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(54) METHOD FOR PRODUCING METAL TUBE

(57) In this method, the inner surface of a metal pipe containing, by mass percent, 20 to 55% of Cr and 20 to 70% of Ni is subjected to mechanical treatment, the metal pipe is subjected to heat treatment such as to be held in a temperature range of 1050 to 1270°C for 0.5 to 60 minutes, and thereby an oxide scale layer consisting mainly of Cr is formed on at least the inner surface of the metal pipe. A metal pipe excellent in carburization resistance and coking resistance in a carburizing gas environment can be obtained by the method.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a method for manufacturing a metal pipe having a scale layer at least on the inner surface thereof. More particularly, the present invention relates to a method for manufacturing a metal pipe excellent in high-temperature strength and corrosion resistance. The metal pipe obtained by the present invention is suitably used as a pipe used in a carburizing gas atmosphere containing hydrocarbon gas, CO gas, and the like, such as a pyrolytic furnace pipe, a reforming furnace pipe, a heating furnace pipe, and a heat exchanger pipe in an oil refining plant, a petrochemical plant, and the like.

BACKGROUND ART

[0002] In recent years, a metal pipe containing 20 to 35 mass % of Cr and 20 to 70 mass % of Ni has been used as a pyrolytic furnace pipe, a reforming furnace pipe, a heating furnace pipe, a heat exchanger pipe, and the like used in a carburizing gas atmosphere containing hydrocarbon gas, CO gas, and the like in, for example, an oil refining plant or a petrochemical plantmass %mass %. The reason is that this metal pipe is excellent in high-temperature strength and corrosion resistance.

[0003] The inner surface of the metal pipe is exposed to a carburizing atmosphere. Therefore, an oxide scale layer consisting mainly of Cr is preferably formed on the inner surface of the metal pipe in order to prevent carburization. The oxide scale layer consisting mainly of Cr is highly dense, and has an effect of shielding the intrusion of carbon into the metal pipe. The oxide scale layer consisting mainly of Cr has a weak catalytic action against coking (deposit of carbon). Therefore, the oxide scale layer consisting mainly of Cr also has an effect of restraining coking on the surface of metal pipe. As a result, the thermal conductivity to a fluid introduced into the metal pipe can be kept for a long period of time. Therefore, for example, in the case where such a metal pipe is used as a decomposition reaction tube, the yield of a reaction product such as olefin is stabilized. This oxide scale layer consisting mainly of Cr is also formed in an environment in which the metal pipe is used. However, because carbon intrudes into the metal pipe simultaneously as described above, it is difficult to form the oxide scale layer consisting mainly of Cr uniformly on the inner surface of metal pipe. For this reason, it is effective to form the oxide scale layer consisting mainly of Cr in advance on the inner surface of metal pipe.

[0004] Patent Document 1 discloses a method in which when a stainless steel pipe containing 12 to 20 mass % of Cr and 40 mass % or less of Ni is used in a high temperature and pressure water environment, the steel pipe is subjected to heat treatment of being heated to 800 to 1100°C under an inert gas atmosphere containing 0.01 to 0.5 vol% of oxygen and being held at that temperature for 2 to 20 minutes to form a scale layer on the surface of the steel pipe in order to prevent the Ni release from the steel pipe. Patent Document 2 discloses an invention in which an austenitic stainless steel containing 14 mass % or less of Cr is heat treated at a temperature not lower than 1100°C while the CO concentration in a barrel furnace is controlled to at least 150 ppm to prevent unevenness of scale caused by abnormal oxidation of the steel surface.

[0005] Patent Document 3 discloses an invention relating to a stainless steel used in a carburizing gas atmosphere, the stainless steel having an oxide scale layer consisting mainly of Cr, in which the Cr concentration in a Cr depleted zone is at least 10% by mass, on the surface of a base metal containing 20 to 55 mass % of Cr, and further having an oxide scale layer consisting mainly of Cr, in which the Cr content is at least 50% by mass, on the outside thereof.

[0006] Patent Document 4 relates to a method for manufacturing an ethylene pyrolytic furnace pipe excellent in coking resistance, and discloses an invention in which a pipe containing 15 to 30 mass % of Cr and 15 to 50 mass % ofNi is subjected to cold working of at least 50 μm depth from the surface, and then the pipe is heated to a temperature not lower than 1100°C in an atmosphere containing less than 5 vol% of oxygen and at least 20 vol% of nitrogen.

[0007]

[Patent Document 1]: JP2-47249A
[Patent Document 2]: JP3-197617A
[Patent Document 3]: JP2005-48284A
[Patent Document 4]: JP2-263895A

DISCLOSURE OF THE INVENTION

Problems to be Solved by the Invention

[0008] In the inventions described in Patent Documents 1 and 2, because the Cr content is as low as 20 mass % or less, it is difficult to form the oxide scale layer consisting mainly of Cr.

[0009] The stainless steel having the oxide scale layer as described in Patent Document 3 is excellent in carburization resistance and coking resistance. However, in actual manufacturing, it is difficult to uniformly form the oxide scale layer consisting mainly of Cr over the entire inner surface of pipe.

[0010] The invention described in Patent Document 4 describes that a fine-grained layer of not less than No. 7 in the austenitic crystal grain size can be created to a depth of at least 30 μm from the surface with cold working and nitrogen permeating heat treatment, so that the stability of Cr_2O_3 oxide film produced during the use under an actual operation condition of 750 to 1100°C can be improved. In this method, the oxide scale produced in the nitrogen permeating heat treatment is removed, and a stable Cr_2O_3 oxide film is formed on the fine-grained layer in the actual operation. However, the formation of oxide film during the actual operation requires a long period of time. In this method, therefore, carburization or coking may occur before the stable oxide film is formed.

[0011] The present invention has been made to solve the above problems with prior arts, and accordingly an objective thereof is to provide a method for manufacturing a metal pipe having excellent resistance to carburization or coking caused by a carburizing gas by forming a uniform oxide scale layer consisting mainly of Cr on the inner surface of metal pipe.

MEANS FOR SOLVING THE PROBLEMS

[0012] The present inventors earnestly conducted studies on the method for uniformly forming the oxide scale layer consisting mainly of Cr having carburization resistance and coking resistance over the entire inner surface of metal pipe, and resultantly obtained the findings concerning the cause for the formation of nonuniform scale and the method for preventing the formation of nonuniform scale, as described below.

[0013]

(A) Various studies were carried out on the oxide scale layer formed on the inner surface of metal pipe, such as observation using an optical microscope and a scanning electron microscope (SEM), and quantitative analysis of elements using energy dispersive X-ray spectrometry (EDX). As the result, on the surface of nonuniform scale, either one or both of alkali metal and alkaline earth metal were detected.

[0014]

(B) According to the results of studies by the present inventors, it was revealed that these elements are derived from a lubricant used at the time of cold working, and the lubricant remaining on the surface of metal pipe is a cause that hinders the formation of the oxide scale layer consisting mainly of Cr.

[0015]

(C) After cold working, an attempt was made to remove the lubricant sticking to the inner surface of pipe by carrying out degreasing, cleaning, and the like method. With these methods, however, in some cases, the lubricant could not be removed sufficiently throughout the overall length of metal pipe. Accordingly, various methods were tested for removing the lubricant. As the result, it was found that by subjecting the inner surface of metal pipe to mechanical treatment such as blasting, the lubricant on the inner surface of metal pipe can be removed uniformly throughout the overall length of metal pipe.

[0016] The present invention was completed on the basis of the above-described findings, and the gist thereof is methods for manufacturing a metal pipe given in the items (1) to (4) listed below.

[0017]

(1) A method for manufacturing a metal pipe containing, by mass percent, 20 to 55% of Cr and 20 to 70% ofNi, wherein
the inner surface of the metal pipe is subjected to mechanical treatment;
the metal pipe is subjected to heat treatment such as to be held in a temperature range of 1050 to 1270°C for 0.5 to 60 minutes; and thereby
an oxide scale layer consisting mainly of Cr is formed on at least the inner surface of the metal pipe.

[0018]

(2) The method for manufacturing a metal pipe according to the above item (1), wherein the metal pipe has a chemical composition consisting of, by mass percent, C: 0.01 to 0.6%, Si: 0.1 to 5%, Mn: 0.1 to 10%, P: 0.08% or less, S: 0.05% or less, Cr: 20 to 55%, Ni: 20 to 70%, N: 0.001 to 0.25%, O (oxygen): 0.02% or less, and the balance being Fe and impurities.

[0019]

(3) The method for manufacturing a metal pipe according to the above item (2), wherein
the metal pipe further contains at least one selected from the elements, by mass percent, given in the following items (a) to (g):

(a) Cu: 5% or less
(b) Co: 5% or less
(c) At least one selected from Mo: 3% or less, W: 6% or less, and Ta: 6% or less
(d) One or two selected from Ti: 1% or less and Nb: 2% or less
(e) At least one selected from B: 0.1% or less, Zr: 0.1% or less, and Hf: 0.5% or less
(f) At least one selected from Mg: 0.1 % or less, Ca: 0.1 % or less, and Al: 1% or less
(g) At least one selected from Y: 0.15% or less and Ln group elements: 0.15% or less.

[0020]

(4) The method for manufacturing a metal pipe according to any one of the above items (1) to (3), wherein the metal pipe has a rib-shaped protrusion on the inner surface of pipe.

EFFECT OF THE INVENTION

[0021] According to the present invention, a metal pipe having an oxide scale layer consisting mainly of Cr formed uniformly on the inner surface of the metal pipe can be manufactured. The metal pipe obtained by the manufacturing method of the present invention is excellent in carburization resistance and coking resistance in a carburizing gas environment.

MODE FOR CARRYING OUT THE INVENTION

[0022] The present invention provides a method for manufacturing a metal pipe, wherein the inner surface of a metal pipe having a predetermined chemical composition is subjected to mechanical treatment; the metal pipe is subjected to heat treatment such as to be held in a temperature range of 1050 to 1270°C for 0.5 to 60 minutes; and thereby an oxide scale layer consisting mainly of Cr is formed on at least the inner surface of the metal pipe. Hereunder, the chemical composition of the metal pipe obtained by the manufacturing method of the present invention, and the mechanical treatment and heat treatment to which the metal pipe is subjected are described. In the description below, "%" relating to the content of each element means "mass %".

1. Chemical composition of metal pipe

[0023] The metal pipe obtained by the manufacturing method of the present invention must contain 20 to 55% of Cr and 20 to 70% ofNi.

Cr: 20 to 55%

[0024] Cr (Chromium) must be contained in an amount of at least 20%. The reason is that the oxide scale layer consisting mainly of Cr is formed stably on at least the inner surface of the metal pipe. However, if Cr is contained excessively, it is difficult to manufacture the metal pipe, and the micro-structure may become unstable during the use at high temperature. Therefore, the upper limit of Cr content is set to 55%. To ensure the workability and to prevent the structural stability from deteriorating, the upper limit of Cr content is preferably set to 35%. The further preferable range of Cr content is 22 to 33%.

Ni: 20 to 70%

[0025] Ni (Nickel) is an element necessary for obtaining a stable austenitic structure. Ni should be contained in an appropriate amount depending on the Cr content. Ni has an effect of reducing the intrusion rate of carbon into the metal material. This effect is achieved in the case where the Ni content is set to at least 20%. However, even if Ni is added excessively, the effect saturates, and the manufacturing cost is increased. Excessive Ni makes the manufacture of pipe difficult. Therefore, the Ni content is set to 20 to 70%. The lower limit of Ni content is preferably set to 23%, and the upper limit thereof is preferably set to 60%, further preferably 50%.

[0026] The starting material for a metal pipe for manufacturing ethylene (ethylene cracking tube) preferably contains Cr: 20 to 35% and Ni: 20 to 60%.

[0027] The metal pipe obtained by the manufacturing method of the present invention has the above-described chemical composition, and other components are not limited. However, the metal pipe preferably has a chemical composition consisting of C: 0.01 to 0.6%, Si: 0.1 to 5%, Mn: 0.1 to 10%, P: 0.08% or less, S: 0.05% or less, Cr: 20 to 55%, Ni: 20 to 70%, N: 0.001 to 0.25%, O (oxygen): 0.02% or less, the balance being Fe and impurities. Hereunder, the reasons for restricting the content of each element are described.

[0028] The impurities are components that mixedly enter from raw ore, scrap, and the like when the metal pipe is manufactured on an industrial basis, and are permitted as far as the content range does not adversely affect the present invention.

C: 0.01 to 0.6%

[0029] C (Carbon) is an element effective in ensuring the high-temperature strength. This effect is remarkable when at least 0.01% of C is contained. If the C content exceeds 0.6%, the toughness may be deteriorated extremely. Therefore, the C content is preferably set to 0.01 to 0.6%. The lower limit of C content is further preferably set to 0.02%, and the upper limit thereof is further preferably set to 0.45%, still further preferably 0.3%.

Si: 0.1 to 5%

[0030] Si (Silicon) has an effect of assisting the uniform formation of the oxide scale layer consisting mainly of Cr because the affinity of Si for oxygen is high. This effect is remarkable when at least 0.1% of Si is contained. However, if the Si content exceeds 5%, the weldability is deteriorated, and the micro-structure may become unstable. Therefore, the Si content is preferably set to 0.1 to 5%. The upper limit of Si content is preferably set to 3%, further preferably 2%, and the lower limit thereof is preferably set to 0.3%.

Mn: 0.1 to 10%

[0031] Mn (Manganese) is an element effective for deoxidation and in improving the workability. Also, because Mn is an austenite producing element, some of Ni can be replaced with Mn. To achieve these effects, at least 0.1 % of Mn is preferably contained. However, if Mn is contained excessively, the formation of the oxide scale layer consisting mainly of Cr may be hindered. Therefore, the Mn content is preferably set to 0.1 to 10%. The upper limit of Mn content is preferably set to 5%, further preferably 2%.

P: 0.08% or less

S: 0.05% or less

[0032] P (Phosphorus) and S (Sulfur) are preferably reduced in amount as far as possible because these elements segregate at the crystal grain boundary and deteriorate the hot workability. However, because the excessive reduction leads to an increase in cost, the P content is preferably 0.08% or less, and the S content is preferably 0.05% or less. The P content is further preferably set to 0.05% or less, and the S content is further preferably set to 0.03% or less. The P content is still further preferably set to 0.04% or less, and the S content is still further preferably set to 0.015% or less.

N: 0.001 to 0.25%

[0033] N (Nitrogen) is an element effective in improving the high-temperature strength. This effect is remarkable when at least 0.001 % of N is contained. However, the excessive addition of N may hinder the workability greatly. Therefore, the N content is preferably set to 0.001 to 0.25%. The upper limit ofN content is preferably set to 0.2%.

O (Oxygen): 0.02% or less

[0034] O (Oxygen) is an element existing as an impurity. If the O content exceeds 0.02%, the oxide-base inclusions in the metal material precipitate in large amounts, which decrease the workability, so that the inclusions are a cause for the surface defects of pipe. Therefore, the O content is preferably set to 0.02% or less.

[0035] The above-described metal pipe may further contain one element selected from the elements given in the items (a) to (g) listed below.

(a) Cu: 5% or less

[0036] Cu (Copper) is an element for stabilizing the austenitic phase. Cu is also an element effective in improving the high-temperature strength. Therefore, Cu may be contained in the above-described metal pipe. However, if the Cu content is excessive, the hot workability may be decreased. Therefore, if Cu is contained, the content thereof is preferably set to 5% or less. The upper limit of the Cu content is further preferably set to 3%. The above-described effects are remarkable when 0.1% or less of Cu is contained.

(b) Co: 5% or less

[0037] Co (Cobalt) is an element for stabilizing the austenitic phase. If Co is contained, some of Ni can be replaced with Co. Therefore, Co may be contained in the above-described metal pipe. However, if the Co content is excessive, the hot workability may be decreased. Therefore, if Co is contained, the content thereof is preferably set to 5% or less. The upper limit of the Co content is further preferably set to 3%. The above-described effect is remarkable when 0.1 % or less of Co is contained.

(c) At least one selected from Mo: 3% or less, W: 6% or less, and Ta: 6% or less

[0038] Mo (Molybdenum), W (Tungsten) and Ta (Tantalum) are elements contributing to solid-solution strengthening and effective in improving the high-temperature strength. Therefore, at least one selected from these elements may be contained in the above-described metal pipe. However, if the contents of these elements are excessive, the workability is deteriorated, and the structural stability may be hindered. Therefore, if at least one of these elements is contained, the Mo content is preferably set to 3% or less, and the W and Ta contents each are preferably set to 6% or less. The upper limit of each of these elements is further preferably set to 2.5%, still further preferably 2% or less. For each of these elements, the above-described effects are remarkable when at least 0.01% of each of these elements is contained. When these elements are contained compositely, the upper limit of the total amount is preferably set to 10%.

(d) One or two selected from Ti: 1% or less and Nb: 2% or less

[0039] Ti (Titanium) and Nb (Niobium) have great effects of improving the high-temperature strength, ductility, and toughness even if minute amounts of them are contained. Therefore, one or two selected from these elements may be contained in the above-described metal pipe. However, if the contents of these elements are excessive, the workability and weldability may be deteriorated. Therefore, if one or two of these elements are contained, the Ti content is preferably set to 1% or less, and the Nb content is preferably set to 2% or less. For each of these elements, the above-described effects are remarkable when at least 0.01% of each of these elements is contained. When these elements are contained compositely, the upper limit of the total amount is preferably set to 2%.

(e) At least one selected from B: 0.1% or less, Zr: 0.1% or less, and Hf: 0.5% or less

[0040] B (Boron), Zr (Zirconium) and Hf (Hafnium) are elements effective in strengthening the grain boundary and improving the hot workability and high-temperature strength. Therefore, at least one selected from these elements may be contained in the above-described metal pipe. However, if the contents of these elements are excessive, the weldability may be deteriorated. Therefore, if at least one of these elements is contained, the B and Zr contents each are preferably set to 0.1% or less, and the Hf content is preferably set to 0.5% or less. For each of these elements, the above-described effects are remarkable when at least 0.001 % of each of these elements is contained. When these elements are contained compositely, the upper limit of the total amount is preferably set to 0.3%.

(f) At least one selected from Mg: 0.1% or less, Ca: 0.1% or less, and Al: 1% or less

[0041] Mg (Magnesium), Ca (Calcium) and Al (Aluminum) are elements effective in improving the hot workability. Therefore, at least one selected from these elements may be contained in the above-described metal pipe. However, if the contents of these elements are excessive, the weldability may be deteriorated. Therefore, if at least one of these elements is contained, the Mg content is preferably set to 0.1% or less, the Ca content is preferably set to 0.1 % or less, and the Al content is preferably set to 1% or less. The upper limits of the Mg content and the Ca content each are further preferably set to 0.05%, and the upper limit of the Al content is further preferably set to 0.6%. The above-described effect is remarkable when at least 0.001% of each of Mg and Ca is contained and when at least 0.01% of Al is contained. The lower limits of the Mg content and the Ca content each are preferably set to 0.002%. When these elements are contained compositely, the upper limit of the total amount is preferably set to 0.5%.

(g) At least one selected from Y: 0.15% or less and Ln group elements: 0.15% or less

[0042] Y (Yttrium) and Ln (Lanthanide) group elements are elements effective in improving the oxidation resistance. Therefore, at least one selected from these elements may be contained in the above-described metal pipe. However, if the contents of these elements are excessive, the workability is deteriorated. Therefore, if at least one of these elements is contained, the content of each element is preferably set to 0.15% or less. The above-described effect is remarkable when at least 0.0005% of each of these elements is contained. The upper limit of the content of each of these elements is further preferably set to 0.10%. When these elements are contained compositely, the upper limit of the total amount is preferably set to 0.15%. The Ln group elements are elements of La, which is element number 57, through Lu, which is element number 71. Among the Ln group elements, at least one of La, Ce and Nd is preferably used.

2. Mechanical treatment

[0043] When the metal pipe is worked, a lubricant is used to reduce the friction between the metal pipe and a working tool. The lubricant is usually removed by degreasing and cleaning after working. However, some of the lubricant remains on the inner surface of pipe. As described above, the lubricant remaining on the surface of the metal pipe hinders the formation of the oxide scale layer consisting mainly of Cr. In the present invention, therefore, mechanical treatment is performed to remove the remaining lubricant. In some cases, in addition to the lubricant, the oxide scale produced at the time of hot pipe-making, dirt, and the like are adhered and remain on the surface of the metal pipe. Such remainder is preferably removed because it hinders the uniform formation of the oxide scale layer consisting mainly of Cr.

[0044] The mechanical treatment is treatment for enhancing the cleanliness of surface by physically removing deposits such as the lubricant remaining on the surface of metal pipe, dirt, and oxide scale. The mechanical treatment includes, for example, blasting treatment, grinding treatment (or friction treatment) for removing the deposits by bringing an abrasive into direct contact with the inner surface of metal pipe and rubbing the inner surface thereof with the abrasive, and a process for removing the deposits by spraying high-pressure water without the use of abrasive. As the blasting treatment, for example, there are available air-blasting in which blast media are propelled by compressed air, sandblasting (one kind of air-blasting) in which sand is used as the blast media, shotblasting in which blast media are propelled by the centrifugal force of an impeller made of an abrasion-resistant alloy, shotpeening (one kind of shotblasting) mainly used for giving strain to the metal surface, wet blasting, and the like. In the shotpeening, deposits on the surface can be removed simultaneously with the giving of strain. Wet blasting in which blast media are propelled together with high-pressure water can also be applied.

[0045] Although the abrasive used for the mechanical treatment is not limited, a nonmetal such as silica sand (SiO_2), alumina (Al_2O_3), zirconia (ZrO_2), boron nitride (BN), or silicon carbide (SiC), a mixture of these nonmetals or an abrasive containing these nonmetals as principal components is suitably used. Also, an abrasive consisting of a metal such as cast steel, stainless steel, metallic glass (amorphous), or Cr may be used. A nonwoven fabric or the like to which the abrasive is stuck may also be used. The shape of the abrasive is not limited, and the abrasive can take any shape such as a granular shape, a grit shape, or a powder shape. The size of the abrasive is not limited. However, in the case where the surface roughness is restrained to enhance the coking resistance, the average grain size (the average of the major axis and the minor axis) is preferably 300 μm or less, further preferably 150 μm or less.

[0046] In the case where the above-described abrasive is shot blasted onto the inner surface of pipe at a high speed, the abrasive may be shot blasted from one end or both ends of the metal pipe, or may be shot blasted while a blasting nozzle is inserted into the metal pipe and is moved in the pipe. Alternatively, the abrasive or the nonwoven fabric to which the abrasive is stuck may be brought into direct contact with the inner surface of metal pipe in a state of being dry or being wetted by a liquid and may be moved while rubbing the inner surface of metal pipe.

3. Heat treatment

[0047] The metal pipe is subjected to mechanical treatment, subsequently heat treatment, and thereby an oxide scale layer consisting mainly of Cr is formed on the inner surface of the metal pipe. If the heat treatment temperature is lower than 1050°C, the oxide scale layer formed on the surface of metal pipe is thin, so that the shielding property against the intrusion of carbon into metal material is insufficient. If the heat treatment temperature exceeds 1270°C, pores or cracks are occurred in the oxide scale layer, and the denseness is decreased, which results in a decrease in carburization resistance. Therefore, the heat treatment is performed in the temperature range of 1050 to 1270°C. The lower limit of heat treatment temperature is preferably 1120°C, further preferably 1160°C.

[0048] If the holding time of the heat treatment is shorter than 0.5 minute, the oxide scale layer consisting mainly of Cr excellent in carburization resistance cannot be formed uniformly. Even if the holding time exceeds 60 minutes, the thickness of the oxide scale layer merely increases, which leads to a decrease in productivity and an increase in energy cost. Moreover, there also arises a problem of decreased denseness of the oxide scale layer. Therefore, the holding time in the above-described temperature range is set to 0.5 to 60 minutes. The lower limit of the holding time is preferably set to 2 minutes, further preferably 5 minutes. The upper limit of the holding time is preferably set to 30 minutes, further preferably 15 minutes.

[0049] It is preferable to encourage degreasing, cleaning, pickling, and other treatment after the mechanical treatment. Even if heat treatment is performed after these kinds of treatment, the uniform formation of the oxide scale layer consisting mainly of Cr is not hindered. These kinds of treatment are especially effective in the case where there is a concern about decrease in cleanliness caused by the abrasive remaining on the inner surface of pipe. The gas atmosphere in the heat treatment may be any atmosphere in which the oxide scale layer consisting mainly of Cr can be formed. For example, the atmosphere of atmospheric gas or a gas obtained by burning a hydrocarbon fuel (LNG, butane, etc.) and air may be used. Also, the atmosphere of DX gas, NX gas, RX gas, COG (C gas), or hydrogen gas whose dew point is controlled may be used. The atmosphere of a gas obtained by mixing these gases in an arbitrary ratio may also be used.

4. Oxide scale layer consisting mainly of Cr

[0050] The oxide scale layer consisting mainly of Cr is very important from the viewpoints of carburization resistance and coking resistance. In particular, the oxide scale layer containing at least 50% of Cr has a high denseness and is excellent in shielding property against the intrusion of carbon into metal material. The oxide scale layer consisting mainly of Cr restrains coking on the surface of metal material because the catalytic action thereof against coking is weak. As a result, the thermal conductivity to a fluid in the pipe is kept for a long period of time. For example, in the case where the metal pipe is used as a decomposition reaction tube, the yield of a reaction product such as olefin is stabilized.

[0051] The Cr content in the oxide scale layer is preferably at least 80%. The oxide scale layer having a high Cr content is denser and achieves a great effect of shielding the intrusion of carbon into the metal material. The content of element in the oxide scale layer can be measured by EDX. The measurement should be made from the surface of the oxide scale layer. The determination of element is made by the fraction of the detected element excluding C (carbon), O (oxygen), and the like.

5. Others

[0052] The present invention is especially useful in manufacture of a metal pipe having a rib-shaped protrusion on the inner surface thereof. Usually, in the case of such a metal pipe having a rib-shaped protrusion on the inner surface thereof, it is thought that the metal pipe is liable to be attacked by carburizing gas, and the oxide scale is liable to peel off. According to the present invention, however, a metal pipe having high carburization resistance on the inner surface of the pipe and high repairability of the film can be obtained. A pipe having a protrusion on the inner surface thereof, a pipe having fins, and the like are cited as the pipe having the rib-shaped protrusion. The protrusion, the fin, and the like may be formed integrally with the pipe itself or may be formed by welding or the like means.

EMBODIMENTS

[0053] The present invention is explained below more specifically by way of example. The present invention is not limited to the example.

[0054] Metal materials having the chemical composition given in Table 1 were melted by using an electric furnace or a vacuum furnace to form billets. The obtained billets were hot forged and cold rolled to produce metal pipes having an outside diameter of 56 mm and a wall thickness of 6 mm. The metal pipes of specimen Nos. 1 to 10 were subjected to mechanical treatment of the conditions given in Table 2. For some metal pipes, the mechanical treatment was omitted. Then, the metal pipes were subjected to heat treatment under the conditions given in Table 2 to form oxide scale. Some metal pipes were subjected to alumina blasting as the mechanical treatment, and were not subjected to heat treatment. To evaluate uniform carburization resistance and coking resistance in the metal pipe, each of the metal pipes was cut at a total of five places at a 2-m pitch along the pipe longitudinal direction to sample ring-shaped specimens each having a width of 50 mm and specimens for observation of oxide scale (20 × 20 mm square), described later.

[Table 1]

[0055] EDX analysis was made from the surface of the specimen for observation, and the Cr content (mass %) in the oxide scale layer produced on the metal pipe was determined from the average of three measurements. On the other hand, carburization and coking tests were conducted by holding the ring-shaped specimen at 1000°C for 300 hours in the gas atmosphere of 15%CH_4-3%CO_2-82%H_2 by a volume ratio. Concerning the coking resistance, the mass of specimen was measured before and after the test to determine the increase amount due to coke deposit, and deposited coke amount per unit area (mg/cm^2) was determined. Concerning the carburization resistance, the amount of C intruding into the base metal was evaluated. That is, metal chips were sampled at a 0.5-mm pitch in the depth direction from the surface of the specimen having been tested, and the amount of C (mass %) at a depth of 0.5 to 1.0 mm and the amount of C (mass %) at a depth of 1.0 to 1.5 mm were measured by chemical analysis. After the amount of C (mass %) of base metal before testing was subtracted, the average value of both the amounts of C was defined as the amount of intruding C (mass %) at a depth of 1 mm.

[0056] The metal pipe that meets the following criteria for all items was accepted:

(1) Oxide scale layer consisting mainly of Cr:

Cr concentration in EDX analysis $\geq$ 50 mass %

(2) Carburization resistance:

Amount of intruding C at 1-mm depth $\leq$ 1.5 mass %

(3) Coking resistance:

Amount of deposited C $\leq$ 3 mg/cm^2.

These results are summarized in Table 2.

[0057] [Table 2]

[0058] The numeral in Table 2 denotes the number of specimens meeting the criteria of the above items (1), (2) and (3) per five specimens. For example, 3/5 denotes that three of five are acceptable. The present invention aims at excellent carburization resistance and coking resistance throughout the overall length of the inner surface of metal pipe. Therefore, it was determined that each of the criteria of the present invention is met when all of the five specimens are acceptable.

[0059] As shown in Table 2, in examples of Nos. 21 and 22 in which specimen No. 10 that did not meet the conditions of chemical composition defined in the present invention was used, although mechanical treatment was performed, the oxide scale layer consisting mainly of Cr could not be obtained, and both of the carburization resistance and coking resistance were poor. Of examples using specimen Nos. 2 and 3, in examples of Nos. 7 and 14 in which mechanical treatment was omitted, some of five specimens did not meet the criteria, and the carburization resistance and coking resistance in the pipe longitudinal direction were nonuniform. Of examples using specimen No. 2, in examples of No. 8 in which the heat treatment temperature was low and No. 9 in which heat treatment was not performed, carburization and coking occurred in some of the specimens.

[0060] On the other hand, for all of the specimens that used the metal pipes of specimen Nos. 1 to 9 meeting the conditions of chemical composition defined in the present invention, were subjected to mechanical treatment, and were subjected to heat treatment under the conditions defined in the present invention, all of the criteria of the above items (1), (2) and (3) were met, and the carburization resistance and coking resistance were excellent throughout the overall length in the metal pipe longitudinal direction.

INDUSTRIAL APPLICABILITY

[0061] According to the present invention, a metal pipe having an oxide scale layer consisting mainly of Cr formed uniformly on the inner surface of the metal pipe can be manufactured, so that the metal pipe is excellent in carburization resistance and coking resistance in a carburizing gas environment. For this reason, the metal pipe obtained by the present invention is suitably used especially as a pipe used in a carburizing gas atmosphere containing hydrocarbon gas, CO gas, and the like, such as a pyrolytic furnace pipe, a reforming furnace pipe, a heating furnace pipe, and a heat exchanger pipe in an oil refining plant, a petrochemical plant, and the like.

Claims

1. A method for manufacturing a metal pipe containing, by mass percent, 20 to 55% of Cr and 20 to 70% ofNi, wherein
the inner surface of the metal pipe is subjected to mechanical treatment;
the metal pipe is subjected to heat treatment such as to be held in a temperature range of 1050 to 1270°C for 0.5 to 60 minutes; and thereby
an oxide scale layer consisting mainly of Cr is formed on at least the inner surface of the metal pipe.

2. The method for manufacturing a metal pipe according to claim 1, wherein the metal pipe has a chemical composition consisting of, by mass percent, C: 0.01

to 0.6%, Si: 0.1 to 5%, Mn: 0.1 to 10%, P: 0.08% or less, S: 0.05% or less, Cr: 20 to 55%, Ni: 20 to 70%, N: 0.001 to 0.25%, O (oxygen): 0.02% or less, the balance being Fe and impurities.

3. The method for manufacturing a metal pipe according to claim 2, wherein
the metal pipe further contains at least one selected from the elements, by mass percent, given in the following items (a) to (g):

(a) Cu: 5% or less
(b) Co: 5% or less
(c) At least one selected from Mo: 3% or less, W: 6% or less, and Ta: 6% or less
(d) One or two selected from Ti: 1% or less and Nb: 2% or less
(e) At least one selected from B: 0.1% or less, Zr: 0.1% or less, and Hf: 0.5% or less
(f) At least one selected from Mg: 0.1% or less, Ca: 0.1% or less, and Al: 1% or less
(g) At least one selected from Y: 0.15% or less and Ln group elements: 0.15% or less.

4. The method for manufacturing a metal pipe according to any one of claims 1 to 3, wherein the metal pipe has a rib-shaped protrusion on the inner surface of pipe.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/052165

A. CLASSIFICATION OF SUBJECT MATTER

C23C8/10(2006.01)i, *B21C37/20*(2006.01)i, *B21C37/22*(2006.01)i, *B21C37/30*(2006.01)i, *C21D7/06*(2006.01)i, *C21D9/08*(2006.01)i, *C22C19/05*(2006.01)i, *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)

C23C8/00-8/80, B21C37/20, B21C37/22, B21C37/30, C21D7/06, C21D9/08, C22C19/05, C22C38/00, C22C38/60

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	1996-2010
Kokai Jitsuyo Shinan Koho	1971-2010	Toroku Jitsuyo Shinan Koho	1994-2010

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.
X Y	JP 2002-121630 A (Sumitomo Metal Industries, Ltd.), 26 April 2002 (26.04.2002), claims; paragraphs [0001], [0006], [0007], [0016], [0027], [0046], [0053] to [0057], [0065] & US 6482528 B2 & EP 1312688 A1 & WO 2002/014566 A1	1 2-4
X Y	JP 2007-284704 A (Sumitomo Metal Industries, Ltd.), 01 November 2007 (01.11.2007), claims; paragraphs [0001], [0048] to [0050], [0078] to [0080], [0084] & EP 2009133 A1 & WO 2007/119706 A1 & CA 2648711 A	1 2-4

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

*	Special categories of cited documents:
"A"	document defining the general state of the art which is not considered to be of particular relevance
"E"	earlier application or patent but published on or after the international filing date
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"O"	document referring to an oral disclosure, use, exhibition or other means
"P"	document published prior to the international filing date but later than the priority date claimed
"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&"	document member of the same patent family

Date of the actual completion of the international search 02 March, 2010 (02.03.10)	Date of mailing of the international search report 09 March, 2010 (09.03.10)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/052165

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 01-259156 A (Sumitomo Metal Industries, Ltd.), 16 October 1989 (16.10.1989), claims; page 3, upper left column, lines 3 to 12 (Family: none)	4
Y	JP 01-279741 A (Osaka Gas Co., Ltd.), 10 November 1989 (10.11.1989), page 1, lower right column, lines 1 to 15 (Family: none)	4
Y	JP 03-039461 A (Sumitomo Metal Industries, Ltd.), 20 February 1991 (20.02.1991), claims; page 1, lower right column, line 18 to page 2, upper left column, line 7 (Family: none)	4

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

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- JP 3197617 A **[0007]**
- JP 2005048284 A **[0007]**
- JP 2263895 A **[0007]**