	0.35	0.39	0.01	<0.01	0.2Hf, 0.003B, 0.02Zr	0.033
13	0.10	0.87	1.29	0.035	0.0083	22.4	24.8	1.21	0.39	0.75	0.02	<0.01	-	0.047
14	0.12	0.94	1.22	0.021	0.0005	23.2	29.3	0.62	0.88	0.52	0.01	<0.01	0.005Ca	0.029
15	0.16	1.44	1.17	0.009	0.0011	25.0	24.5	3.24	0.42	0.55	0.01	<0.01	0.011La, 0.023Ce	0.139
16	0.18	1.01	0.64	0.019	0.0010	28.6	22.4	2.67	0.46	0.56	0.01	<0.01	5.3Co	0.079
17	0.21	0.89	1.48	0.024	0.0032	26.3	27.5	3.32	0.41	0.51	0.01	<0.01	0.8W, 0.8Nb	0.103
18	0.27	1.16	0.82	0.024	0.0016	26.1	25.6	3.05	0.35	0.50	0.01	<0.01	-	0.111
19	0.24	1.74	1.29	0.019	0.0014	28.6	25.2	2.77	0.39	0.42	0.01	<0.01	-	0.128
20	0.12	0.61	1.16	0.022	0.0012	24.9	27.1	2.58	0.48	0.40	0.01	<0.01	-	0.066
21	0.11	0.97	1.12	0.018	0.0007	25.5	25.8	2.97	0.46	0.48	0.01	<0.01	0.035Y	0.099
22	0.15	0.96	0.52	0.022	0.0009	20.4	27.2	3.05	0.47	0.49	0.01	<0.01	-	0.122
23	0.15	0.92	0.47	0.019	0.0007	18.5	25.7	3.11	0.48	0.52	0.01	<0.01	0.3Nb	0.129
24	0.06*	0.30*	1.20	0.021	0.0014	25.2	25.8	2.97	0.50	0.54	0.01	<0.01	0.002Ca	0.059

(continued)

No.	Chemical composition (mass%, balance being Fe and impurities)													Right-hand side of Expression (1)
	C	Si	Mn	P	S	Cr	Ni	Cu	Al	Ti	N	O	Others	
25	0.12	1.62	0.87	0.020	0.0002	23.6	27.9	3.11	0.31	0.44	0.01	<0.01	-	0.152*
26	0.11	0.40*	0.63	0.017	0.0015	23.5	25.6	2.96	0.52	0.52	0.01	<0.01	0.001B, 0.02Nd	0.071
27	0.09	0.40*	0.63	0.051*	0.0004	24.3	26.7	3.00	0.82	0.43	0.01	<0.01	-	0.070
28	0.17	0.87	1.14	0.021	0.0010	25.2	24.3	0.32*	0.32	0.37	0.01	<0.01	-	0.007
29	0.21	0.68	1.21	0.018	0.0011	25.8	20.5	12.30*	0.44	0.06	0.02	0.04*	2.6W, 0.08Zr	0.382*
30	0.21	2.51*	1.27	0.019	0.0015	26.2	26.6	2.87	0.22	0.49	0.01	<0.01	0.003B, 0.003Ca	0.189
31	0.16	1.15	1.10	0.023	0.0230*	25.7	26.8	3.02	0.35	0.47	0.01	<0.01	1.3Mo	0.111
32	0.17	1.23	1.08	0.025	0.0022	25.5	25.9	2.74	<0.01*	0.56	0.01	<0.01	-	0.108
33	0.15	1.04	0.63	0.024	0.0015	26.1	25.5	2.21	0.52	<0.01*	0.01	<0.01	0.004Mg, 0.5Hf	0.07F
Note: * Mark indicates out of the scope of the present invention.														

[0076] [Table 2]

Table 2

No.	650°C, 200h, in 45%CO-42.5%H_2-6.5%CO_2-6%H_2O	650°C, 10h, in 30%C_3H_6-70%H_2 gas	Restraint weld crack test
	Presence of Pit or not	Presence of Pit or not	(Number ofHAZ cracks) / (Number of cross sections observed)
1	Absent	Absent	0/10
2	Absent	Absent	0/10
3	Absent	Absent	0/10
4	Absent	Absent	0/10
5	Absent	Absent	0/10
6	Absent	Absent	0/10
7	Absent	Absent	0/10
8	Absent	Absent	0/10
9	Absent	Absent	0/10
10	Absent	Absent	0/10
11	Absent	Absent	0/10
12	Absent	Absent	0/10
13	Absent	Absent	0/10
14	Absent	Absent	0/10
15	Absent	Absent	0/10
16	Absent	Absent	0/10
17	Absent	Absent	0/10
18	Absent	Absent	0/10
19	Absent	Absent	0/10
20	Absent	Absent	0/10
21	Absent	Absent	0/10
22	Absent	Absent	0/10
23	Absent	Absent	0/10
24	Present	Present	6/10
25	Absent	Absent	10/10
26	Present	Present	0/10
27	Absent	Present	0/10
28	Present	Present	2/10
29	Absent	Absent	5/10
30	Absent	Absent	10/10
31	Absent	Present	3/10
32	Present	Present	0/10
33	Present	Present	0/10

[0077] Table 2 indicates that, among Nos. 24 to 33 metal materials in which the chemical composition deviates from the condition specified in the present invention, Nos. 24, 26, 28, 32 and 33 metal materials had a pit formed after 200 hours had elapsed. Therefore, the metal dusting resistance is poor in a synthetic gas environment containing CO. On the other hand, in all of the metal materials specified in the present invention, no pit is formed, and therefore, these metal materials have excellent metal dusting resistance.

[Example 2]

[0078] A metal material having a chemical composition given in Table 1 was melted by using a high-frequency heating vacuum furnace, and a metal plate having a plate thickness of 6 mm was manufactured by hot forging and hot rolling. The metal plate was subjected to solid-solution heat treatment at 1160 to 1230°C for 5 minutes, a part of which was cut to produce a test piece. From the metal material described in Table 1, a test piece measuring 15 mm wide and 20 mm long was cut. This test piece was isothermally maintained at 650°C in a 30%C_3H_8-70%H_2 (percent by volume) gas atmosphere. The test piece was taken out after 10 hours had elapsed, and the presence of a pit formed on the surface of test piece was examined by visual observation and by optical microscope observation. The results are summarized in Table 2.

[0079] Table 2 indicates that, among Nos. 24 to 33 metal materials in which the chemical composition deviates from the condition specified in the present invention, Nos. 24, 26 to 28, and 31 to 33 metal materials had a pit formed in the 10-hour test. Therefore, the metal dusting resistance is poor in a hydrocarbon gas environment. On the other hand, in all of the metal materials specified in the present invention, no pit is formed, and therefore, these metal materials have excellent metal dusting resistance.

[Example 3]

[0080] A metal material having a chemical composition given in Table 1 was melted by using a high-frequency heating vacuum furnace, and two metal plates each having a plate thickness of 12 mm, a width of 50 mm, and a length of 100 mm was manufactured from each metal material by hot forging and hot rolling. The metal plates were subjected to solid-solution heat treatment at 1200°C for 5 minutes, a part of which was cut to produce a test piece.

[0081] Then, on one side in the lengthwise direction of the test piece, a V-type edge having an angle of 30 degrees and a root thickness of 1.0 mm was prepared. Thereafter, the periphery of the test pieces was restraint-welded onto a commercially available metal plate of SM400C specified in JIS G3106(2004) measuring 25 mm thick, 150 mm wide, and 150 mm long by using a covered electrode of DNiCrMo-3 specified in JIS Z3224(1999). Subsequently, multi-layer welds were made by TIG welding under a condition of heat input of 6 kJ/cm by using a TIG welding wire of YNiCrMo-3 specified in JIS Z3334(1999). After the aforementioned welding, ten test pieces for observing the sectional microstructure of joint were cut from each test piece, and the cross sections thereof were mirror polished and corroded. Thereby, the presence of cracks in the HAZ was observed by an optical microscope at x500 magnification. The results are summarized in Table 2.

[0082] Table 2 indicates that in No. 24 metal material in which the C content deviates from the condition specified in the present invention and No. 25 metal material that does not satisfy Expression (1), HAZ cracks are recognized. Also, it is indicated that for Nos. 28 to 31 metal materials in which the Cu, Si and S contents deviate from the condition specified in the present invention though the C content meets the specified condition, the HAZ crack restraining effect is small. On the other hand, in all of the metal materials specified in the present invention, HAZ cracks are not generated. Therefore, the weldability thereof is excellent.

Industrial Applicability

[0083] There is provided a metal material that has an effect of restraining reaction between carburizing gas and the metal surface, has excellent metal dusting resistance, carburization resistance, and coking resistance, and further has improved weldability. This metal material can be used for welded structure members of cracking furnaces, reforming furnaces, heating furnaces, heat exchangers, etc. in petroleum refining, petrochemical plants, and the like, and can significantly improve the durability and operation efficiency of apparatus.

Claims

1. A carburization resistant metal material **characterized by** consisting of, by mass%, C: 0.08 to 0.4%, Si: 0.6 to 2.0%, Mn: 0.05 to 2.5%, P: 0.04% or less, S: 0.015% or less, Cr: 22 to 30%, Ni: 20% or higher and less than 30%, Cu: 0.5 to 10.0%, Al: 0.01 to 1%, Ti: 0.01 to 1%, N: 0.15% or less, and O (oxygen): 0.02% or less , the balance being

Fe and impurities, and satisfying Expression (1).

$$C \geq 0.062\times Si + 0.033\times Cu - 0.004\times Cr + 0.043 \quad ... (1)$$

in which the symbol of element in Expression (1) represents the content of that element in mass%.

2. A carburization resistant metal material **characterized by** consisting of, by mass%, C: 0.08 to 0.4%, Si: 0.6 to 2.0%, Mn: 0.05 to 2.5%, P: 0.04% or less, S: 0.015% or less, Cr: 18 to 30%, Ni: 20% or higher and less than 30%, Cu: 0.5 to 10.0%, Al: 0.01 to 1%, Ti: 0.01 to 1%, N: 0.15% or less, and O (oxygen): 0.02% or less , the balance being Fe and impurities, and satisfying Expression (1).

$$C \geq 0.062\times Si + 0.033\times Cu - 0.004\times Cr + 0.043 \quad ... (1)$$

in which the symbol of element in Expression (1) represents the content of that element in mass%.

3. The carburization resistant metal material according to claim 1 or 2, **characterized by** further containing, by mass%, at least one kind of a component selected from at least one group of the first group to the fifth group described below:

first group: Co: 10% or less,
second group: Mo: 2.5% or less and W: 5% or less,
third group: B: 0.1% or less, V: 0.5% or less, Zr: 0.1% or less, Nb: 2% or less, and Hf: 0.5% or less,
fourth group: Mg: 0.1 % or less and Ca: 0.1 % or less,
fifth group: Y: 0.15% or less, La: 0.15% or less, Ce: 0.15% or less, and Nd: 0.15% or less.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/053212

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/58*(2006.01)i

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C38/00, C22C38/58

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2007-186727 A (Sumitomo Metal Industries, Ltd.), 26 July, 2007 (26.07.07), & EP 1975267 A1	1-3
A	JP 2007-186728 A (Sumitomo Metal Industries, Ltd.), 26 July, 2007 (26.07.07), & EP 1975267 A1	1-3
A	WO 2005/078148 A1 (Sumitomo Metal Industries, Ltd.), 25 August, 2005 (25.08.05), & EP 1717330 A1	1-3

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
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"&" document member of the same patent family

Date of the actual completion of the international search 19 May, 2009 (19.05.09)	Date of mailing of the international search report 26 May, 2009 (26.05.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/053212

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 59-38365 A (Kubota Tekko Kabushiki Kaisha), 02 March, 1984 (02.03.84), (Family: none)	1-3

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

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