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(54) METALLIC MATERIAL HAVING EXCELLENT METAL DUSTING RESISTANCE

(57) [Objective] To provide a metal material having excellent metal dusting resistance which is suited for using cracking furnaces, reforming furnaces, heating furnaces or heat exchangers, in petroleum refining, petrochemical plants, etc.

[Means for Solution] A metal material having excellent metal dusting resistance, **characterized in** comprising, by mass %, C: 0.01 to 0.4%, Si: 0.01 to 2.5%, Mn: 0.01 to 2.5%, Cr: 15 to 35%, Ni: 20 to 65%, Cu: 0.05 to 20%, S: not more than 0.1%, N: not more than 0.25% and O (oxygen): not more than 0.02% and the balance Fe and impurities, and also containing, by mass %, one or more selected among the elements of P: more than 0.05% and not more than 0.8%, Sb: 0.001 to 1% and Bi: 0.001 to 0.5. It may further contain one or more selected among the elements of Nd: 0.001 to 0.15%, Co: not more than 10%, Mo: not more than 3%, W: not more than 6%, Ti: not more than 1%, Nb: not more than 2%, B: not more than 0.1%, Zr: not more than 1.2%, Hf: not more than 0.5%, Mg: not more than 0.1%, Ca: not more than 0.1%, Al: not more than 0.8%, Y: not more than 0.15%, La: not more than 0.15% and Ce: not more than 0.15%.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a metal material which is high in strength at elevated temperatures, excellent in corrosion resistance and is to be used in particular in a carburizing gas atmosphere which contains hydrocarbon gases, CO gas, and in particular in a metal material having excellent metal dusting resistance, which is suited for use to cracking furnaces, reforming furnaces, heating furnaces or heat exchangers in petroleum refining or petrochemical plants.

BACKGROUND ART

[0002] The demands for such clean energy fuels as hydrogen, methanol, GTL (gas to liquids) and DME (dimethyl ether) are expected to grow markedly in the future. Therefore, the refining apparatus for producing such synthesis gases will become larger-sized and will be required to be much higher in thermal efficiency and suited for mass production. Also, the conventional refining apparatus in petroleum refining and petrochemical plants, the conventional ammonia production apparatus or hydrogen production apparatus using petroleum have been improved in functioning heat exchange with recovering exhaust heat in order to raise an energy efficiency.

[0003] In order to efficiently utilizing the heat of these high-temperature gases, heat exchange in the temperature range of 400 to 700°C, which is lower than the conventional target range, becomes more important. However, the heat exchange in the lower temperature range might cause problematic corrosion due to the carburization phenomenon in a Fe alloy containing a high Cr and high Ni, which is used for reactor tubes and heat exchangers.

[0004] Generally, synthesis gases produced in such a reaction apparatus as mentioned above, namely gases containing H_2, CO, CO_2, H_2O and hydrocarbons such as methane, are in contact with a metal material constituting reactor tubes whose temperature is around 1000°C or higher. In this temperature range, because Cr and Si have a higher oxidation tendency than Fe and Ni, Cr and Si are selectively oxidized on the metal surface to form dense oxide layers having Cr oxide and Si oxide thereon, which result in suppressing corrosion. However, the surface of those parts in a relatively low temperature within heat exchanger causes carburization due to the penetration of C from the metal surface, because the forming of the oxidized dense layers effective in suppressing corrosion are delayed due to the insufficient diffusion of Cr and Si to the metal surface from the inside, and also because the gases containing hydrocarbons are converted to carburizing ones.

[0005] When carburization proceeds to form a carburized layer of Cr carbide and Fe carbide, the volume of the carburized part increases in an ethylene cracking furnace pipe. As a result, fine cracks tend to appear and, in the worst case, the metal pipe in use will burst. Further, when the metal surface is exposed, a coking, deposition of carbon on the metal surface, is caused by the metal functioning as a catalyst, which is accompanied by decreases in the passage area in the pipe and this decreases the heat transfer characteristics.

[0006] On the other hand, the metal of the reforming furnace pipes or heat exchanger pipes in an environment where the carburizing effect of the gases is more serious is supersaturated with carbides. Then the graphite deposits and the corrosive wear, called metal dusting proceeds, and the base metal exfoliates and falls off reducing the base metals thickness. Furthermore, the metal powder formed upon exfoliation acts as a catalyst, which causes coking.

[0007] Extension of such cracking, wear and clogging in the pipe may lead to a failure of the apparatus, and, as a result, there arises the possibility that the operation has to be discontinued; therefore, due care should be exercised in selecting the manufacturing apparatus parts.

[0008] Various measures have so far been investigated to prevent such corrosion due to carburization or metal dusting.

[0009] Regarding the metal dusting resistance in a gaseous atmosphere containing H_2, CO, CO_2 and H_2O at 400 to 700°C, Patent Document 1 proposes a Fe-based alloy or Ni-based alloy containing 11-60% of Cr. More specifically, it is shown that an invention relating to a Fe-based alloy containing at least 24% of Cr and at least 35% of Ni, a Ni-based alloy containing at least 20% of Cr and at least 60% of Ni and alloy s resulting from the further addition of Nb to those alloys, produces excellent effects. However, no sufficient effect for suppressing carburization can be obtained by merely increasing the contents of Cr or Ni in Fe-based alloys or Ni-based alloys; a metal material more resistant to metal dusting is demanded.

[0010] The method disclosed in Patent Document 2 is to protect the surface of a high-temperature alloy containing iron, nickel and chromium against corrosion due to metal dusting by causing one or more metals selected from among the metals of the groups VIII, IB, IV and V of the periodic table of the elements, either solely or in admixture, to adhere to the surface by a conventional physical or chemical means, followed by annealing in an inert atmosphere to form a thin layer which has a thickness of 0.01 to 10 μm. It is alleged that Sn, Pb and Bi are especially effective in this case. However, while this method may be effective in the initial stage but, during a long period of use, the thin layer may possibly spall and accordingly, the effect may possibly be lost.

[0011] In Patent Document 3, it is disclosed that, as a result of investigations concerning the interaction with C, from the viewpoint of solute elements in iron in relation to the metal dusting resistance of metal materials in a gaseous atmosphere, containing H_2, CO, CO_2 and H_2O at 400 to 700°C, the addition of an element or elements forming stable carbides in the metal, such as Ti, Nb, V and Mo, or the addition of an alloying element or elements whose interaction auxiliary coefficient Ω shows a positive value, such as Si, Al, Ni, Cu and Co, was found to be effective in suppressing metal dusting in addition to the enhanced protective effect of the oxide layers. However, increased contents of Si and Al may lead to a decrease in hot workability and weldability in some instances; from the production stability and plant construction viewpoint, there is room for improvement.

[0012] Further, methods comprising subjecting a metal material in advance to oxidation treatment or surface treatment in order to avoid contact of the metal surface with a carburizing gas have been disclosed.

[0013] Patent Document 4 and Patent Document 5 disclose a method comprising subjecting a low Si-25%Cr-20%Ni (HK40) heat-resisting steel or a low Si-25%Cr-35Ni heat-resisting steel species to preliminary oxidation in the air at a temperature in the vicinity of 1000°C for at least 100 hours, and Patent Document 6 discloses a method comprising carrying out preliminary oxidation of an austenitic heat-resisting steel species containing 20 to 35% Cr in the air. Furthermore, Patent Document 7 proposes a method of improving the carburization resistance by heating a high Ni-Cr alloy under vacuum to cause the formation of a scale layer. In addition, Patent Document 8 proposes a method of improving the carburization resistance by forming a Si- or Cr-enriched layer by surface treatment.

[0014] Moreover, a method of suppressing metal dusting has also been contemplated which comprises adding H_2S to the gaseous atmosphere in pipes of an apparatus for reforming or producing synthesis gas, without improving the metal material itself.

[0015]

[Patent Document 1] JP-A-H09-78204
[Patent Document 2] JP-A-H11-172473
[Patent Document 3] JP-A-2003-73763
[Patent Document 4] JP-A-S53-66832
[Patent Document 5] JP-A-S53-66835
[Patent Document 6] JP-A-S57-43989
[Patent Document 7] JP-A-H11-29776
[Patent Document 8] JP-A-2000-509105

DISCLOSURE OF INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0016] As mentioned above, various technologies for increasing the metal dusting resistance of metal materials have so far been proposed. However, all of them require special heat treatment or surface treatment, which cost excessive money, and are also laborious. Further, there is no function for repairing preliminarily oxidized scales or surface-treated layers (scale regeneration) after exfoliation thereof, so that once they are damaged, the subsequent metal dusting cannot be suppressed.

[0017] As mentioned above, a method of suppressing metal dusting has also been contemplated which comprises adding H_2S to the gaseous atmosphere in the pipes of an apparatus for reforming or producing synthesis gas, without improving the metal material itself. However, there is a possibility that H_2S markedly reduces the activity of the catalyst used in reforming hydrocarbons; therefore, the technique of suppressing metal dusting by adjusting the composition of the gaseous atmosphere is applied to only to a limited extent.

[0018] Thus, in spite of various investigations made so far, a technique of sufficiently suppressing metal dusting is not available at the present time.

[0019] It is an objective of the present invention, which has been made in view of the above-discussed state of the art, to provide a metal material which has a good metal dusting resistance through the suppression of the surface reactions between the carburizing gases and the metal in cracking furnace pipes or reforming furnace pipes in ethylene plants.

MEANS FOR SOLVING THE PROBLEMS

[0020] The present inventors made various investigations in an attempt to find a method of suppressing metal dusting from occurring and, as a result, obtained the following findings (a) to (i).

[0021] (a) The occurrence of metal dusting is influenced by the protective effect of the oxide layer formed on the surface and the development of the carburized layer formed inside the oxide layer. Thus, when a crack is caused in the oxide layer or the oxide layer spalls, C penetrates from the surface site into the metal material and forms a carburized layer and, on that occasion, metal dusting occurs as a result of a change in the volume or a formation and decomposition of the carbides.

[0022] (b) Similar to the ordinary method of increasing the oxidation resistance, there is another method for enhancing the protective effect of oxide layers, the method comprising increasing the Cr content and adding an element having strong affinity for oxygen, such as Si and Al. When this method is applied, however, the penetration of C into the metal material can be prevented only for a certain period of time. Since it is impossible to realize no cracking of the oxide layer and no exfoliation thereof for a long period of time, the penetration of C into the metal material cannot be completely avoided by merely enhancing the protective effect of the oxide layer. Accordingly, adding an element or elements such as Ti, Nb, V and Mo that forms stable carbides in the metal material, in addition to the enhancement of the protective effect of the oxide layer, can lead to suppressing the penetration of C into the metal material and also reducing the rate of the penetration of C, which result in suppressing the growth of the carburized layer formed inside the oxide layer.

[0023] (c) Alternatively, adding an element or elements such as Si, Al and Ni that have little affinity for carbon, in addition to enhancement of the protective effect of the oxide layer, can lead to suppressing the growth of the carburized layer formed inside the oxide layer. The elements that have little affinity for carbon may be an element effective in increasing the activity of C solutable in Fe, in other words, an alloying element such as Co, Cu, Ag, As, P, S and N whose interaction auxiliary coefficient Ω shows a positive value. In particular, Co and Cu, when contained as alloy elements in the metal material, are effective in improving the metal dusting resistance since they will not deteriorate such properties of the metal material as hot workability and toughness and they can also be used within the content range acceptable from the cost viewpoint. However, it is difficult to use Ag from the cost viewpoint and As from the toxicity viewpoint; further, it is difficult to contain P, S and N as alloy elements since they deteriorate such properties of the metal material as hot workability and toughness.

[0024] The findings mentioned above under (a) to (c) have already been disclosed in Patent Document 3.

[0025] (d) At this time, the present inventors made further detailed investigations concerning the phenomenon of the growth of the carburized layer formed inside the oxide layer. As a result, they found the reason why the carburized layer formed inside the oxide layer can be prevented from growing due to the addition of an element having little affinity for carbon, in other words, an alloying element whose interaction auxiliary coefficient Ω shows a positive value is that the adsorption and dissociation reactions of carburizing gases on the metal surface can be suppressed and therefore the penetration of C into metal material can be markedly reduced. They also found that, in addition to noble metals such as Cu, Ag and Pt, elements of the group VA or VIA of the periodic table of the elements are excellent as alloying elements capable of suppressing the adsorption and dissociation reactions of carburizing gases on the metal surface. Further experiments revealed that, in particular, adding P, S, Sb or Bi, could produce metal materials having excellent metal dusting resistance. P, S, Sb or Bi may be added solely or in combination.

[0026] Here, since P, S, Sb and Bi are elements segregating along grain boundaries in the metal structure, it is expected that they may also segregate on the metal surface and, therefore, it is estimated that they can efficiently suppress the surface reactions between carburizing gases and the metal. Therefore, it is considered that there is no need for intentionally adding P, S, Sb and/or Bi in an excessive amount.

[0027] (e) As for P and S, they have already been mentioned in Patent Document 3 as elements having little affinity for carbon, and which, when added, can suppress the carburized layer formed inside the oxide layer from growing. Since S and P are elements segregating along grain boundaries and deteriorate such properties of the metal material as hot workability, it is considered difficult to add them as alloy elements. P and S have so far been regarded as detrimental elements which deteriorate the hot workability of metal, promoting the exfoliation of oxide scales and adversely affecting welding; therefore, it has been attempted to reduce these impurities as far as possible in the refining process and, further, to fix the trace amounts of P and S in metal material grains by adding an element capable of fixing P and S. However, as a result of the subsequent investigations and experiments, it has been revealed that P, when added at levels exceeding 0.05%, can give metal materials having excellent metal dusting resistance and that a content of P up to 0.3% is acceptable from the hot workability and weldability points of view. As for S, it is necessary, from the hot workability and weldability viewpoint, to set the upper limit to the content thereof at 0.1% and, therefore, the addition of S alone may possibly be insufficient to provide metal materials with metal dusting resistance, so that it is considered preferable to add P, Sb or Bi.

[0028] (f) As mentioned above, the suppression of the adsorption and dissociation reactions of carburizing gases on the metal surface is effective in order to increase the metal dusting resistance of metal materials, and metal materials containing one or more of P, Sb and Bi, in particular, are suited for that purpose.

[0029] (g) It is further possible, in addition to adding one or more of P, Sb and Bi as alloy elements, used in combination with the conventional technique, such as the method comprising forming protective oxide scales on the metal surface or forming a thin layer by surface treatment to enhance the protective effect of the oxide layer, or the method comprising the addition of elements such as Si or Al that have a strong affinity for oxygen. These methods can enhance the metal dusting resistance and also increase the carburization resistance and coking resistance

[0030] (h) Thus, it was found that metal materials containing one or more of P, S, Sb and Bi as alloy elements are excellent in metal dusting resistance. Various investigations were made to further provide the metal materials with workability, in particular hot workability, while maintaining the metal dusting resistance of those metal materials. As a result, it was found that the addition of an appropriate amount of Nd is effective in suppressing the grain boundary segregation of these added elements. While the function of Nd is not yet fully clear, it presumably forms compounds with P, S, Sb or Bi to thereby prevent these elements to be concentrated along grain boundaries.

[0031] (i) It was also found that, based on the metal materials having excellent metal dusting resistance as obtained by addition of one or more of alloy element such as P, S, Sb and Bi, or based on the metal materials excellent not only in metal dusting resistance but also in workability as obtained by further addition of an appropriate amount of Nd, one or more of Co, Mo, W, Ti, Nb, B, Zr, Hf, Mg, Ca, Al, Y, La and Ce can be added in order to improve the strength, ductility and toughness.

[0032] The present invention has been completed based on such findings. The gist of the present invention is shown in the following described under (1) to (3). Hereinafter, for convenience sake, the followings (1) to (3) are referred to as the inventions (1) to (3), respectively. The gist of the invention is sometimes collectively referred to as the present inventi on.

[0033] (1) A metal material having excellent metal dusting resistance, characterized in comprising, by mass %, C: 0.01 to 0.4%, Si: 0.01 to 2.5%, Mn: 0.01 to 2.5%, Cr: 15 to 35%, Ni: 20 to 65%, Cu: 0.05 to 20%, S: not more than 0.1%, N: not more than 0.25% and O (oxygen): not more than 0.02% and the balance Fe and impurities, and also containing, by mass %, one or more selected among the elements of P: more than 0.05% and not more than 0.3%, Sb: 0.001 to 1% and Bi: 0.001 to 0.5.

[0034] (2) The metal material having excellent metal dusting resistance according to (1) above, characterized in further containing, by mass %, Nd: 0.001 to 0.15%.

[0035] (3) The metal material having excellent metal dusting resistance according to (1) or (2) above, characterized in further comprising at least one element selected from at least one group among the first to sixth groups defined below.
First group: by mass %, Co: not more than 10%;
Second group: by mass %, Mo: not more than 3% and W: not more than 6%;
Third group: by mass %, Ti: not more than 1% and Nb: not more than 2%;
Fourth group: by mass %, B: not more than 0.1%, Zr: not more than 1.2% and
Hf: not more than 0.5%;
Fifth group: by mass %, Mg: not more than 0.1%, Ca: not more than 0.1% and
Al: not more than 0.8%;
Sixth group: by mass %, Y: not more than 0.15%, La: not more than 0.15% and Ce: not more than 0.15%.

EFFECTS OF THE INVENTION

[0036] The metal material according to the present invention has an effect of suppressing the surface reactions between carburizing gases and the metal and is excellent in metal dusting resistance and therefore can be used for constructing cracking furnaces, reforming furnaces, heating furnaces, heat exchangers in petroleum refining or petrochemical plants and can markedly improve the durability of apparatus and the operation efficiency.

BEST MODES FOR CARRYING OUT THE INVENTION

[0037] The reasons for restricting the content ranges for the respective elements in the metal material in accordance with the present invention are as follows. In the description that follows, the designation "%" for the content of each element means "mass % ".

[0038] C: 0.01 to 0.4%
A C content of 0.01% is necessary for securing the strength at elevated temperatures. However, at levels exceeding 0.4%, the toughness of the metal markedly deteriorates, so that the upper limit is set at 0.4%. A preferred range is 0.03 to 0.35%, and a more preferred range is 0.03 to 0.3%.

[0039] Si: 0.01 to 2.5%
Si has strong affinity for oxygen and encourages uniform formation of protective layers of oxide scales such as Cr_2O_3. Further, it forms Si-based oxide scales under the Cr_2O_3 layer, which shuts off carburizing gases. This effect is produced at content levels not lower than 0.01%. At levels exceeding 2.5%, however, the toughness decreases, so that the upper limit is set at 2.5%. A preferred range is 0.1 to 2.5%, and a more preferred range is 0.3 to 2%.

[0040] Mn: 0.01 to 2.5%
Mn is necessary for deoxidation and improvement in workability and a content level of not lower than 0.01% is necessary to obtain such effects. Since Mn is an austenite-forming element, it is also possible to replace part of Ni with Mn. However, an excessive content of Mn impairs the carburizing gas shut-off performance of the protective layer of oxide scale, so that the upper limit is set at 2.5%. A preferred Mn content range is 0.1 to 2%.

[0041] Cr: 15 to 35%

Cr stably forms oxide scales such as Cr_2O_3 and therefore it is effective in shutting off carburizing gases. For producing such effect, a content of not lower than 15% is necessary. Since an excessive content deteriorates the workability and also deteriorates the structural stability, the upper limit to the content thereof is set at 35%. A preferred range is 18 to 33%, and a more preferred range is 23 to 33%.

[0042] Ni: 20 to 65%
Ni is an element necessary for obtaining a stable austenitic structure depending on the Cr content. When C penetrates into metal, it reduces the rate of penetration. Further, it also functions in securing the strength at elevated temperatures of the metal structure. However, unnecessarily high content levels result in an increased cost and difficulty in production, therefore an appropriate content range is 20 to 65%. A preferred range is 25 to 65%, and a more preferred range is 28 to 50%.

[0043] Cu: 0.05 to 20%
Cu is one of the important elements in the practice of the present invention. Cu suppresses the surface reactions between carburizing gases and the metal and also markedly improves the metal dusting resistance. Further, since it is an austenite-forming element, it is also possible to replace part of Ni with Cu. In order to improve the metal dusting resistance, a content level not lower than 0.05% is necessary. Since, however, levels exceeding 20% tend to cause marked decreases in weldability, the upper limit is set at 20%. A preferred content range is 0.2 to 15%, and a more preferred content range is 0.5 to 10%.

[0044] S: not more than 0.1%
S is effective in suppressing the reactions between the carburizing gases and the metal. However, an excessive content markedly impairs the hot workability and weldability and, therefore, it is necessary to set the upper limit to the content thereof at 0.1%. Since S has a catalyst poisoning effect, the content thereof, in the case of a catalyst being used in the concerned plant, is desirably as low as possible; therefore, the upper limit to the S content is preferably set at 0.015%.

[0045] As mentioned above, it is necessary to set the upper limit of the S content at 0.1% and, if a catalyst is being used in the plant, the upper limit to the S content is preferably set at 0.015%. Therefore, the use of S alone may become insufficient to produce the effect of suppressing the reactions between carburizing gases and the metal in certain cases. Thus, in order to suppress the reactions between carburizing gases and the metal, it is necessary to add one or more of P, Sb and Bi, as described below.

[0046] In cases where one or more of P, Sb and Bi is to be contained in the metal material, no content of S is necessary. Therefore, when the adverse influence of S is not allowable, when the catalyst is used in the plant, the content of S is desirably as low as possible. When the adverse influence of S can be tolerated, it is of course possible to keep S contained, provided that the level thereof is not more than 0.1%; in this case, the S content is at least 0.005%, the suppressing effect of S adds to the effect of suppressing the reactions between carburizing gases and the metal as produced by the addition of one or more of P, Sb and Bi.

[0047] N: not more than 0.25%
N can be contained. When contained, it is effective in increasing the strength at elevated temperatures of the metal material. If content levels exceed 0.25%, however, it significantly impairs the workability Therefore, the upper limit to the N content is set at 0.25%. A preferred upper limit thereto is 0.2%. For obtaining the effect of enhancing the strength at elevated temperatures of the metal material, a content of at least 0.001% is preferred.

[0048] O (oxygen): not more than 0.02%
O (oxygen) is an impurity element coming from raw materials on the occasion of melting the metal material and, when oxidic inclusions occur abundantly in metal, they not only cause decreases in workability but also cause defects on the metal surface. Therefore, it is desirable to reduce the oxygen content to a level as low as possible. The O content allowable in the practice of the present invention is up to 0.02%.

[0049] P: in excess of 0.05% but not more than 0.3%
As well as Sb and Bi, P is one of the most important elements in the present invention. These elements all are active in suppressing the reactions between carburizing gases and the metal. These elements produce that effect when contained either solely or when contained in combination.

[0050] For producing this effect, it is necessary that the P content be in excess of 0.05%. Since, at excessive content levels, P markedly impairs the hot workability and weldability, it is necessary to set the upper limit of the P content to 0.3%. A preferred P content range is 0.06 to 0.25%, and a more preferred P content range is 0.085 to 0.2%.

[0051] Sb: 0.001 to 1%
As well as P and Bi, Sb is one of the most important elements in the present invention. These elements all are active in suppressing the reactions between carburizing gases and the metal. These elements produce that effect when contained solely or when contained in combination.

[0052] For producing this effect, it is necessary that the Sb content be not lower than 0.001%. Since, at excessive content levels, Sb markedly impairs the hot workability and weldability, it is necessary to set the upper limit of the Sb content to 1%. A preferred Sb content range is 0.005 to 0.8%, and a more preferred Sb content range is 0.01 to 0.7%.

[0053] Bi: 0.001 to 0.5%

As well as P and Sb, Bi is one of the most important elements in the practice of the present invention. These elements all are active in suppressing the reactions between carburizing gases and the metal. These elements produce that effect when contained either solely or when contained in combination.

[0054] For producing this effect, it is necessary that the Bi content be not lower than 0.001%. Since, at excessive content levels, Bi markedly impairs the hot workability and weldability, it is necessary to set the upper limit of the Bi content to 0.5%. A preferred Bi content range is 0.005 to 0.3%, and a more preferred Bi content range is 0.01 to 0.2%.

[0055] The invention (1) relating to a metal material having excellent metal dusting resistance by adding one or more of P, Sb and Bi have been described hereinabove.

[0056] A metal material according to the invention (2) in addition to the technique of that invention (1), which is also improved in workability, in particular in hot workability, while maintaining the metal dusting resistance obtainable according to the invention (1), is now described.

[0057] That is, the invention (2) provides a metal material having excellent metal dusting resistance which is characterized in that it is provided with workability as well by further adding Nd, as described below.

[0058] Nd: 0.001 to 0.15%

Nd is an element optionally added when it is desired that the workability of the above-mentioned metal material having excellent metal dusting resistance, be secured. For marked improvements in metal dusting resistance, it is necessary to cause one or more of P: more than 0.05% and not more than 0.3%, Sb: 0.001 to 1% and Bi: 0.001 to 0.5% to be contained, as mentioned above, whereas Nd is effective in suppressing the reduction in hot workability as resulting from the addition of these elements or further from the content of S. For producing the effect of suppressing such reduction in workability, it is necessary that the Nd content be not lower than 0.001%. At excessive content levels, however, Nd combines with O (oxygen) to form inclusions abundantly, which cause not only reductions in workability but also cause defects on the metal surface. Therefore, it is necessary to set the upper limit to the Nd content at 0.15%. The Nd content is preferably 0.005 to 0.12%, more preferably 0.01 to 0.10%.

[0059] Now, the invention (3) is described which relates to a metal material improved in strength, ductility and toughness in addition to the techniques according to the inventions (1) and (2).

[0060] The invention (3) relates to a metal material having excellent metal dusting resistance, which is characterized in further comprising at least one element selected from at least one group among the following first to sixth groups in the metal material defined in the invention (1) or invention (2).

First group: by mass %, Co: not more than 10%,
Second group: by mass %, Mo: not more than 3% and W: not more than 6%,
Third group: by mass %, Ti: not more than 1% and Nb: not more than 2%,
Fourth group: by mass %, B: not more than 0.1%, Zr: not more than 1.2% and Hf: not more than 0.5%,
Fifth group: by mass %, Mg: not more than 0.1%, Ca: not more than 0.1% and Al: not more than 0.8%,
Sixth group: by mass %, Y: not more than 0.15%, La: not more than 0.15% and Ce: not more than 0.15%.

[0061] In the following explanations, the elements to be optionally added are described in the above order.

[0062] First group (Co: not more than 10%)

Co is effective in stabilizing the austenitic phase, so that it can substitute for part of the Ni element; thus, the metal material may contain it if necessary. At content levels exceeding 10%, however, it lowers the hot workability; therefore, when Co is added, the content thereof should be not more than 10%. From the hot workability viewpoint, a preferred range is 0.01 to 5%, and a more preferred range is 0.01 to 3%.

[0063] Second group (Mo: not more than 3% and W: not more than 6%)

Both Mo and W are solid solution strengthening elements, so that one or both may be added if necessary. When Mo is added, Mo, at content levels exceeding 3%, causes a decrease in workability and also threatens the structural stability; therefore, when Mo is added, the content level thereof should be not more than 3%. The Mo content is preferably 0.01 to 2.5%. When W is added, W, at content levels exceeding 6%, causes a decrease in workability and also threatens the structural stability; therefore, when W is added, the content thereof should not be more than 6%. The W content is preferably 0.01 to 2.5%.

[0064] Third group (Ti: not more than 1% and Nb: not more than 2%)

Both Ti and Nb, at very low content levels, improve the strength at elevated temperatures as well as ductility and toughness and, when P, S or Bi coexists, they improve the creep strength and, therefore, one or both of them may be added if necessary. When Ti is added, Ti, at content levels exceeding 1%, causes a decrease in workability and weldability; therefore, when Ti is added, the content thereof should be not more than 1%. The Ti content is preferably 0.01 to 1%. When Nb is added, Nb, at content levels exceeding 2%, causes a decrease in workability and weldability; therefore, when Nb is added, the content thereof should be not more than 2%. The Nb content is preferably 0.01 to 2%.

[0065] Fourth group (B: not more than 0.1%, Zr: not more than 1.2% and Hf: not more than 0.5%)

B, Zr and Hf all strengthen grain boundaries and show the effects of improving the hot workability and high-temperature strength characteristics and, therefore, one or more of them may be added if necessary. When B is added, B, at content levels exceeding 0.1%, causes a decrease in weldability; therefore, when B is added, the content thereof should be not more than 0.1%. The B content is preferably 0.001 to 0.1%. When Zr is added, Zr, at content levels exceeding 1.2%, causes a decrease in weldability; therefore, when Zr is added, the content thereof should be not more than 1.2%. The Zr content is preferably 0.001 to 1.0%. When Hf is added, Hf, at content levels exceeding 0.5%, causes a decrease in weldability; therefore, when Hf is added, the content thereof should be not more than 0.5%. The Hf content is preferably 0.001 to 0.5%.

[0066] Fifth group (Mg: not more than 0.1%, Ca: not more than 0.1% and Al: not more than 0.8%)

Mg, Ca and Al all have the effects of improving the hot workability and, therefore, one or more of these may be added if necessary. When Mg is added, Mg, at content levels exceeding 0.1%, causes a decrease in weldability; therefore, when Mg is added, the content thereof should be not more than 0.1%. The Mg content is preferably 0.0005 to 0.1%. When Ca is added, Ca, at content levels exceeding 0.1%, causes a decrease in weldability; therefore, when Ca is added, the content thereof should be not more than 0.1%. The Ca content is preferably 0.0005 to 0.1%. When Al is added, Al, at content levels exceeding 0.8%, causes a decrease in weldability; therefore, when Al is added, the content thereof should be not more than 0.8%. The Al content is preferably 0.001 to 0.8%.

[0067] Sixth group (Y: not more than 0.15%, La: not more than 0.15% and Ce: not more than 0.15%)

Y, La and Ce all have the effects of improving the oxidation resistance and, therefore, one or more of these may be added if necessary. When these elements are added at respective content levels exceeding 0.15%, they cause decreases in workability; therefore, when they are added, the content of each of them should be not more than 0.15%. The content is preferably 0.0005 to 0.15%.

[0068] The metal material according to the present invention is excellent in metal dusting resistance, in particular in atmospheres containing 1% or more, by volume, of hydrocarbons and carbon monoxide, either solely or in total or even 25% or more, by volume, of hydrocarbons, carbon monoxide and hydrogen either solely or in combination, at a temperature not higher than 1000°C. Therefore, when weld joints made of this metal material are applied in such parts as reactor pipes or peripheral devices in heat exchanger-type hydrocarbon reformers, an exhaust heat recovering apparatus in petroleum refining, the weldability, durability and safety of the apparatus can be markedly improved.

[0069] The metal material according to the present invention can be molded into the required shapes such as plates, sheets, seamless pipes, welded pipes, forgings and wires by such means as melting, casting, hot working, cold working and welding. It can be formed into required shapes also by such means as powder metallurgy and centrifugal casting. Further, the metal surface after final heat treatment can be subjected to a surface processing treatment such as pickling, shot blasting, shot peening, mechanical grinding, grinder buffing and electrolytic grinding. The metal material according to the present invention can also be molded into irregular profiles having one or more projections on the surface. Furthermore, the metal material according to the present invention can be made into multi-layer or composite s in combination with various carbon steel, stainless steel, Ni-based alloy, Co-based alloy and Cu-based alloy species; the shaped articles manufactured from that metal material are not particularly restricted in shape or form. In this case, the method of joining the metal material according to the present invention to various steel or alloy species is not particularly restricted but includes mechanical joining such as pressure welding or caulking; it is also possible to give the metal material such shapes suited for thermal joining such as welding or diffusion treatment.

[0070] The following examples illustrate the present invention more specifically. These examples are, however, by no means limitative of the scope of the present invention.

[EXAMPLE 1]

[0071] Metal materials which have the respective chemical compositions shown in Table 1 and Table 2 were prepared by melting, using a high-frequency induction vacuum furnace and made into billets, which were subjected to hot forging and cold rolling to give the metal pipes with an outside diameter of 56 mm and a wall thickness of 6 mm. The metal pipes were subjected to a solution treatment under the conditions given below, and test specimens were prepared by cutting a part of each metal pipe. The solution heat treatment was carried out under the conditions of 1160 to 1230°C for 10 minutes. Some of the metals according to the present invention were pressure-welded to the alloy 800H to produce clad materials, and test specimens were prepared in the same manner.

[0072] [Table 1]

Table 1

Test specimen No.	Chemical composition						(mass%, the balance:Fe and impurities)						
	C	Si	Mn	Cr	Ni	Cu	S	N	O	P	Sb	Bi	Others
1	0.09	0.15	0.52	25.2	34.6	1.55	<0.001	0.11	0.02	0.024	0.45	<0.001	-
2	0.12	0.64	2.22	27.4	37.4	1.11	<0.001	0.01	<0.01	0.128	<0.001	<0.001	-
3	0.12	1.37	1.05	24.1	36.9	0.17	<0.001	0.22	<0.01	0.022	<0.001	0.013	-
4	0.11	1.68	0.43	25.2	37.6	0.55	<0.001	0.02	<0.01	0.094	<0.001	<0.001	-
5	0.11	0.36	0.74	24.5	23.8	17.50	0.009	0.05	<0.01	0.016	0.08	<0.001	-
6	0.36	1.53	0.08	23.5	32.4	0.79	<0.001	0.16	<0.01	0.055	<0.001	0.022	-
7	0.22	0.67	0.32	33.7	57.9	3.67	0.007	0.02	<0.01	0.092	0.13	0.053	-
8	0.12	1.59	0.32	25.5	38.2	1.93	<0.001	0.02	<0.01	0.114	<0.001	<0.001	-
9	0.13	1.68	0.45	25.1	37.3	1.86	<0.001	0.01	<0.01	0.081	<0.001	<0.001	-
10	0.07	1.12	0.76	23.8	33.7	2.34	<0.001	0.03	<0.01	0.275	<0.001	<0.001	-
11	0.11	0.88	0.47	24.5	35.1	7.44	<0.001	0.02	0.01	0.222	<0.001	<0.001	-
12	0.07	1.39	0.32	26.0	36.8	2.03	<0.001	0.02	0.02	0.021	0.008	<0.001	-
13	0.11	1.88	029	24.8	38.2	1.77	<0.001	0.02	<0.01	0.022	0.13	<0.001	-
14	0.15	1.64	0.22	24.7	42.5	0.59	<0.001	0.04	<0.01	0.021	0.35	<0.001	-
15	0.13	1.62	0.68	24.0	41.9	0.22	0.002	0.02	<0.01	0.033	0.78	<0.001	-
16	0.06	1.48	1.16	25.7	39.5	2.01	<0.001	0.01	<0.01	0.024	<0.001	0.007	-
17	0.10	1.66	0.44	26.3	36.3	1.77	<0.001	0.02	0.01	0.020	<0.001	0.035	-
18	0.11	1.80	0.61	25.5	36.9	4.52	<0.001	0.02	<0.01	0.028	<0.001	0.112	-
19	0.05	1.27	0.31	22.1	38.1	3.55	0.001	0.06	0.02	0.116	0.34	<0.001	-
20	0.09	1.61	0.28	27.9	38.0	10.50	0.025	0.17	<0.01	0.094	0.51	0.081	-
21	0.12	1.63	0.33	26.2	36.3	1.62	<0.001	0.02	<0.01	0.025	<0.001	<0.001	-
22	0.13	1.54	0.41	25.4	37.4	0.03	<0.001	0.03	<0.01	0.091	<0.001	<0.001	-
23	0.03	1.41	0.21	13.6	60.3	1.78	<0.001	0.01	0.01	0.026	0.88	<0.001	-

(continued)

Test specimen No.	Chemical composition					(mass%, the balance:Fe and impurities)							
	C	Si	Mn	Cr	Ni	Cu	S	N	O	P	Sb	Bi	Others
24	0.11	1.57	3.20	25.3	38.1	1.56	<0.001	0.03	<0.01	0.094	<0.001	<0.001	-

Note: Test specimen Nos. 1 to 20 show the present invention, and Nos. 21 to 24 the comparative.

[0073] [Table 2]

Table 2

Test specimen	Chemical composition									(mass%, the balance:Fe and impurities)		
No.	C	Si	Mn	Cr	Ni	Cu	S	N	O	P	Sb	Bi	Others
25	0.08	1.27	0.44	24.5	36.5	0.55	0.002	0.02	0.01	0.142	<0.001	<0.001	6.5Co
26	0.12	1.67	0.33	25.2	37.4	1.89	<0.001	0.02	<0.01	0.101	<0.001	<0.001	1.3Mo, 0.13Ti, 0.002Mg, 0.03La
27	0.15	1.45	0.32	23.8	45.3	1.38	0.010	0.02	<0.01	0.095	<0.001	<0.001	0.21Ti
28	0.11	1.37	0.37	25.6	38.5	1.13	<0.001	0.02	<0.01	0.115	023	<0.001	0.03Zr
29	0.09	1.52	0.36	24.4	35.7	1.90	0.008	0.02	<0.01	0.022	<0.001	0.09	0.004Ca
30	0.16	1.53	025	27.3	44.9	1.75	<0.001	0.01	0.01	0.021	025	<0.001	22W
31	0.11	1.43	0.22	25.6	33.0	1.34	<0.001	0.02	<0.01	0.081	0.74	0.03	1.5Mo, 0.3Nb
32	0.08	1.98	0.26	25.0	36.7	4.52	<0.001	0.02	<0.01	0.025	0.48	<0.001	3.5Co, 0.01B
33	0.12	1.55	0.16	24.6	34.6	221	<0.001	0.02	<0.01	0.093	<0.001	<0.001	2.6Mo, 0.002Mg, 0.04A1
34	0.11	1.60	0.19	24.2	32.7	3.06	<0.001	0.06	0.02	0.114	<0.001	0.08	0.5Co, 0.04La
35	0.12	1.67	0.19	24.8	40.1	8.45	0.011	0.01	<0.01	0.013	0.66	0.002	0.26Ti, 0.004Ca
36	0.14	1.19	024	25.8	37.8	1.96	<0.001	0.02	<0.01	0.125	<0.001	0.042	0.32Nb,0.02Hf
37	0.08	1.55	0.26	28.9	49.5	2.05	<0.001	0.01	<0.01	0.014	0.16	0.003	2.4Mo, 0.13Ti, 0.002Mg
38	0.06	1.57	0.16	25.5	35.5	1.68	0.009	0.02	<0.01	0.052	0.11	0.012	0.01B, 0.08Al, 0.02Ce
39	0.05	1.51	0.42	25.0	36.5	1.71	<0.001	0.02	<0.01	0.023	0.22	<0.001	0.6Co, 0.45Nb, 0.06Zr
40	0.08	0.55	0.33	21.3	30.5	1.59	<0.001	0.03	<0.01	0.121	<0.001	<0.001	0.4Al, 0.37Ti
41	0.06	0.58	1.20	25.1	20.4	0.55	<0.001	0.02	<0.01	0.112	<0.001	<0.001	0.04Y
42	0.10	1.64	0.18	23.6	35.9	0.88	<0.001	0.05	<0.01	0.081	<0.001	0.012	2.1Mo, 0.3Ti, 0.02Zr, 0.002Ca, 0.04Al 0.05Ce
43	0.06	1.60	0.47	24.8	36.6	0.45	0.009	0.177	0.01	0.090	<0.001	<0.001	0.03Ce,0.12Zr
44	0.10	1.49	0.09	26.5	39.8	3.54	<0.001	0.01	<0.01	0.144	<0.001	<0.001	1.2Co, 4.8W, 0.5Ti, 0.1Zr, 0.01Ca, 0.001Y
Note: Test specimen Nos. 25 to 44 show the present invention.													

[0074] Test specimens with a width of 15 mm and a length of 20 mm were cut out from each of the metal materials described in Table 1 and Table 2. The test specimens were maintained in a gas atmosphere containing, on the % by volume basis, 60%CO-26%H_2-11.5%CO_2-2.5%H_2O at a constant temperature of 620°C for a maximum of 1000 hours. The test specimens were taken out at timed intervals and the specimen surfaces were observed; the point of time at which pitting of a test specimen was confirmed was regarded as the pitting time of the test specimen. The results thus obtained are summarized in Table 3 and Table 4.

[0075] [Table 3]

Table 3

Test specimen No.	Remarks	In the gas of 60%CO-26%H_2-11.5%CO_2-2.5%H_2O at 620°C
		Pitting time (hour)
1		1000
2		1000
3		1000
4		>1000
5		1000
6		1000
7		1000
8		>1000
	Clad materials with Alloy800H	>1000
9		1000
10		>1000
11		>1000
12		1000
13		>1000
14		>1000
15		>1000
16		1000
17		>1000
18		>1000
19		>1000
20		>1000
21		500
22		200
23		200
24		500
Note : Test specimen Nos. 1 to 20 show the present invention, and Nos. 21 to 24 the comparative.		

[0076] [Table 4]

Table 4

Test specimen No.	Remarks	In the gas of 60%CO-26%H_2-11.5%CO_2-2.5%H_2O at 620°C
		Pitting time (hour)
25		>1000
26		>1000
27		>1000
28		>1000
29		>1000
30		>1000
31		>1000
32		>1000
33		>1000
34		>1000
35		>1000
36		>1000
37		>1000
38		>1000
39		>1000
40		>1000
41		>1000
42		>1000
43		>1000
44		>1000
Note: Test specimen Nos. 25 to 44 show the present invention.		

[0077] As seen in Table 3, the metal materials in Test Nos. 21 to 24 which failed to satisfy the chemical composition requirements specified herein gave pitting times as short as 500 hours at the longest and thus were inferior in metal dusting resistance. On the contrary, the metal materials according to the present invention in Test Nos. 1 to 20 and 25 to 44 all showed pitting times longer than 1000 hours and were excellent in metal dusting resistance, as seen in Table 3 and Table 4.

[EXAMPLE 2]

[0078] Metal materials having the respective chemical compositions shown in Table 5 were prepared by melting using a high-frequency induction vacuum furnace and made into billets, which were subjected to hot forging and cold rolling to produce metal plates with a thickness of 12 mm. The metal plates were subjected to solution heat treatment under the conditions given below, and test specimens were prepared by cutting a part of each metal plate. The solution heat treatment was carried out under the conditions of 1160 to 1230°C for 10 minutes.

[0079] [Table 5]

Table 5

Test specimen No.	Chemical composition								(mass%, the balance:Fe and impurities)					
	C	Si	Mn	Cr	Ni	Cu	Nd	S	N	O	P	Sb	Bi	Others
45	0.12	1.64	0.33	25.1	36.8	1.47	0.025	<0.001	0.03	<0.01	0.103	<0.001	<0.001	-
46	0.14	0.88	0.42	24.5	36.2	0.69	0.032	<0.001	0.01	0.01	0.021	0.35	<0.001	-
47	0.04	1.55	0.29	25.8	38.3	2.03	0.003	<0.001	0.01	0.01	0.023	<0.001	0.012	-
48	0.06	1.75	0.27	24.6	39.2	1.33	0.046	0.008	0.01	0.02	0.094	<0.001	<0.001	1.1Mo
49	0.12	1.44	0.35	21.6	32.1	14.3	0.018	0.002	0.02	0.01	0.132	<0.001	<0.001	0.4Ti
50	0.08	1.10	0.34	25.6	37.8	0.66	0.034	0.012	0.17	<0.01	0.018	<0.001	0.018	1.7W, 0.2Nb,0.003Ca
51	0.04	1.62	1.26	30.4	53.7	3.57	0.042	0.008	0.01	<0.01	0.081	<0.001	<0.001	0.04La, 0.02Zr
52	0.06	1.57	0.68	25.8	38.6	1.67	0.008	0.007	0.03	<0.01	0.032	0.46	<0.001	1.2Mo, 0.3Ti, 0.04Al, 0.9Co
53	0.04	1.26	0.24	20.4	25.3	1.48	0.032	<0.001	0.08	<0.01	0.015	0.22	0.022	0.02Ce, 0.05Hf, 0.002Mg
54	0.16	2.45	0.11	23.6	34.6	2.21	0.028	0.001	0.02	<0.01	0.091	0.06	<0.001	0.45Ti, 0.03Zr, 0.002Ca, 0.35Al
55	0.16	1.65	0.34	24.2	37.2	2.55	0.038	0.008	0.01	0.01	0.022	<0.001	0.015	0.35Nb, 1.9Mo
56	0.09	0.55	0.39	27.7	39.6	1.68	0.075	0.007	0.02	0.01	0.083	0.012	0.011	-
57	0.06	1.16	0.46	24.5	36.5	1.92	0.046	0.012	0.03	0.01	0.025	<0.001	0.009	-
58	0.03	1.46	0.16	24.9	34.6	2.46	0.024	0.009	0.02	<0.01	0.096	<0.001	<0.001	-
59	0.05	0.36	0.64	24.2	36.7	1.13	0.042	<0.001	0.01	<0.01	0.025	1.5	<0.001	-
60	0.07	0.94	0.22	24.8	36.9	1.35	0.052	<0.001	0.02	<0.01	0.432	<0.001	<0.001	-
61	0.09	1.64	0.21	25.2	37.2	1.05	0.041	<0.001	0.02	<0.01	0.011	<0.001	<0.001	-

Note : Test specimen Nos. 45 to 58 show the present invention, and Nos. 59 to 61 the comparative.

[0080] Round bar test specimens with a diameter of 10 mm and a length of 130 mm were cut out from each metal material described in Table 5. The test specimens were heated at 1200°C for 5 minutes, then cooled to 900°C at a cooling rate of 100°C/minute, then pulled at a strain rate of 5 second^{-1} and, after breakage, cooled to room temperature under He gas. Thereafter, the specimens were taken out of the apparatus and measured for a percent reduction in area. The results thus obtained are shown in Table 6. When the percent reduction in area is 60% or larger, such plates as mentioned above can be produced in hot working for mass production scale without the occurrence of cracking; therefore, when the percent reduction in area is 60% or larger, the metal material can be judged to have good quality.

[0081] Further, test specimens with a width of 15 mm and a length of 20 mm were cut out from each metal material described in Table 5. The test specimens were maintained in a gas atmosphere containing, on the % by volume basis, $60\%CO-26\%H_2-11.5\%CO_2-2.5\%H_2O$ at a constant temperature of 620°C for a maximum of 1000 hours, the test specimens were taken out at timed intervals and the specimen surfaces were observed; the point of time at which pitting of a test specimen was confirmed was regarded as the pitting time of the test specimen. The results thus obtained are shown in Table 6.

[0082] [Table 6]

Table 6

Test specimen No.	Percent reductions in area at 900°C	In the gas of $60\%CO-26\%H_2-11.5\%CO_2-2.5\%H_2O$ at 620°C
		Pitting time (hour)
45	79	>1000
46	78	1000
47	68	1000
48	77	>1000
49	73	>1000
50	76	1000
51	80	1000
52	72	>1000
53	85	1000
54	78	>1000
55	75	>1000
56	80	1000
57	80	1000
58	77	>1000
59	50	>1000
60	42	>1000
61	88	200
Note: Test specimen Nos. 45 to 58 show the present invention, and Nos. 59 to 61 the comparative.		

[0083] As seen in Table 6, the metal materials according to the present invention in Test Nos. 45 to 58 showed percent reductions in the area at 900°C of not smaller than 60%, hence satisfied the hot workability requirement and, in addition, all showed pitting times longer than 1000 hours and were excellent in metal dusting resistance.

[0084] On the other hand, as seen in Table 6, the metal materials in Test Nos. 59 and 60 which failed to satisfy the chemical composition requirements specified herein gave pitting times longer than 1000 hours and thus were excellent in metal dusting resistance but showed percent reductions in area at 900°C of lower than 60% and were therefore inferior in hot workability. Further, the metal material in Test No. 61 which also failed to satisfy the chemical composition requirements specified herein was excellent in hot workability but gave a pitting time as short as 200 hours and thus was inferior in metal dusting resistance.

INDUSTRIAL APPLICABILITY

[0085] The metal material of the present invention has the effect of suppressing the surface reactions between carburizing gases and the metal and is excellent in metal dusting resistance and therefore can be utilized for cracking furnaces, reforming furnaces, heating furnaces, heat exchangers in petroleum refining and petrochemical plants to markedly improve the durability of apparatus and the operation efficiency.

Claims

1. A metal material having excellent metal dusting resistance, **characterized in** comprising, by mass %, C: 0.01 to 0.4%, Si: 0.01 to 2.5%, Mn: 0.01 to 2.5%, Cr: 15 to 35%, Ni: 20 to 65%, Cu: 0.05 to 20%, S: not more than 0.1%, N: not more than 0.25% and O (oxygen): not more than 0.02% and the balance Fe and impurities, and also containing, by mass %, one or more selected among the elements of P: more than 0.05% and not more than 0.3%, Sb: 0.001 to 1% and Bi: 0.001 to 0.5.

2. The metal material having excellent metal dusting resistance according to Claim 1, **characterized in** further containing, by mass %, Nd: 0.001 to 0.15%.

3. The metal material having excellent metal dusting resistance according to Claim 1 or 2, **characterized in** further comprising at least one element selected from at least one group among the first to sixth groups defined below.
   First group: by mass %, Co: not more than 10%;
   Second group: by mass %, Mo: not more than 3% and W: not more than 6%;
   Third group: by mass %, Ti: not more than 1% and Nb: not more than 2%;
   Fourth group: by mass %, B: not more than 0.1%, Zr: not more than 1.2% and
   Hf: not more than 0.5%;
   Fifth group: by mass %, Mg: not more than 0.1%, Ca: not more than 0.1% and
   Al: not more than 0.8%;
   Sixth group: by mass %, Y: not more than 0.15%, La: not more than 0.15% and Ce: not more than 0.15%.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2007/050101

A. CLASSIFICATION OF SUBJECT MATTER
C22C38/00(2006.01)i, *C22C38/60*(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)
C22C38/00-38/60

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

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Kokai Jitsuyo Shinan Koho	1971-2007	Toroku Jitsuyo Shinan Koho	1994-2007

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 2003-073763 A (Sumitomo Metal Industries, Ltd.), 12 March, 2003 (12.03.03), Full text & WO 2002/103072 A1 & EP 1403392 A1 & US 6623869 B1	1-3
A	JP 2005-048284 A (Sumitomo Metal Industries, Ltd.), 24 February, 2005 (24.02.05), Full text & EP 1498508 A1 & US 2005-45251 A1	1-3
A	JP 2003-247049 A (Daido Steel Co., Ltd.), 05 September, 2003 (05.09.03), Full text (Family: none)	1-3

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

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