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(54) HEAT-RESISTANT PIPE HAVING ALUMINA BARRIER LAYER

HITZEBESTÄNDIGES ROHR MIT ALUMINIUMSPERRSCHICHT

TUYAU RÉSISTANT À LA CHALEUR COMPORTANT UNE COUCHE BARRIÈRE D’ALUMINE

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(56) References cited:
EP-A1- 1 717 330
WO-A1-2004/067788
WO-A1-2005/078148
WO-A1-2012/054377
WO-A2-01/94664
JP-A- H01 153 887
JP-A- H05 195 161
JP-A- 2003 535 976
JP-A- 2013 227 655
JP-A- 2014 501 620
US-A1- 2011 308 669

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Description

Technical Field

[0001] The present invention relates to a heat-resistant tube having an alumina barrier layer, and more specifically to a heat-resistant tube having an alumina barrier layer with a stable structure on the tube inner surface.

Background Art

[0002] An austenite-based heat-resistant alloy having excellent high-temperature strength is used in heat-resistant tubes to be exposed to a high-temperature atmosphere, such as reaction tubes for production of ethylene or propylene and decomposition tubes used for thermal decomposition of hydrocarbons.

[0003] While this type of austenite-based heat-resistant alloy is used in a high-temperature atmosphere, a portion of components (e.g., Cr, Si, Al, and Fe) contained in the base material is oxidized, and thus a metal oxide layer is formed on the surface. This oxide layer serves as a barrier and suppresses further oxidation of the base material.

[0004] However, when the metal oxide layer made of Cr-oxides (mainly constituted by Cr_2O_3 (chromia)) is formed, a function for preventing the entry of oxygen and carbon is insufficient due to the oxides having a low denseness, thus causing the internal oxidation of the base material in a high-temperature atmosphere and the thickening of the oxide layer. Moreover, the thickened oxide layer is likely to be removed during repeated cycles of heating and cooling. Even in a case where the oxide layer is not removed, since the function for preventing the entry of oxygen and carbon from an outside atmosphere is insufficient, there is a disadvantageous situation in which oxygen and carbon pass through the oxide layer and cause the internal oxidation or carburization of the base material.

[0005] For this reason, an attempt has been made to increase the Al content compared with that in a general austenite-based heat-resistant alloy for the purpose of forming a useful oxide layer made of alumina (Al_2O_3) in order to prevent carburization or internal oxidation. It is known that Al-oxides have a high denseness, which makes it difficult for oxygen and carbon to pass therethrough, and therefore, it is proposed to form an oxide layer including alumina (Al_2O_3) as a main component (i.e., "alumina barrier layer") on the tube inner surface (see Patent Documents 1 and 2, for example).

[0006] Patent Document 3 discloses a coated stainless steel tube, the steel tube consisting of 18-38% Cr, 18-48 Ni, the balance being Fe and alloying additives, usable for thermal decomposition of hydrocarbons such as ethane. An inner protective coating comprises predominantly alumina.

[0007] Patent Document 4 discloses a bimetallic tube for the transport of hydrocarbon feedstocks through the radiant coils of refinery process furnaces, comprising an outer tube layer being formed from carbon steels or low chromium steels, an inner tube layer being formed from alumina forming bulk alloy and an oxide layer formed on the surface of the inner tube layer, wherein the oxide layer comprises alumina.

Citation List

Patent Document

[0008]

[Patent Document 1]: JP S52-78612A
[Patent Document 2]: JP S57-39159A
[Patent Document 3]: WO 01/94664 A2
[Patent Document 4]: WO 2012/054377 A1

Summary of Invention

Technical Problem

[0009] As a result of increasing the Al content, a barrier function can be expected to be improved by the alumina barrier layer. However, Al is a ferrite-forming element, and therefore, an increase in the Al content causes a problem in that the mechanical characteristics of the heat-resistant tube, such as creep rupture strength and tensile ductility, deteriorate and a problem in that weldability deteriorates.

[0010] It is an object of the present invention to provide a heat-resistant tube in which an alumina barrier layer is favorably provided on the tube inner surface and that is excellent in mechanical characteristics such as creep rupture strength and tensile ductility.

Solution to Problem

[0011] A heat-resistant tube according to the present invention is defined in claim 1. It comprises a heat-resistant tube having an alumina barrier layer to be used for thermal decomposition of hydrocarbons, the alumina barrier layer including an Al oxide and being provided on an inner surface of a tube body,
wherein, in the tube body, an Al content on an inner diameter side is larger than that on an outer diameter side.

[0012] It should be noted that the outer diameter side refers to an outer circumferential side of the cross-sectional thickness of a heat-resistant tube shown in FIG. 1, and the inner diameter side refers to an inner circumferential side thereof. A portion near the center of the cross-sectional thickness is taken as the center in a thickness direction (middle diameter side).

[0013] In the tube body, the Al content on the inner diameter side is larger than that on the outer diameter side by a factor of 2 or more.

[0014] It is desirable that, in the tube body, the Al content on the inner diameter side is larger by 1.3 mass% or more than that on the outer diameter side.

Advantageous Effects of the Invention

[0015] With the heat-resistant tube having an alumina barrier layer of the present invention, the Al content on the inner diameter side of the tube body is larger than that on the outer diameter side thereof, and therefore, an alumina barrier layer can be favorably formed on the inner surface of the tube body by heating. Accordingly, the tube inner surface to be brought into contact with a high-temperature hydrocarbon gas during thermal decomposition of hydrocarbon can be provided with excellent oxidation resistance, carburization resistance, nitridation resistance, corrosion resistance, and the like.

[0016] On the other hand, the Al content on the outer diameter side of the tube body is small, and therefore, the deterioration of mechanical characteristics such as creep rupture strength and tensile ductility due to the contained Al can be prevented. Moreover, reducing the Al content on the outer diameter side of the tube body makes it possible to prevent the deterioration of weldability on the outer diameter side of the tube.

[0017] Accordingly, since the heat-resistant tube having an alumina barrier layer of the present invention includes the tube body in which an oxide layer including alumina (Al_2O_3) as a main component is provided on the tube inner surface, and is provided with improved oxidation resistance, carburization resistance, and the like and excellent mechanical characteristics such as the creep rupture strength, it is preferable to apply the heat-resistant tube to a heating furnace to be used in a high-temperature environment.

[0018] In addition, in the heat-resistant tube having an alumina barrier layer of the present invention, the Al content on the inner diameter side of the tube body is increased, and therefore, the alumina barrier layer can be favorably regenerated by action of the contained Al even if a portion of the alumina barrier layer inside the tube is removed during the operation or the like.

Brief Description of Drawings

[0019]

FIG. 1 shows a heat-resistant tube including an alumina barrier layer according to an embodiment of the present invention and a cross-sectional view thereof.

FIG. 2 is an explanatory diagram of a centrifugal casting apparatus for manufacturing a heat-resistant tube including an alumina barrier layer according to an embodiment of the present invention.

FIG. 3 shows SEM photographs showing regeneration states of alumina barrier layers of an inventive example and a comparative example. FIGS. 3(a) and 3(a') are SEM photographs of Inventive Example 7 and Comparative Example 1, respectively, after alumina barrier layer removing processing, and FIGS. 3(b) and 3(b') are SEM photographs of Inventive Example 7 and Comparative Example 1, respectively, after the alumina barrier layer regenerating processing.

Description of Embodiments

[0020] Hereinafter, embodiments of the present invention will be described in detail.

[0021] A heat-resistant tube of the present invention is used as a reaction tube for manufacturing ethylene, a decomposition tube for thermal decomposition of hydrocarbons, and the like, and is to be provided in a heating furnace for manufacturing hydrocarbons such as ethylene, for example.

[0022] As shown in FIG. 1, in a heat-resistant tube 10 of the present invention, an alumina barrier layer 14 that contains an Al-oxide including alumina as a main component is formed on the inner surface of a tube body 12. The heat-resistant tube 10 may have an inner diameter of 30 to 300 mm, a length of 1000 to 6000 mm, and a thickness of 5 to 30 mm, for example. It will be appreciated that there is no limitation to these dimensions.

Centrifugal Casting

[0023] The heat-resistant tube 10 can be manufactured using a centrifugal casting apparatus 20 as shown in FIG. 2. For example, the centrifugal casting apparatus 20 may have a configuration in which a tubular metal framework 22 that is rotated at a high speed by casting machine rollers 21 is provided, and a molten alloy 23 is poured into the metal framework 22 from a ladle 24 via a casting pail 25.

[0024] The heat-resistant tube 10 of the present invention is characterized in that the Al content on the inner diameter side (see FIG. 1) of the tube body 12 is larger than that on the outer diameter side (see FIG. 1).

[0025] The Al content in the molten alloy poured into the metal framework from the casting pail is changed over time in order to increase the Al content on the inner diameter side of the tube body compared with that on the outer diameter side, thus making it possible to manufacture the heat-resistant tube of the present invention. For example, the pouring time is divided into the early stage, the middle stage, and the last stage, and the Al content in the molten alloy at the middle stage and/or the last stage of casting is increased compared with that at the early stage of casting, thus making it possible to manufacture the heat-resistant tube of the present invention. The early stage, the middle stage, and the last stage of casting can be set by dividing the pouring time into substantially equal three stages, for example. It will be appreciated that the pouring time may be divided into the first half and the latter half of casting, and the Al content in the molten alloy at the latter half may be increased.

[0026] The Al content in the molten alloy in the casting pail can be adjusted by preparing a ladle containing a molten alloy including a small amount of Al or no Al and a ladle containing a molten alloy including a large amount of Al. Alternatively, at the middle stage or the last stage, molten Al may be directly added to the ladle or the casting pail using a dipper, or a lump of Al or an Al alloy may be charged into the ladle.

[0027] Increasing the Al content in the molten alloy poured into the metal framework at the middle stage and/or the last stage of casting as described above makes it possible to increase the Al content on the inner diameter side of the tube body in the heat-resistant tube casted compared with that on the outer diameter side.

[0028] It should be noted that the Al content on the inner diameter side of the tube body casted through centrifugal casting can also be increased by pouring the molten alloy including a large amount of Al at only the middle stage, not at the middle and last stages or only the last stage. The reason for this is that the molten alloy poured at the middle stage is mixed with the molten alloy poured at the last stage by convection of the molten alloy.

[0029] The tube body is made of a heat-resistant alloy containing at least Cr in an amount of 15 to 50%, Ni in an amount of 18 to 70%, and Al in an amount of 1 to 6%.

[0030] It is desirable that the tube body is made of a heat-resistant alloy containing C in an amount of 0.05 to 0.7%, Si in an amount of more than 0% to 2.5% or less, Mn in an amount of more than 0% to 5% or less, Cr in an amount of 15 to 50%, Ni in an amount of 18 to 70%, Al in an amount of 1 to 6%, a rare earth element in an amount of 0.005 to 0.4%, and W in an amount of 0.5 to 10% and/or Mo in an amount of 0.1 to 5%, and

[0031] Fe and inevitable impurities as the balance.

[0032] It is desirable that the above heat-resistant alloy contains at least one selected from the group consisting of Nb in an amount of 0.1 to 3%, Ti in an amount of 0.01 to 0.6%, and Zr in an amount of 0.01 to 1%.

[0033] At least one rare earth element selected from La, Y, and Ce can be used.

[0034] It is desirable that the above heat-resistant alloy contains B in an amount of 0.001 to 0.5%.

[0035] Furthermore, it is desirable that the above heat-resistant alloy contains N in an amount of 0.005 to 0.2%.

[0036] In addition, it is desirable that the above heat-resistant alloy contains Ca in an amount of 0.001 to 0.5%.

Explanation of Reasons for Component Restrictions

Cr: 15 to 50%

[0037] The Cr content is set to 15% or more for the purpose of contribution to the improvement of high-temperature strength and cyclic oxidation resistance. However, if the content is too large, high-temperature creep rupture strength deteriorates, and therefore, the upper limit is set to 50%. It should be noted that the Cr content of 20 to 45% is more desirable.

Ni: 18 to 70%

[0038] Ni is an element that is necessary to secure cyclic oxidation resistance and the stability of a metal structure. If the Ni content is small, the Fe content relatively becomes large. As a result, a Cr-Fe-Mn-oxide is likely to be formed on the surface of the cast body, thus inhibiting the formation of the alumina barrier layer. Therefore, the Ni content is set to at least 18%. Even if the Ni content exceeds 70%, it is impossible to obtain the efficacy corresponding to the increasing amount, and therefore, the upper limit is set to 70%. It should be noted that the Ni content of 20 to 50% is more desirable.

Al: 1 to 6%

[0039] The Al content refers to an average content in the entire tube body. That is, in the present invention, the Al content on the inner diameter side of the tube body in the heat-resistant tube is increased compared with that on the outer diameter side as described above, and therefore, when the Al content is 3%, for example, the Al content on the inner diameter side is larger than 3%, whereas the Al content on the outer diameter side is smaller than 3%.

[0040] The reason for adding Al is to form an alumina barrier layer having excellent oxidation resistance, carburization resistance, coking resistance, and the like on the inner surface of the tube body. On the other hand, an increase in the Al content causes the deterioration of the mechanical characteristics such as creep rupture strength and a tensile characteristic, and the deterioration of weldability. Therefore, in the present invention, the Al content on the inner diameter side of the tube body is larger than that on the outer diameter side as described above.

[0041] The Al content is set to at least 1% in order to favorably form the alumina barrier layer on the inner diameter side of the tube body. However, the Al content exceeds 6%, an effect of forming the alumina barrier layer on the inner diameter side of the tube body becomes substantially saturated, and therefore, the upper limit is set to 6% in the present invention. It should be noted that the Al content of 2.0 to 4.0% is more desirable.

[0042] In the tube body, the Al content on the inner diameter side is preferably set to be larger than that on the outer diameter side by a factor of 2 or more, desirably 2.5, and more preferably 4.0. Adjusting the Al content in this manner makes it possible to favorably form the alumina barrier layer on the inner surface of the tube body and to prevent the deterioration of the mechanical characteristics of the tube body.

[0043] An adjustment is performed on the tube body such that the Al content on the inner diameter side is preferably larger by 1.3 mass% or more, and more desirably larger by 2.0 mass% or more than that on the outer diameter side. It should be noted that, in this specification, "%" refers to "mass%" unless otherwise stated. Adjusting the Al content in this manner makes it possible to favorably form the alumina barrier layer on the inner surface of the tube body and to prevent the deterioration of the mechanical characteristics of the tube body.

[0044] Furthermore, it is preferable that the Al content on the inner diameter side of the tube body is set to 1.5% or more, and the Al content on the outer diameter side thereof is set to 5% or less. When the Al content on the inner diameter side is smaller than the lower limit, a favorable alumina barrier layer is not formed, and when the Al content on the outer diameter side exceeds the upper limit, it is difficult to maintain the mechanical characteristics.

C: 0.05 to 0.7%

[0045] C acts to improve castability and enhance high-temperature creep rupture strength. Therefore, the C content is set to at least 0.05%. However, if the content is too large, a primary carbide of Cr_7C_3 is likely to be extensively formed, and thus the movement of Al, which forms the alumina barrier layer, in the base material is suppressed. As a result, Al is insufficiently supplied to the surface portion of a cast body and the alumina barrier layer locally splits, and thus the continuity of the alumina barrier layer is impaired. Moreover, a secondary carbide is excessively deposited to cause the deterioration of tensile ductility and toughness. Therefore, the upper limit is set to 0.7%. It should be noted that the C content of 0.2 to 0.6% is more desirable.

Si: more than 0% to 2.5% or less

[0046] Si is contained for the purpose of using Si as a deoxidizer for molten alloy and enhancing the fluidity of the molten alloy. If the content is too large, high-temperature creep rupture strength deteriorates, or Si is oxidized to form an oxide layer having a low denseness, and therefore, the upper limit is set to 2.5%. It should be noted that the Si content of 2% or less is more desirable.

Mn: more than 0% to 5% or less

[0047] Mn is contained for the purpose of using Mn as a deoxidizer for molten alloy and fixing S in the molten alloy. If the content is too large, high-temperature creep rupture strength deteriorates, and therefore, the upper limit is set to 5%. It should be noted that the Mn content of 1.6% or less is more desirable.

Rare earth element: 0.005 to 0.4%

[0048] The term "rare earth element" means 17 elements including 15 elements of the lanthanide series ranging from La to Lu in the periodic table, and Y and Sc. It is preferable that at least one rare earth element selected from the group consisting of La, Y and Ce is contained in the heat-resistant alloy of the present invention. The rare earth element contributes to the formation of the alumina barrier layer and the enhancement of stability thereof.

[0049] When the alumina barrier layer is formed by heating in a high-temperature oxidizing atmosphere, the rare earth element that is contained in an amount of 0.005% or more effectively contributes to the formation of the alumina barrier layer.

[0050] On the other hand, if the content is too large, the tensile ductility and toughness deteriorate, and therefore, the upper limit is set to 0.4%.

W: 0.5 to 10% and/or Mo: 0.1 to 5%

[0051] W and Mo form a solid solution in a matrix and strengthen an austenite phase in the matrix, thus improving creep rupture strength. At least one of W and Mo is contained in order to achieve this efficacy. The W content is set to 0.5% or more, and the Mo content is set to 0.1% or more.

[0052] However, if the W content and the Mo content are too large, tensile ductility deteriorates and carburization resistance deteriorates. Moreover, as in the case where the C content is large, a primary carbide of $(Cr, W, Mo)_7C_3$ is likely to be extensively formed, and thus the movement of Al, which forms the alumina barrier layer, in the base material is suppressed. As a result, Al is insufficiently supplied to the surface portion of the cast body and the alumina barrier layer locally splits, and thus the continuity of the alumina barrier layer is likely to be impaired. Furthermore, since W and Mo have a large atomic radius, when they form a solid solution in the matrix, the movement of Al in the base material is suppressed and the formation of the alumina barrier layer is inhibited. Therefore, the W content is set to 10% or less, and the Mo content is set to 5% or less. It should be noted that when both elements are contained, the total content is preferably set to 10% or less.

[0053] In addition, the following components may be contained.

[0054] At least one selected from the group consisting of Nb in an amount of 0.1 to 3%, Ti in an amount of 0.01 to 0.6%, and Zr in an amount of 0.01 to 1%

[0055] Nb, Ti, and Zr are elements that are likely to form carbides, and form less solid solutions in the matrix than W and Mo. Therefore, Nb, Ti, and Zr do not exhibit any particular action of forming the alumina barrier layer, but improve creep rupture strength. At least one of Ti, Zr and Nb may be contained as needed. The Nb content is set to 0.1% or more, and the Ti content and the Zr content are set to 0.01% or more.

[0056] However, if they are excessively added, tensile ductility deteriorates. Furthermore, Nb reduces the removing resistance of the alumina barrier layer. Therefore, the upper limit of the Nb content is set to 1.8%, and the upper limits of the Ti content and the Zr content are set to 0.6%.

B: 0.001 to 0.5%

[0057] Since B exhibits an action of strengthening the particle boundaries of the cast body, B may be contained as needed. It should be noted that if the B content is large, creep rupture strength deteriorates, and therefore, the B content is set to 0.5% or less even in the case where B is added.

N: 0.005 to 0.2%

[0058] N forms a solid solution in an alloy matrix and improves high-temperature tensile strength. However, the N content is large, N binds to Al to form AlN, and tensile ductility deteriorates. Therefore, the N content is set to 0.2% or less. The N content of 0.06 to 0.15% is preferable.

Ca: 0.001 to 0.5%

[0059] Ca serves as a desulfurizing element or a deoxidizing element. Therefore, Ca contributes to the improvement of the yields of Ti and Al. This effect can be obtained when Ca is added in an amount of 0.001% or more. However, if a large amount of Ca is added, weldability is impaired, and therefore, Ca is added in an amount of 0.5% or less.

[0060] In the heat-resistant tube of the present invention, the heat-resistant alloy constituting the tube body includes the above-described components and Fe as the balance. P, S, and other impurities that are inevitably mixed in the alloy when melting the alloy may be present as long as the contents of such impurities are within a range that is usually allowable to this type of alloy material.

[0061] In the obtained tube body, the Al content on the inner diameter side is larger than that on the outer diameter side.

Machining Processing

[0062] An unsound layer that has protrusions and depressions or ununiformly includes impurities is present on the inner surface of the tube body obtained through centrifugal casting, and therefore, machining processing is performed on this unsound layer. It should be noted that the machining processing preferably includes polishing processing that is performed such that the surface roughness (Ra) of the inner surface of the tube body is 0.05 to 2.5 μm. Setting the surface roughness (Ra) as mentioned above makes it possible to suppress the formation of Cr-oxides (e.g., Cr_2O_3) on the inner surface of the tube body.

Heat Processing

[0063] The alumina barrier layer is formed on the inner surface of the tube body by heating the tube body in an oxidizing atmosphere after the machining processing is performed on the inner surface. It should be noted that this heat processing can also be performed as an independent step or performed in a high-temperature atmosphere in which the tube body installed in a heating furnace is used.

[0064] The heat processing is performed in an oxidizing atmosphere. The "oxidizing atmosphere" refers to an oxidizing environment in which an oxidizing gas containing oxygen in an amount of 20 vol% or more, steam, and CO_2 are mixed. The heat processing is performed at a temperature of 900°C or higher, preferably 1000°C or higher, and more preferably 1050°C or higher, and heating time is one hour or more.

[0065] When the heat processing is performed, the inner surface of the tube body comes into contact with oxygen to oxidize Al, Cr, Ni, Si, and Fe that have diffused on the surface of the matrix, and an oxide layer is thus formed. When the heat processing is performed within the above temperature range, Al forms oxides prior to Cr, Ni, Si, and Fe.

[0066] In the present invention, the Al content on the inner diameter side of the tube body is large, and therefore, Al located near the inner surface of the tube body favorably binds to oxygen by being heated as described above to form, as the oxide layer, an alumina barrier layer including an Al-oxide (Al_2O_3) as a main component.

[0067] When the tube body is heated as described above, an alumina barrier layer is favorably formed on the inner surface due to the Al content on the inner diameter side being large, whereas the tube body forms a heat-resistant tube that is excellent in mechanical characteristics such as creep rupture strength and tensile ductility due to the Al content on the outer diameter side being small.

[0068] Al is a component that causes defective welding and reduces weldability. However, in the heat-resistant tube of the present invention, the Al content on the outer diameter side is small, thus making it possible to suppress the deterioration of the weldability when the heat-resistant tube is installed in a heating furnace.

[0069] When the heat-resistant tube of the present invention is used in a high-temperature atmosphere, excellent oxidation resistance, carburization resistance, nitridation resistance, and corrosion resistance can be maintained for a long period of time due to the alumina barrier layer formed on the inner surface, and the mechanical characteristics are excellent. Furthermore, when the heat-resistant tube is installed in a heating furnace, weldability is also excellent. Accordingly, the lifetime of the heat-resistant tube can be improved significantly, and the operation efficiency can be enhanced to a level as high as possible.

Examples

[0070] Molten alloy was produced through atmospheric melting in a highfrequency induction melting furnace, and the centrifugal casting apparatus shown in FIG. 2 was used to form tube bodies having alloy compositions shown in Table 1 below (unit: %; it should be noted that an average content is used for Al) in the following conditions, followed by machining processing. The tube bodies each had an inner diameter of 80 mm, an outer diameter of 100 mm, and a length of 250 mm prior to the machining processing. It should be noted that "-" shown in Table 1 means that the component is not contained in the tube body or is inevitably contained in the tube body.

Table 1

	C	Si	Mn	Cr	Ni	Mo	W	Al	Nb	Ti	N	Zr	La	Y	B	Ce	Ca
Inv. Ex. 1	0.6	0.3	0.5	30	42	0.5	-	1	1.5	-	-	-	-	0.1	-	-	-
Inv. Ex. 2	0.5	0.6	0.6	37	40	2.5	-	4	0.5	0.1	-	-	0.1	-	0.01	-	-
Inv. Ex. 3	0.45	0.5	0.3	24	35	3.3	-	6	0.8	0.15	-	0.2	0.03	-	-	-	0.05

(continued)

	C	Si	Mn	Cr	Ni	Mo	W	Al	Nb	Ti	N	Zr	La	Y	B	Ce	Ca
Inv. Ex. 4	0.2	0.3	0.5	45	33	0.3	-	2	-	-	0.01	-	-	-	-	-	-
Inv. Ex. 5	0.4	0.8	0.8	25	20	0.5	2	5	0	0	-	-	0.1	-	-	-	-
Inv. Ex. 6	0.4	0.3	0.5	20	46	1.4	-	2	0.8	0.1	-	-	0.05	0.05	-	0.05	-
Inv. Ex. 7	0.5	0.5	3	24	34	-	1	3	-	0.15	-	0.1	0.03	-	-	-	-
Comp. Ex. 1	0.3	0.8	0.4	20	37	0.1	-	1	-	-	-	0.1	-	0.05	-	-	-
Comp. Ex. 2	0.5	0.6	0.6	24	34	0.2	1	4	-	0.1	0.05	0.2	-	0.1	0.01	-	-

[0071] Each of the tube bodies of inventive examples and comparative examples was produced by setting the total weight of molten alloy to be poured into a casting pail to 40 kg, preparing three types of molten alloy including an early-stage molten alloy, an middle-stage molten alloy, and the last-stage molten alloy in which the Al contents (Al inputs) were different or the same as shown in Table 2 below, and pouring the early-stage molten alloy, followed by pouring the middle-stage molten alloy and the last-stage molten alloy in this order. It should be noted that the reason why the composition of the manufactured tube body is inconsistent with the total weight of the alloy and the Al input is that a portion of Al adhered to a dipper or a melting pot and remained thereon.

Table 2

Al input (kg)			
	Early-stage molten alloy	Middle-stage molten alloy	Last-stage molten alloy
Inv. Ex. 1	0	0	0.5
Inv. Ex. 2	0	1.0	0
Inv. Ex. 3	0	1.0	0.5
Inv. Ex. 4	0	0	0.8
Inv. Ex. 5	0	1.3	0
Inv. Ex. 6	0	0.8	0
Inv. Ex. 7	0	1.0	0
Comp. Ex. 1	0.5	0	0
Comp. Ex. 2	1.5	0	0

[0072] Regarding the pouring time, the total time of the early stage, the middle stage, and the last stage was set to 14 to 16 seconds. Zero second to fifth second was the early stage, fifth second to seventh second was the middle stage, and seventh second and onward was the last stage.

[0073] After the centrifugal casting, 2.5-mm inner surface processing was performed on the unsound layer on the inner surface side of each obtained tube bodies such that the thickness was 7.5 mm, and paper polishing was performed such that the surface roughness (Ra) of the inner surface was 2.0 μm.

[0074] Then, regarding Inventive Examples 1 to 7 and Comparative Examples 1 and 2, the Al contents at three points that were respectively located on the outer diameter side, at the center in a thickness direction (middle diameter side), and on the inner diameter side were measured. The measurement was performed using a fluorescent X-ray analysis apparatus after the tube body was cut, the surfaces on the outer diameter side and the inner diameter side were polished away so as to reduce the thickness by 1 to 2 mm, and the the middle diameter side was polished after the cutting. The measurement was performed at six positions in total, namely two positions at each of the three points that were portions near the two ends and the center in the longitudinal direction. Table 3 shows the average Al contents (unit: %) in Inventive Examples 1 to 3 and Comparative Example 1 out of the tube bodies measured.

Table 3

	Inv. Ex. 1	Inv. Ex. 2	Inv. Ex. 3	Comp. Ex. 1
Outer diameter side	0.48	1.40	2.88	1.00
Middle diameter side	1.38	5.24	6.36	1.00
Inner diameter side	1.85	6.36	7.34	1.00

[0075] The Al contents obtained through the above measurements were used to calculate a ratio of the Al content on the inner diameter side with respect to that on the outer diameter side (inner-outer content ratio), and a ratio of the Al content on the middle diameter side with respect to that on the outer diameter side (middle-outer content ratio). Table 4 shows the results.

Table 4

	Inv. Ex. 1	Inv. Ex. 2	Inv. Ex. 3	Inv. Ex. 4	Inv. Ex. 5	Inv. Ex. 6	Inv. Ex. 7	Comp. Ex. 1	Comp. Ex. 2
Inner-outer content ratio	3.85	4.56	2.55	3.20	2.93	2.65	4.87	1.00	1.00
Middle-outer content ratio	2.88	3.75	2.21	2.53	2.30	2.09	3.63	1.00	0.99
Layer regeneration	B	A	A	B	A	B	A	C	B
Tensile ductility	7.2%	6.4%	3.6%	10.4%	4.0%	11.2%	8.4%	9.2%	2.8%
Comprehensive evaluation	A	A	A	A	A	A	A	B	B

[0076] As shown in Tables 3 and 4, the Al contents on the inner diameter side and the middle diameter side were larger than that on the outer diameter side in all of Inventive Examples 1 to 7. The reason for this is that molten alloy containing a large amount of Al was used in the middle stage and/or the last stage of the casting in the inventive examples. On the other hand, in Comparative Examples 1 and 2, the Al contents on the inner diameter side and the middle diameter side were the same as that on the outer diameter side, or the Al content on the middle diameter side was smaller than that on the outer diameter side. The reason for this is that Al was poured at the early stage of the casting in the comparative examples, and Al was uniformly diffused in the molten alloy in the casting pail.

[0077] For example, the Al contents in Inventive Example 1 and Comparative Example 1 were 1%, but Tables 3 and 4 show that the Al content on the outer diameter side in Inventive Example 1 was smaller than that in Comparative Example 1, and the Al contents on the middle diameter side and the inner diameter side could be increased. The same applies to Inventive Example 2 and Comparative Example 1.

Alumina Barrier Layer Forming Processing

[0078] The tube bodies of Inventive Examples 1 to 7 and Comparative Examples 1 and 2 were heated in the atmosphere (containing oxygen in an amount of about 21%) at 950°C for 24 hours and then cooled in the furnace.

[0079] The cross sections of the inner surfaces of the obtained tube bodies were observed using a scanning electron microscope (SEM). The results show that, in all of Inventive Examples 1 to 7 and Comparative Example 2, the alumina barrier layer of 80 area% or more was formed. On the other hand, in Comparative Example 1, the alumina barrier layer of smaller than 80 area% was formed. The reason for this is that, in all of Inventive Examples 1 to 7 and Comparative Example 2, the Al content on the inner diameter side of the tube body could be increased, and in Comparative Example 1, the Al content on the inner diameter side of the tube body was as small as 1%.

[0080] It should be noted that when Inventive Examples 1 to 7 and Comparative Example 2 were compared, the alumina barrier layer was formed on substantially the entire surface in Inventive Examples 2, 3, 5, and 7.

Alumina Barrier Layer Removing Processing

[0081] Regarding the inventive examples and comparative examples, the alumina barrier layer formed on the inner surface of the tube body was removed in the following conditions in order to determine whether or not a favorable alumina barrier layer was formed again at a position where the alumina barrier layer had been removed.

[0082] The removing conditions were as follows: all the tube bodies were heated in the atmosphere (containing oxygen in an amount of about 21%) at 1200°C (which is higher than the operation temperature of a heating furnace for manufacturing ethylene) for 60 hours and then cooled in the furnace. As a result, while the tube body was being cooled, the alumina barrier layer was removed from the inner surface of the tube body due to the difference in heat shrinkage percentage between the tube body and the alumina barrier layer.

[0083] FIGS. 3(a) and 3(a') are SEM photographs of the tube bodies 12 of Inventive Example 7 and Comparative Example 1, respectively, after alumina barrier layer removing processing. These photographs show that an Al-oxide (Al_2O_3) on the inner surface of the tube body 12 did not take a layered form, and only a portion of the Al-oxide remained on the inner surface of the tube body 12.

Alumina Barrier Layer Regenerating Processing

[0084] Subsequently, the tube bodies on which the above alumina barrier layer removing processing had been performed were heated in the atmosphere (containing oxygen in an amount of about 21%) at 950°C for 24 hours and then cooled in the furnace. The inner surface of the tube body was observed to check whether or not an alumina barrier layer was formed again thereon.

[0085] Table 4 (Layer regeneration) above shows the results. In Table 4, "A" shows that an alumina barrier layer was regenerated on substantially the entire inner surface (90 area% or more) of the tube body, "B" means that an Al-oxide of 80 area% or more and less than 90 area% was formed, and an Al-oxide was not regenerated or Cr-oxides were formed on the remaining area, and "C" means that an Al-oxide of less than 80 area% was regenerated, and an Al-oxide was not regenerated or Cr-oxides were formed on the remaining area.

[0086] As shown in Table 4, Inventive Examples 2, 3, 5, and 7 were evaluated as "A" for layer regeneration, meaning that substantially the entire alumina barrier layer was regenerated. This was due to the Al contents on the inner diameter side of the tube bodies of these inventive examples being 4.0% or more. Al contained in a large amount on the inner diameter side bound to oxygen taken in through heat processing, and thus a favorable alumina barrier layer was regenerated. Inventive Examples 1, 4, and 6 and Comparative Example 2 were inferior to the above inventive examples, and were evaluated as "B" for layer regeneration, meaning that an alumina barrier layer of 80 area% or more could be regenerated. On the other hand, Comparative Example 1 was evaluated as "C" for layer regeneration due to the Al content on the inner diameter side of the tube body being small, meaning that an alumina barrier layer was regenerated insufficiently.

[0087] FIGS. 3(b) and 3(b') are SEM photographs of the inner surfaces of the tube bodies 12 of Inventive Example 7 and Comparative Example 1, respectively, after alumina barrier layer regenerating processing. In Inventive Example 7, the alumina barrier layer 14 constituted by an Al-oxide (Al_2O_3) was observed on substantially the entire surface of the tube body 12, and the formation of Cr-oxides was not observed. On the other hand, as shown in FIG. 3(b'), in Comparative Example 1, an Al oxide was partially regenerated, and Cr-oxides were also formed. It is thought that the Al content on the inner diameter side of the tube body of Comparative Example 1 was as small as 1%, and therefore, Cr, Ni, Si, Fe, and the like formed oxides while an Al oxide was formed.

[0088] Discussions of the above alumina barrier layer regenerating processing will be given. It is found that even when the alumina barrier layer is removed for one reason or another while each of the inventive examples is used in an ethylene manufacturing apparatus, the alumina barrier layer can be regenerated immediately, and oxidation resistance, carburization resistance, nitridation resistance, corrosion resistance, coking resistance, and the like can be provided.

Tensile Testing

[0089] Test pieces were produced from the tube bodies of Inventive Examples 1 to 7 and Comparative Examples 1 and 2, and tensile testing was performed thereon to measure tensile ductility.

[0090] The tube body was cut in the thickness direction, and the test piece was produced based on JIS Z 2201 (flat test piece). The distance between marks in the thickness direction of the test piece is $5.65\sqrt{S}$ (S: cross-sectional area). The tensile testing was performed in conformity with JIS Z 2241 (metallic materials tensile testing method). It should be noted that the testing was performed at room temperature because a clear difference can be observed compared with a case where the testing is performed at a high temperature. Table 4 (Tensile ductility) above shows the results.

[0091] Table 4 shows that Inventive Examples 1, 2, 4, 6, and 7 and Comparative Example 1 had a tensile ductility of higher than 6% and thus were favorable. Inventive Examples 3 and 5 had a tensile ductility of higher than 3% and thus were also favorable. On the other hand, Comparative Example 2 had a tensile ductility of lower than 3%.

[0092] The reason for this is that the Al contents on the outer diameter side could be reduced in the inventive examples and Comparative Example 1. On the other hand, in Comparative Example 2, the Al content on the outer diameter side was large. Therefore, Al acted as a ferrite-forming element, and in addition, a compound of Ni and Al was deposited, causing the deterioration of the tensile ductility.

[0093] It is found from these results that reducing the Al contents on the outer diameter side of the tube bodies of the inventive examples made it possible to prevent the deterioration of the mechanical characteristics such as creep rupture strength and tensile ductility.

Comprehensive Evaluation

[0094] The inventive examples and comparative examples were evaluated comprehensively. Comprehensive evaluation was determined as follows: in a case where an alumina barrier layer of 80 area% or larger was formed through the alumina barrier layer forming processing, the layer of 80 area% or more was regenerated (evaluation for layer regeneration was "A" or "B") through the alumina barrier layer regenerating processing, and the tensile ductility measured in the tensile testing was 3% or more, the comprehensive evaluation was "A", and in a case where at least one of the above criteria was not satisfied, the comprehensive evaluation was "B".

[0095] As shown in Table 4 (Comprehensive evaluation), the comprehensive evaluation was "A" for all the inventive examples, and these results show that the inventive examples had a high ability to form and regenerate the alumina barrier layer and a high tensile ductility. The reason why the ability to form and regenerate the alumina barrier layer could be enhanced is that the Al content on the inner diameter side of the tube body could be increased. In addition, the reason why excellent mechanical characteristics could be provided is that the Al content on the outer diameter side of the tube body could be reduced. It is found from the description above that the Al content on the inner diameter side of the tube body is preferably larger than that on the outer diameter side by a factor of 2 or more, and the Al content on the inner diameter side is preferably larger by 1.3 mass% or more than that on the outer diameter side.

[0096] On the other hand, regarding Comparative Example 1 in which the Al content in the tube body was merely reduced, the mechanical characteristics could be secured, but the ability to form and regenerate the alumina barrier layer deteriorated, and therefore, the comprehensive evaluation was "B". Regarding Comparative Example 2 in which the Al content in the tube body was merely increased, the ability to form and regenerate the alumina barrier layer could be enhanced, but the mechanical characteristics deteriorated, and therefore, the comprehensive evaluation was "B". In addition, regarding Comparative Example 2, the Al content on the outer diameter side was large, and therefore, the weldability was not favorable. Accordingly, when comprehensively evaluated as heat-resistant tubes to be used in a high-temperature environment, these comparative examples were inferior to the inventive examples.

[0097] As described above, with the heat-resistant tube having an alumina barrier layer of the present invention, the alumina barrier layer is less likely to be removed even when subjected to repeated cycles of heating and cooling, Even if the alumina barrier layer is removed, the alumina barrier layer is regenerated immediately. Accordingly, even when used in a high-temperature atmosphere, the heat-resistant tube having an alumina barrier layer of the present invention can exhibit excellent oxidation resistance, carburization resistance, nitridation resistance, corrosion resistance, coking resistance, and the like for a long period of time, and is excellent in mechanical characteristics such as creep rupture strength and tensile ductility. Furthermore, the Al content on the outer diameter side is small, and therefore, the heat-resistant tube also exhibits excellent weldability when installed in a heating furnace. Accordingly, the lifetime of the heat-resistant tube can be improved significantly, and the operation efficiency can be enhanced to a level as high as possible because a time and a frequency of maintenance such as a coking removing operation can be reduced.

[0098] The foregoing description is intended to illustrate the present invention, and should not be construed as limiting the invention defined in the claims. Also, the configuration of each element of the invention is not limited to the foregoing examples, and various modifications can be made within the technical scope of the claims.

List of Reference Numerals

[0099]

10	Heat-resistant tube
12	Tube body
14	Alumina barrier layer

Claims

1. A heat-resistant tube having an alumina barrier layer to be used for thermal decomposition of hydrocarbons, the alumina barrier layer comprising an Al oxide and being provided on an inner surface of a tube body,
   wherein the tube body comprises at least:

15 to 50 mass% Cr,
18 to 70 mass% Ni,
1 to 6 mass% Al,
optionally option (1) : 0.05 to 0.7 mass% C, more than 0 mass% to 2.5 mass% or less Si, more than 0 mass% to 5 mass% or less Mn, 0.005 to 0.4 mass% of a rare earth element ;
0.5 to 10 mass% W and/or 0.1 to 5 mass% Mo; and when option (1), than optionally at least one selected from the group consisting of 0.1 to 3 mass% Nb, 0.01 to 0.6 mass% Ti, and 0.01 to 1 mass% Zr,
optionally 0.001 to 0.5 mass% B,
optionally 0.005 to 0.2 mass% N,
optionally 0.001 to 0.5 mass% Ca,
with the balance being Fe and inevitable impurities,

wherein, in the tube body, an Al content on an inner diameter side is larger than that on an outer diameter side.

2. The heat-resistant tube having an alumina barrier layer according to claim 1,
wherein, in the tube body, the Al content on the inner diameter side is larger than that on the outer diameter side by a factor of 2 or more.

3. The heat-resistant tube having an alumina barrier layer according to claim 1 or 2,
wherein, in the tube body, the Al content on the inner diameter side is larger by 1.3 mass% or more than that on the outer diameter side.

4. The heat-resistant tube having an alumina barrier layer according to any one of claims 1 to 3
wherein at least one of La, Y, and Ce is used as the rare earth element.

5. A heating furnace comprising the heat-resistant tube having an alumina barrier layer according to any one of claims 1 to 4.

Patentansprüche

1. Hitzebeständiges Rohr mit einer Aluminiumoxid-Sperrschicht, das für die thermische Zersetzung von Kohlenwasserstoffen zu verwenden ist, wobei die Aluminiumoxid-Sperrschicht ein Al-Oxid umfasst und auf einer inneren Oberfläche eines Rohrkörpers vorgesehen ist,
wobei der Rohrkörper mindestens umfasst:

15 bis 50 Masse-% Cr,
18 bis 70 Masse-% Ni,
1 bis 6 Masse-% Al,
wahlweise Option (1): 0,05 bis 0,7 Masse-% C,
mehr als 0 Masse-% bis 2,5 Masse-% oder weniger Si,
mehr als 0 Massse-% bis 5 Masse-% oder weniger Mn,
0,005 bis 0,4 Masse-% eines Seltenerdelements;
0,5 bis 10 Masse-% W und/oder 0,1 bis 5 Masse-% Mo; und
im Falle von Option (1), dann
wahlweise mindestens eines, gewählt aus der Gruppe, bestehend aus 0,1 bis 3 Masse-% Nb, 0,01 bis 0,6 Masse-% Ti und 0,01 bis 1 Masse-% Zr,

wahlweise 0,001 bis 0,5 Masse-% B,

wahlweise 0,005 bis 0,2 Masse-% N,
wahlweise 0,001 bis 0,5 Masse-% Ca,
wobei der Rest Fe und unvermeidbare Verunreinigungen sind,

wobei in dem Rohrkörper ein Al-Gehalt auf einer Innendurchmesserseite größer ist als derjenige auf einer Außendurchmesserseite.

2. Hitzebeständiges Rohr mit einer Aluminiumoxid-Sperrschicht nach Anspruch 1, wobei in dem Rohrkörper der Al-

Gehalt auf der Innendurchmesserseite durch einen Faktor von zwei oder mehr größer ist als der auf der Außendurchmesserseite.

3. Hitzebeständiges Rohr mit einer Aluminiumoxid-Sperrschicht nach Anspruch 1 oder 2, wobei in dem Rohrkörper der Al-Gehalt auf der Innendurchmesserseite um 1,3 Masse-% oder mehr höher ist als der auf der Außendurchmesserseite.

4. Hitzebeständiges Rohr mit einer Aluminiumoxid-Sperrschicht nach irgendeinem der Ansprüche 1 bis 3, wobei mindestens eines aus La, Y und Ce als das Seltenerdelement verwendet wird.

5. Heizofen, umfassend das hitzebeständige Rohr mit einer Aluminiumoxid-Sperrschicht nach irgendeinem der Ansprüche 1 bis 4.

Revendications

1. Tube résistant à la chaleur ayant une couche barrière d'alumine à utiliser pour la décomposition thermique d'hydrocarbures, la couche barrière d'alumine comprenant un oxyde d'Al et étant disposée sur une surface interne d'un corps de tube,
dans lequel le corps de tube comprend au moins :

15 à 50 % en masse de Cr ;
18 à 70 % en masse de Ni ;
1 à 6 % en masse d'Al ;
facultativement option (1) :

0,05 à 0,7 % en masse de C ;
plus de 0 % en masse à 2,5 % en masse ou moins de Si ;
plus de 0 % en masse à 5 % en masse ou moins de Mn ;
0,005 à 0,4 % en masse d'un élément des terres rares ;
0,5 à 10 % en masse de W et / ou 0,1 à 5 % en masse de Mo ; et
lors de l'option (1), alors

facultativement au moins l'un choisi dans le groupe consistant en 0,1 à 3 % en masse de Nb, 0,01 à 0,6 % en masse de Ti et 0,01 à 1 % en masse de Zr, facultativement 0,001 à 0,5 % en masse de B ;

facultativement 0,005 à 0,2 % en masse de N ;
facultativement 0,001 à 0,5 % en masse de Ca ;
le reste étant Fe et les impuretés inévitables,
dans lequel, dans le corps de tube, une teneur en Al sur un côté diamètre interne est plus grande que celle sur un côté diamètre externe.

2. Tube résistant à la chaleur ayant une couche barrière d'alumine, selon la revendication 1,
dans lequel, dans le corps de tube, la teneur en Al sur le côté diamètre interne est plus grande que celle sur le côté diamètre externe d'un facteur de 2 ou plus.

3. Tube résistant à la chaleur ayant une couche barrière d'alumine, selon l'une des revendications 1 ou 2,
dans lequel, dans le corps de tube, la teneur en Al sur le côté diamètre interne est supérieure de 1,3 % en masse ou plus à celle sur le côté diamètre externe.

4. Tube résistant à la chaleur ayant une couche barrière d'alumine, selon l'une quelconque des revendications 1 à 3, dans lequel au moins l'un parmi La, Y et Ce est utilisé comme l'élément des terres rares.

5. Four de chauffage comprenant le tube résistant à la chaleur ayant une couche barrière d'alumine selon l'une quelconque des revendications 1 à 4.

Fig. 1

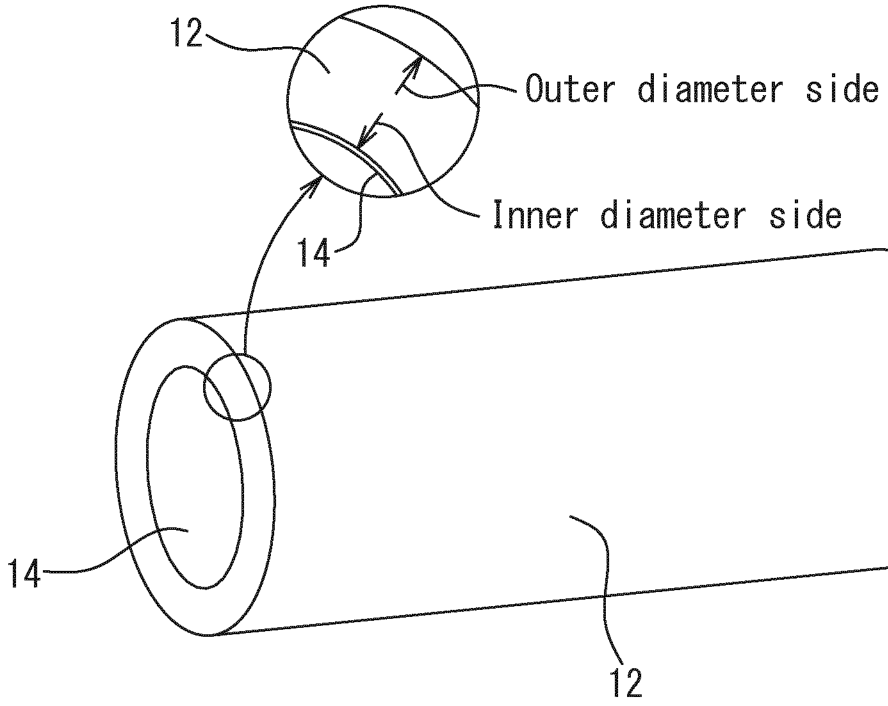

12
Outer diameter side
Inner diameter side
14
10
14
12

Fig. 2

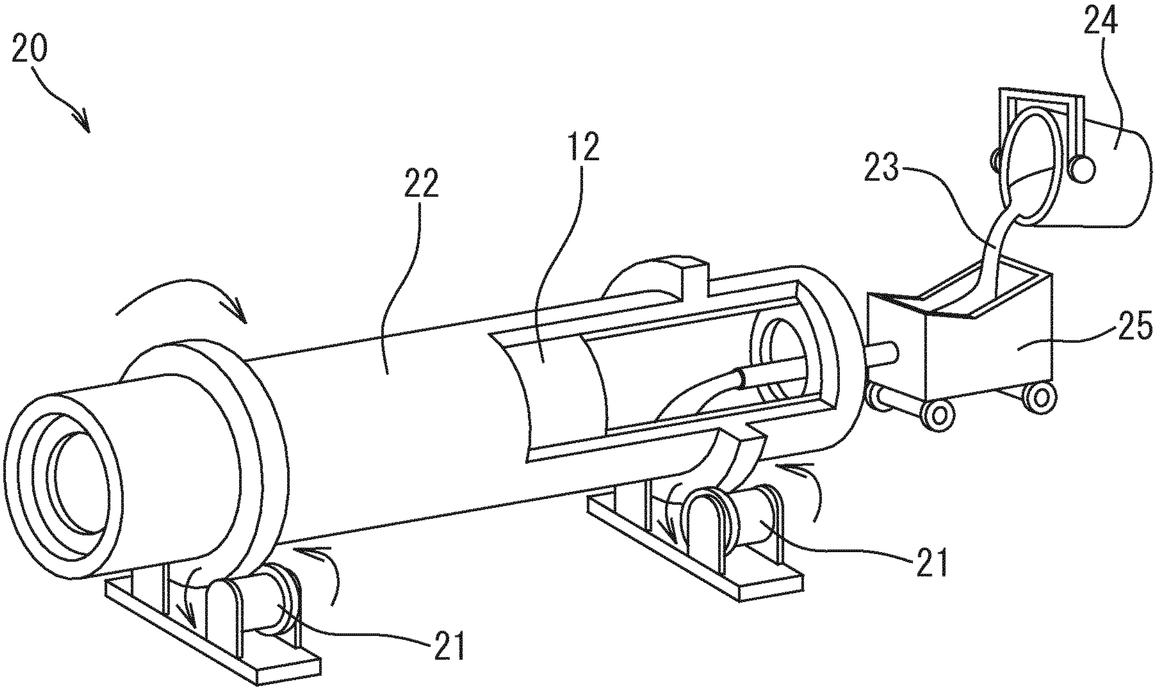
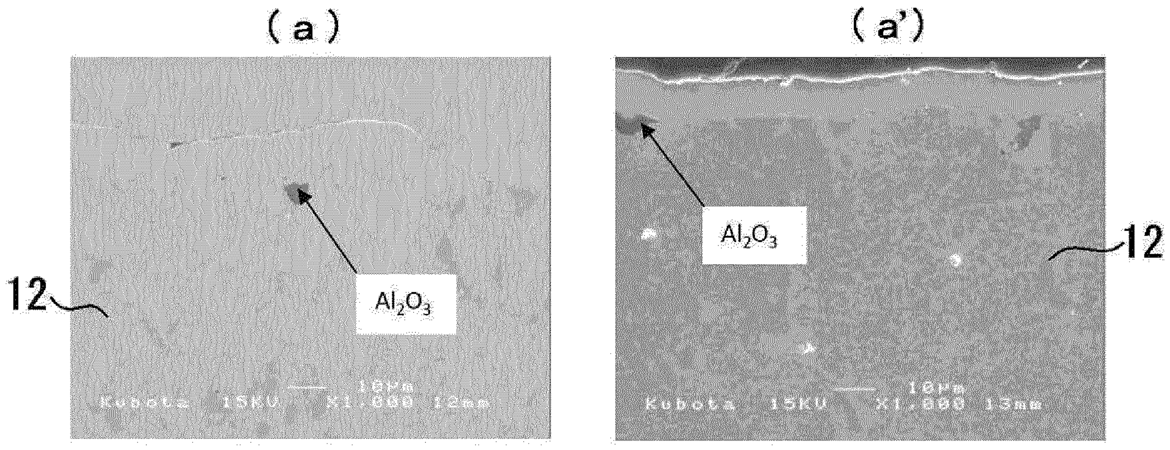
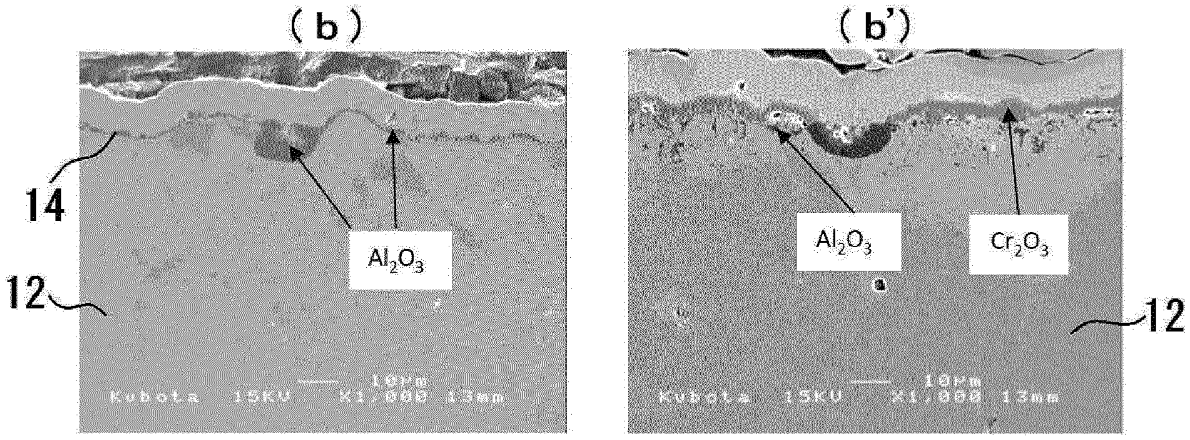

20
24
12
22
23
25
21
21

Fig 3



Inventive Example 7

Comparative Example 1



Inventive Example 7

Comparative Example 1

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP S5278612 A **[0008]**
- JP S5739159 A **[0008]**
- WO 0194664 A2 **[0008]**
- WO 2012054377 A1 **[0008]**