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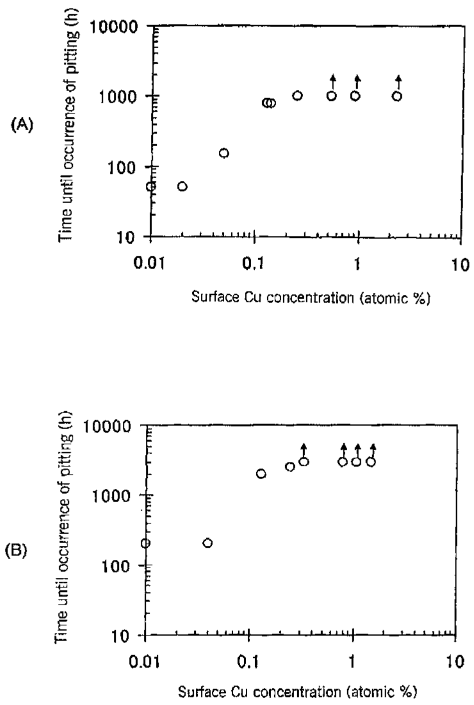
(54) METAL TUBE FOR USE IN CARBURIZING GAS ATMOSPHERE

(57) A metal tube having the ability to protect against carburizing gas and having improved resistance to metal dusting, to carburization, and to coking has a Cu-enriched layer with a Cu concentration of at least 0.1 atomic percent and a thickness of at least 0.3 nm in a surface region of the metal tube. The alloy composition of the base metal of the metal tube contains, in mass percent, Cr: 15 - 35%, Ni: 30 - 75%, Al: 0.001 - 10%, and Cu: 0.01 - 10%. An oxide scale comprising predominantly Cr with a Cr content of at least 50% or an oxide scale comprising predominantly Cr and Al with a total content of Cr + Al of at least 50% may further be provided on the outer side of the Cu-enriched layer, and between this oxide scale and the Cu-enriched layer, a second oxide scale comprising predominantly Si with an Si content of at least 50% may be provided.

Fig. 1



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Description

Technical Field

[0001] This invention relates to a metal tube which has good high-temperature strength and excellent corrosion resistance and which can be used in a carburizing gas atmosphere containing hydrocarbon gases or CO gas. A metal tube according to the present invention has improved protecting ability against carburizing gases, and it is suitable for use as a material for tubes for pyrolysis furnaces or reforming furnaces, tubes for heating furnaces, or heat exchanger tubes in petroleum refinery or petrochemical plants.

[0002] The present invention makes it possible to control the ability of a metal tube used in a carburizing gas atmosphere to be protected against carburizing gas.

Background Art

[0003] The demand for fuels for providing clean energy such as hydrogen, methanol, gas to liquids (GTL), and dimethyl ether (DME) is expected to greatly increase in the future. Accordingly, reforming equipment for manufacturing synthesis gas (syngas) is becoming larger, and there is a demand for equipment suitable for mass production with a higher thermal efficiency. In addition, in order to increase the energy efficiency of reforming equipment used in conventional petroleum refinery or petrochemical plants or of ammonia manufacturing equipment or hydrogen manufacturing equipment using petroleum or the like as a raw material, it has become common to perform heat exchange for recovering waste heat.

[0004] In order to effectively utilize the heat of high temperature gas, it is important to carry out heat exchange in a temperature range of 400 - 700° C, which is lower than the range which has been used in the past. Therefore, corrosion accompanying carburization which is exhibited in such a temperature range by high-Cr, high-Ni metals used in metal tubes such as reaction tubes and heat exchanger tubes is becoming a problem.

[0005] Contact of synthesis gases manufactured in reforming equipment, i.e., gases containing H_2, CO, CO_2, and H_2O, and hydrocarbons such as methane with metals constituting reaction tubes and the like which form the main part of reforming equipment occurs at a high temperature of around 1000° C or higher. In such a high temperature range, a dense oxide film made of oxides of elements such as Cr and Si (chromium oxide and silicon oxide) which have a greater tendency to oxidize than Fe or Ni forms on the surface of the metal, and it protects the metal material from corrosion. However, in those parts in which the temperature is relatively low such as parts for heat exchange, diffusion of elements from the interior of the material to its surface is inadequate so that the formation of an oxide film which has the effect of suppressing corrosion is delayed. In addition, although the elemental composition of the gas is the same, the gas has been modified by the reforming reaction so as to exhibit carburizing properties, and carburization of the metal occurs by penetrating C from the metal surface.

[0006] In a pyrolysis furnace for ethylene production or similar apparatus, if carburization of the metal which constitutes a tube of the furnace proceeds and a carburized layer made of carbides of metals such as Cr or Fe forms on the inner surface of the tube, the carburized portion has an expanded volume. As a result, fine cracks tend to form easily in that portion, and in the worst case, the cracks lead to rupture of the tube. In addition, on the metal surface which is freshly exposed by the cracks, carbon deposition (coking) catalyzed by the metal takes place, resulting in a decrease in the cross-sectional area of the flow path in the tube or a decrease in heat transfer properties.

[0007] In an environment which is exposed to a gas having a greater tendency to produce carburization as encountered in reforming furnaces or heat exchangers, due to a phenomenon in which carbides formed by carburization on the inner surface of a tube become supersaturated and then graphite is directly deposited thereon, corrosive wear of the metal material referred to as metal dusting occurs in which the base metal spalls or peels off from the tube surface and the wall thickness of the tube decreases. The above-described coking also occurs since the metal powder which spalls serves as a catalyst.

[0008] If crack formation, corrosion, and clogging of the interior of a tube caused by the above-described carburization continues, it may be necessary to stop operation due to problems such as equipment malfunctions. Accordingly, sufficient attention must be paid when a material for a metal tube which is used in a carburizing gas atmosphere is selected.

[0009] Various countermeasures against carburization and corrosion due to metal dusting of metals have been proposed in the past.

[0010] For example, JP H09-78204A indicates that an Fe-based alloy or an Ni-based alloy containing 11 - 60% (here and below, percent refers to mass percent) of Cr has improved resistance to metal dusting in an atmospheric gas containing H_2, CO, CO_2, and H_2O at 400 - 700° C. The materials disclosed in that patent document are an Fe-based alloy containing at least 24% of Cr and at least 35% of Ni, an Ni-based alloy containing at least 20% of Cr and at least 60% of Ni, and these alloys to which Nb is further added. However, in general, it is not possible to sufficiently suppress carburization just by increasing the content of Cr and Ni, and a greater degree of protection against metal dusting is desired.

[0011] In JP H11-172473A, in order to suppress corrosion due to metal dusting of a high-temperature alloy containing iron, nickel, and chromium, at least one metal selected from Group VIII, Group IB, Group IV, or Group V of the periodic table or mixtures thereof is deposited on the surface of a metallic material by a conventional physical or chemical method, and the material is subjected to annealing in an inert atmosphere to form a thin layer with a thickness of 0.01 - 10 micrometers on the surface thereof. Sn, Pb, Bi, and the like are particularly effective in this method. However, even though this method is initially effective, its effect seems to disappear during long periods of use due to spalling of the thin layer.

[0012] In JP 2003-73763A, as a result of investigating the interaction of C with dissolved elements in iron with respect to resistance to metal dusting in an atmospheric gas containing H_2, CO, CO_2, and H_2O at 400 - 700 ° C, it is described that an alloying element which has a positive value of the interaction coefficient Ω is effective at suppressing metal dusting. In that patent document, a metallic material is disclosed in which the contents of Si, Al, and Ni as well as Cu and Co are controlled. These alloying elements serve to greatly increase resistance to metal dusting, but increasing the content of alloying elements such as Si, Al, and Cu decreases hot workability and weldability of the material. Therefore, in view of stable supply and manufacture and plant layout, there is room for improvement.

[0013] In order to protect a metal from carburizing gas, a method or technique in which a material is preliminarily subjected to oxidation or surface treatment is proposed in the prior art.

[0014] For example, JP S53-66832A and JP S53-66835A disclose a method in which a 25Cr-20Ni (HK40) low-Si heat resistant steel or a 25Cr-35Ni low-Si heat resistant steel is subjected to pre-oxidation for at least 100 hours at around 1000° C in air. JP S57-43989A discloses a technique in which an austenitic heat-resistant steel containing 20 - 35% Cr is subjected to pre-oxidation in air. JP H11-29776A discloses a method for increasing resistance to carburization by heating a high Ni-Cr alloy in a vacuum to form a scale coating. JP 2000-509105 discloses a method of increasing resistance to carburization by forming a surface layer enriched with Si and Cr by surface treatment.

[0015] Each of these methods requires special heat treatment or surface treatment, so they are uneconomical. In addition, they do not take into consideration healing of scale after the scale formed by pre-oxidation or the surface treatment layer has spalled. Therefore, after the surface is once damaged, the effect of the method can no longer be expected.

[0016] A method in which H_2S is added to an atmospheric gas has also been conceived. However, since H_2S can markedly decrease the activity of a catalyst used for reforming, its use is limited.

[0017] Accordingly, there is still a demand for a metallic material which can adequately suppress metal dusting and can provide necessary properties such as manufacturability and weldability.

Disclosure of the Invention

[0018] The present invention provides a metal tube which has the ability to protect against a carburizing gas, thereby exhibiting improved resistance to metal dusting, resistance to carburization, and resistance to coking, and which is suitable for use as a tube for a pyrolysis furnace for use in an ethylene plant or a reforming furnace or the like.

[0019] In order to investigate the behavior in which metal dusting, carburization, and coking (carbon deposition) locally occur even with a metal tube having a high Cr content, the present inventors analyzed the surface condition of various metal tube materials. They found that if an oxide layer which forms on the surface of a metal tube is dense, the above-described corrosive phenomena do not occur, but if the oxide layer has locally formed defects such as cracking or spalling, C which is present in a gas penetrates through these defects, and at the same time, the exposed metal serves as a catalyst to induce deposition of carbon.

[0020] As a result of detailed investigation of the phenomenon of penetration of C, it was found that the penetration of C proceeds through a dissociative adsorption process in which a hydrocarbon or CO gas is adsorbed by the metal surface and then dissociated to liberate C, and the liberated adsorbed C penetrates into the steel. Upon further investigation of the dissociative adsorption, it was found that the presence of Cu, Ag, or Pt is effective at suppressing this dissociative adsorption.

[0021] In light of the above-described mechanism, as a third means in order to suppress carburization and metal dusting, in addition to (1) forming a protective oxide scale or a thin layer by surface treatment on the metal surface for protecting against C and (2) lowering the flux of penetration of C, it is effective to suppress the dissociative adsorption of a gas. For this purpose, it is important that the elements Cu, Ag, and Pt be present on the surface of the metal.

[0022] However, if these elements are added to an alloy, they are very likely to impair properties such as manufacturability and weldability, and Ag and Pt lead to an increase in cost. Accordingly, the content of these elements is preferably made as low as possible without losing the above-described resistance to carburization, resistance to metal dusting, and resistance to coking.

[0023] The present inventors noted that the gas adsorption is a phenomenon which occurs on the surface of a metal material, and thought that if a Cu-enriched layer is present only on a metal surface, it should be possibly to essentially reduce dissociation of adsorbed gas to suppress carburization and metal dusting. They carried out experiments to confirm whether a desired performance can be obtained by limiting the Cu content in a metal material (alloy) to a level which does not cause problems with respect to manufacturability and weldability and at the same time treating the material to increase the Cu concentration in the surface portion.

[0024] Figure 1(A) and Figure 1(B) show the relationship between the Cu concentration at the surface and the length of time until the occurrence of pitting of plate-shaped test pieces made of 25% Cr-35% Ni-bal. Fe alloys [Figure 1(A)] and 25% Cr-55% Ni-2.5% Al-bal. Fe alloys [Figure 1(B)] which are different in Cu content and hence in Cu concentration at the surface when they were subjected to a corrosion test which was carried out in a 60% CO-26% H_2-11.5% CO_2-2.5% H_2O (volume %) gas at 650° C. From these figures, it can be seen that the effect of suppressing pitting, i.e., metal dusting appears when the Cu concentration in the metal surface exceeds 0.1 atom percent. The Cu concentration was obtained by converting into atomic percent the measured value of elemental analysis which was performed in the depth direction from the surface of the metal by AES (Auger electron spectroscopy). When an oxide scale comprising predominantly Cr or Cr and Al, or this oxide scale and a second oxide scale comprising predominantly Si are present on a surface, the measured value on the metal surface where these oxide scales have been substantially removed is made the Cu concentration.

[0025] Figure 2(A) and Figure 2(B) show the relationship between the thickness of a Cu-enriched layer and the occurrence of pitting when a Cu-enriched layer is formed under different conditions on the surface of a 25% Cr-35% Ni-0.5% Cu-bal. Fe alloy [Figure 2(A)] or a 25% Cr-55% Ni-2.5% Al-0.3% Cu-bal. Fe alloy [Figure 2(B)]. The corrosion test conditions were the same as those described above. The Cu concentration in the Cu-enriched layer of the test alloys was in the range of approximately 0.4 - 0.8 atomic percent [Figure 2(A)] or approximately 0.2 - 0.5 atomic percent [Figure 2(B)]. From these figures, it can be seen that if the thickness of the Cu-enriched layer is at least 0.3 nm (nanometers), the time until the occurrence of pitting is increased i.e., the Cu-enriched layer has an effect on resistance to metal dusting.

[0026] In order to ascertain whether a Cu-enriched layer immediately beneath an oxide scale formed on a metal surface has an effect on resistance to metal dusting resistance, plate-shaped test pieces which were the same as those used for the test shown in Figure 1(A) and Figure 1(B) were subjected to oxidation treatment in air for 5 minutes at 1100° C to form an oxide scale, and then a corrosion test was performed thereon under the same conditions as described above. Figure 3(A) shows the results obtained with a 25% Cr-35% Ni-bal. Fe alloy, and Figure 3(B) shows the results obtained with a 25% Cr-55% Ni-2.5% Al-bal. Fe alloy. The abscissa shows the Cu concentration in atomic % immediately beneath the preliminarily-formed oxide scale. From these figures, it can be seen that the occurrence of pitting is suppressed if an oxide scale is previously present on the metal surface, and that the occurrence of pitting is further suppressed if the Cu concentration immediately beneath the scale is at least 0.1 atomic percent.

[0027] As can be seen from these results, even if an oxide scale is previously formed on a surface, when defects develop in the scale, the metal surface is exposed, and the formation of pits cannot be prevented. In contrast, if a Cu-enriched layer is present immediately beneath a preliminarily-formed oxide scale, even if defects develop in the scale so that the metal is exposed, the exposed metal surface is a Cu-enriched layer, so dissociative adsorption of a gas is suppressed and pitting is prevented.

[0028] In a first aspect, an invention based on these findings is a metal tube for use in a carburizing gas atmosphere formed from a base metal containing, in mass percent, Cr: 15 - 35%, Ni: 30 - 75%, Al: 0.001 - 10%, and Cu: 0.01 - 10%, characterized in that the metal tube has a Cu-enriched layer in a surface region, the Cu-enriched layer having a Cu concentration of at least 0.1 atomic percent and a thickness of at least 0.3 nm.

[0029] This metal tube may further have a layer of an oxide scale on the outside of the Cu-enriched layer, the oxide scale having a Cr content of at least 50 mass percent or a total content of Cr + Al of at least 50 mass percent. In this case, the metal tube may have a second layer of an oxide scale having an Si content of at least 50 mass percent between the first oxide scale and the Cu-enriched layer.

[0030] The inner surface and/or the outer surface of a metal tube according to the present invention may have an irregular shape.

[0031] The base metal preferably has a chemical composition comprising, in mass percent, C: 0.01 - 0.6%, Si: 0.01 - 5%, Mn: 0.01 - 10%, P: at most 0.08%, S: at most 0.05%, Cr: 15 - 35%, Ni: 30 - 75%, Cu: 0.01 - 10%, N: 0.001 - 0.25%, Al: 0.001 - 10%, O (oxygen): at most 0.02%, and a remainder of Fe and impurities. This chemical composition may further contain, in mass percent, at least one element selected from below-described (i) through (vi).

(i) Co: 0.01 - 5%,
(ii) One or both of Mo: 0.01 - 10% and W: 0.01 - 10%,
(iii) One or both of Ti: 0.01 - 2% and Nb: 0.01 - 2%,
(iv) One or more of B: 0.001 - 0.1 %, Zr: 0.001 - 0.1 %, and Hf: 0.001 - 0.5%,
(v) One or both of Mg: 0.0005 - 0.1% and Ca: 0.0005 - 0.1%, and
(vi) One or more ofY: 0.0005 - 0.15%, La: 0.0005 - 0.15%, Ce: 0.0005 - 0.15%, and Nd: 0.0005 - 0.15%.

[0032] In another aspect, the present invention is a method of improving the resistance to metal dusting, resistance to carburization, and resistance to coking of a metal tube used in a carburizing gas atmosphere and comprising a base metal containing, in mass percent, Cr: 15 - 35%, Ni: 30 - 75%, Al : 0.001 - 10%, and Cu: 0.01 - 10%, characterized by forming a Cu-enriched layer in a surface region of the metal tube, wherein the Cu-enriched layer has a Cu concentration of at least 0.1 atomic percent and a thickness of at least 0.3 nm.

[0033] In this method, an oxide scale having a Cr content of at least 50% or having a total content of Cr + Al of at least 50 mass percent may be formed on the outer side of the Cu-enriched layer, and an Si-based second oxide scale having an Si content of at least 50% may be formed between the above-described oxide scale and the Cu-enriched layer.

[0034] A metal tube according to this invention has the ability to protect against a carburizing gas, and it has improved resistance to metal dusting, to carburization, and to coking. Therefore, it can be used in tubes for pyrolysis furnaces, tubes for reforming furnaces, tubes for heating furnaces, piping, or heat exchanger tubes or the like in petroleum refinery or petrochemical plants, and it can greatly increase the durability and operating efficiency of equipment.

Brief Description of the Drawings

[0035]

Figure 1(A) and Figure 1(B) are graphs showing the relationship between the surface Cu concentration and the occurrence of pitting in 25% Cr-35% Ni-bal. Fe alloys and 25% Cr-55% Ni-2.5% Al-bal. Fe alloys, respectively, having different Cu contents.

Figure 2(A) and Figure 2(B) are graphs showing the relationship between the thickness of a Cu-enriched layer and the occurrence of pitting in a 25% Cr-35% Ni-0.5% Cu-bal. Fe alloy and a 25% Cr-55% Ni-2.5% Al-0.3% Cu-bal. Fe alloy, respectively.

Figure 3(A) and Figure 3(B) are graphs showing the relationship between the Cu concentration immediately beneath an oxide scale and the occurrence of pitting in 25% Cr-35% Ni-bal. Fe alloys and 25% Cr-55% Ni-2.5% Al-bal. Fe alloys, respectively, having different Cu contents.

Best Mode for Carrying Out the Invention

[0036] Next, this invention will be explained in greater detail. In the following explanation, percent with respect to the content of elements are mass percent.

[0037] A metal tube according to the present invention is formed from a base metal containing Cr: 15 - 35%, Ni: 30 - 75%, Al: 0.001 - 10%, and Cu: 0.01 - 10%, and it has a Cu-enriched layer in its surface region.

[0038] A Cu-enriched layer can be provided on one or both of the inner and outer surfaces of a metal tube. The object of the present invention can be achieved if a Cu-enriched layer is formed only on the surface of the metal tube which is exposed to a carburizing gas atmosphere. For example, a Cu-enriched layer can be formed on the inner surface of a reaction tube or a pyrolysis furnace tube, or can be formed on the outer surface of a heat exchanger tube. However, in any of these cases, a Cu-enriched layer may be formed on both surfaces of a metal tube.

(i) Cu-enriched layer

[0039] A Cu-enriched layer refers to a region having a Cu concentration (mass percent) which is higher than the average Cu concentration (mass percent) of the base metal. The thickness of the Cu-enriched layer is the distance in the depth direction (namely, in the radial direction of the metal tube) from the metal surface (when at least one layer of oxide scale is present on the metal surface, from the interface with the innermost oxide scale) to a position where the Cu concentration is the same as the average Cu concentration of the base metal (namely, the interface between the Cu-enriched layer and the base metal).

[0040] Examples of oxide scales which can be formed or present on the surface of a metal tube according to the present invention include an oxide scale comprising predominantly Cr (with a Cr content of at least 50%), an oxide scale comprising predominantly Cr and a second oxide scale on the inner side thereof comprising predominantly Si (with an Si content of at least 50%), and an oxide scale comprising predominantly Cr + Al (the total content of Cr + Al being at least 50%).

[0041] The Cu concentration of the Cu-enriched layer means the average value of the Cu concentration inside the layer. When the Cu concentration is measured by AES as in the examples, the average of the measured values in the layer (a value converted to atomic percent) is made the Cu concentration of the Cu-enriched layer.

[0042] The Cu concentration and the thickness of the Cu-enriched layer can be measured using AES. In AES, the surface being measured is irradiated with an electron beam, and the concentration of metallic elements in the surface can be measured by detecting the emission of Auger electrons. A small piece is cut from a portion of the metal tube, and analysis can be carried out in the depth direction from the surface by carrying out AES while the surface is gradually removed by sputtering. In this manner, the thickness of the Cu-enriched layer can be measured by measuring the Cu concentration of the surface of the material in the depth direction up to where the Cu concentration is constant, and the Cu concentration of the Cu-enriched layer can be found as the average Cu concentration within the enriched layer.

[0043] The Cu-enriched layer is provided in a surface region of a metal tube. The surface region of a metal tube means a region in the vicinity of the tube surface. Its location depends upon the method of forming the Cu-enriched layer. There are cases in which the Cu-enriched layer is the outermost layer of the metal tube, but when one or more layers of oxide scales are present on the outer side of the Cu-enriched layer, the Cu-enriched layer is present between the oxide scales and the base metal.

[0044] The Cu concentration of the Cu-enriched layer is at least 0.1 atomic percent. If the Cu concentration of the Cu-enriched layer is less than 0.1 atomic percent, it is not possible to achieve a protecting effect by suppressing adsorption of a C-dissociating gas such as a hydrocarbon or CO gas present in a carburizing gas during plant operation. In addition, even when an oxide scale is present on the metal surface as described above, if the Cu concentration of the Cu-enriched layer immediately beneath the scale layer is less than 0.1 atomic percent, if the oxide scale undergoes damage such as cracking or spalling, it is not possible to suppress adsorption of gas by the exposed metal surface. The Cu concentration of the Cu-enriched layer is preferably at least 0.3 atomic percent, and more preferably it is at least 1.0 atomic percent.

[0045] The thickness of the Cu-enriched layer is at least 0.3 nm. If the thickness of the Cu-enriched layer is less than 0.3 nm, it is not possible to achieve protecting by suppressing adsorption of a C-containing gas such as a hydrocarbon or CO gas in a carburizing gas at the time of plant operation. The thickness of the Cu-enriched layer is preferably at least 0.5 nm. The thickness of the Cu-enriched layer can be easily adjusted by varying the conditions of alternating current electrolysis or controlled atmospheric heat treatment, for example. There is no particular upper limit on the thickness of the Cu-enriched layer, but normally it does not exceed 100 nm.

[0046] Methods of forming a Cu-enriched layer include, but not limited to, alternating current electrolysis, controlled atmospheric heat treatment, and pickling treatment. Two or more of these methods may be used.

[0047] Of these methods, the most preferred is alternating current electrolysis. Alternating current electrolysis is a method in which an applied voltage is swept to a noble potential which causes some alloying elements to dissolve in the electrolytic solution, and then is swept to a base potential to cause Cu to precipitate on the surface. Cu is electrically more noble than Ni, Cr, or Fe, and it is preferentially precipitated by electrolysis in a base potential. This treatment can form a Cu-enriched layer on the surface of a metal tube which is in contact with the electrolytic solution. It can form a Cu-enriched layer with certainty. The thickness and the Cu content of the resulting Cu-enriched layer can be varied based upon the applied voltage and the duration of application of the voltage for each of the noble and base potential.

[0048] When an oxide scale is provided on a metal surface, it is possible to form a Cu-enriched layer by the formation of an oxide scale comprising predominantly Cr or Cr + Al or a second oxide scale comprising predominantly Si by controlled atmospheric heat treatment, since the formation of such an oxide scale causes the concentrations of Cr, Al, and Si in a region immediately beneath the scale to decrease so that the Cu concentration in that region becomes higher than that inside the base metal.

[0049] A Cu-enriched layer can also be formed by utilizing pickling treatment which causes elements other than Cu to preferentially dissolve out so that the Cu concentration in the surface layer is increased.

[0050] When an oxide scale is formed on the surface of the metal tube by oxidative heat treatment after carrying out alternating current electrolysis or pickling treatment, a Cu-enriched layer can be formed between the oxide scale and the base metal alloy.

(ii) Oxide scale

[0051] As an oxide scale (a layer or film of oxide scale), a first oxide scale comprising predominantly Cr or Cr + Al [referred to below as oxide scale (A)] is preferably present on the surface of the metal tube, and a second oxide scale comprising predominantly Si [referred to below as oxide scale (B)] may also be formed on the inner side of layer (A).

[0052] Oxide scale (A) is a layer of an oxide scale comprising predominantly Cr or Cr + Al. Whether this oxide scale comprises predominantly Cr or Cr + Al depends upon the Al content in the alloy. In general, if the Al content of the base metal is at least 1.5%, the oxide scale predominantly comprises Cr + Al, and if the Al content is less than 1.5%, the oxide scale predominantly comprises Cr.

[0053] Oxide scale (A) can be formed by heating a metal tube in an oxidizing atmosphere to a temperature at which surface oxidation takes place. The thickness of the resulting oxide scale can be varied depending upon conditions such as the heating temperature, the heating time, and the partial pressure of oxygen in the atmosphere. The partial pressure of oxygen should be at least the dissociation pressure of an oxide comprising predominantly Cr. The composition of the oxide scale is primarily determined by the alloy composition of the base metal.

[0054] An oxide scale comprising predominantly Cr or Cr + Al is extremely important from the standpoints of resistance to metal dusting, resistance to carburization, and resistance to coking. A Cr-based oxide scale having a Cr content of at least 50% has a high denseness, and it has a good ability to protect against penetration of carbon into steel. A (Cr+Al)-based oxide scale in which the total content of Cr and Al is at least 50% has a still higher denseness, and it exhibits excellent protective properties. Each of these oxide scales is thermodynamically stable up to a high temperature even in a high-temperature carburizing environment as encountered in a pyrolysis furnace for ethylene production, and it has protective properties over a long period. In addition, any of these oxide scales has a low catalyzing effect with respect to coking, and it can suppress coking of the metal surface. As a result, the thermal conductivity to the fluid flowing inside the tube can be maintained at a satisfactory level for long periods, and the yield of reaction products such as olefins is stabilized.

[0055] If the Cr content or the total content of Cr + Al (in the case in which the oxide scale includes Al) of the oxide scale is at least 80%, the scale layer becomes denser, and it acts as a strong protecting layer against penetration of carbon into the steel. As a result, resistance to carburization greatly increases. More preferably, the Cr content or the Cr + Al content is at least 85%.

[0056] Oxide scale (B) is a layer of an oxide scale comprising predominantly Si. This oxide scale can be formed by heating a metal tube in an oxidizing atmosphere at a temperature at which surface oxidation occurs. The thickness of the resulting oxide scale varies in accordance with conditions such as the heating temperature, the heating time, and the partial pressure of oxygen in the atmosphere. The composition of the oxide scale is determined primarily by the steel composition of the base metal.

[0057] If Si-based oxide scale (B) having an Si content of at least 50% is formed, it is preferably present between the Cu-enriched layer and oxide scale (A). Oxide scale (B) serves to promote the uniform formation of oxide scale (A), and when damage such as cracking or spalling of oxide scale (A) occurs, it assists in healing of the damaged portion.

[0058] Oxide scale (B) comprising predominantly Si can be formed between the Cu-enriched layer and oxide scale (A) by heating a metal tube in a gas having a partial pressure of oxygen which is at least the dissociation pressure of oxides comprising predominantly Cr. The dissociation pressure of oxides comprising predominantly Si is smaller than that of oxides comprising predominantly Cr. Therefore, oxide scale (B) on the inner side and oxide scale (A) on the outer side can be formed at the same time. The thickness of each oxide scale varies in accordance with the heating temperature and heating time.

[0059] Formation of oxide scale (B) can be facilitated by increasing the Si content in the base metal alloy (to at least 0.4%, for example).

[0060] The thickness of an oxide scale can be measured by observation with an optical microscope of a sectional specimen for microscopic observation. The content of elements in oxide scale (A) and oxide scale (B) can be measured using an EDX (energy dispersive X-ray) spectrometer. Measurement is usually carried out with a sectional specimen for microscopy having vapor deposition of C on its surface formed before it is subjected to EDX spectroscoy for quantitative analysis of elements. From the results of elemental analysis for each scale layer, the content of Cr, Al, and Si can be found when the total content of metallic elements is made 100%.

[0061] The inner and/or outer surface of a metal tube according to the present invention may be a surface with an irregular shape, such as one having bosses or one having differing dimensions. In general, a surface having such an irregular cross-section easily undergoes attack by carburizing gas, and as a result, damage such as spalling of an oxide scale formed thereon easily takes place. However, according to the present invention, the inner surface and/or the outer surface of a metal tube has high resistance to carburization, and an oxide film formed thereon has an improved ability to heal itself, so the effects of the present invention are particularly marked with a metal tube having an inner surface and/or an outer surface with an irregular cross-section.

[0062] A metal material (base metal) constituting a metal tube according to the present invention is preferably an alloy having the following composition (except for the Cu concentration of the Cu-enriched layer, which is expressed as atomic percent, the composition being expressed as mass percent, and the remainder is Fe and impurities).

C: 0.01 - 0.6%

[0063] It is effective for the C content to be at least 0.0 1 % in order to provide high-temperature strength. If the C content exceeds 0.6%, the toughness of the alloy becomes extremely poor. A preferred range for the C content is 0.01 - 0.45%, and a more preferred range is 0.01 - 0.3%.

Si: 0.01 - 5%

[0064] Si has a strong affinity for oxygen and facilitates the formation of Cr-based oxide scale (A) uniformly. This effect is exhibited when the Si content is at least 0.01 %. However, if the Si content exceeds 5%, weldability worsens, and the structure of the alloy becomes unstable. A preferred range for the Si content is 0.1 - 3%, and a more preferred range is 0.3 - 2.5%.

[0065] However, when the Al content is 1.5% or greater, presence of both Si and Al greatly worsens weldability and makes the alloy structure unstable. Therefore, in this case, the upper limit on the Si content is preferably made 1%. A more preferred range for the Si content in this case is 0.05 - 0.6%.

Mn: 0.01 - 10%

[0066] Mn is added in an amount of at least 0.01% for the purpose of deoxidation and improving workability. Since Mn is an austenite-forming element, it is possible to replace a portion ofNi by Mn. However, excessive addition of Mn impedes the formation of an oxide scale comprising predominantly Cr, so the upper limit of the Mn content is made 10%. A preferred range for the Mn content is 0.1 - 5%, and a more preferred range is 0.1 - 2%.

P: at most 0.08%, S: at most 0.05%

[0067] P and S segregate at grain boundaries and cause hot workability to deteriorate. Therefore, it is preferred that they be reduced as much as possible. However, due to the fact that excessive reduction of these elements leads to an increase in costs, P is made at most 0.08%, and S is made at most 0.05%. Preferably, P is at most 0.05% and S is at most 0.03%, and more preferably, P is at most 0.04% and S is at most 0.015%.

Cr: 15 - 35%

[0068] Cr is an important element in the present invention. It is necessary for the Cr content to be at least 15% in order to stably form an oxide scale comprising predominantly Cr. When the alloy contains at least 1.5% Al, an oxide scale comprising predominantly Cr and Al is formed which is denser and has higher protective properties. However, addition of an excessive amount of Cr deteriorates workability as well as stability in structure. Thus, the upper limit of Cr content is made 35%. A preferred range for the Cr content is 20 - 33%, and a more preferred range is 22 - 32%.

Ni: 30 - 75%

[0069] Ni is present in an amount of 30 - 75% since it is an element which acts to form a stable austenite structure depending on the Cr content. In addition, Ni also acts to reduce the speed of penetration of C when C penetrates into steel. However, an Ni content which is higher than necessary leads to cost increases and difficulty in manufacture. A preferred range for the Ni content is 35 - 70%, and a more preferred range is 40 - 65%.

Cu: 0.01 - 10%

[0070] Cu is one of the most important elements in the present invention. Cu has a very strong effect on suppressing adsorption of a carburizing gas by a metal surface. In order to form a Cu-enriched layer having a Cu concentration of at least 0.1 atomic percent in a surface region, it is necessary to add at least 0.01% of Cu to the base metal alloy. On the other hand, addition of Cu in excess of 10% causes hot workability to markedly decrease. A preferred range for the Cu content is 0.03 - 5%, and a more preferred range is 0.1 - 3%.

N: 0.001 - 0.25%

[0071] N is an element which is effective at improving high-temperature strength. In order to obtain this effect, at least 0.001% of N is contained. Since excessive addition of N greatly impairs workability, the upper limit of the N content is 0.25%. A preferred range for the N content is 0.001 - 0.2%.

[0072] However, when the Al content is at least 1.5%, the N content is preferably at most 0.1% since Al and N form compounds which results in a decrease in creep strength. A more preferred range for the N content in this case is 0.001 - 0.05%.

Al: 0.001 - 10%

[0073] Al is an element which is effective even in minute amounts at improving hot workability. For this purpose, at least 0.001 % of Al is added, and preferably at least 0.01% is added.

[0074] When an oxide scale is previously formed on a surface and it is exposed to a carburizing gas environment, Al contributes to the formation of a dense oxide scale comprising predominantly Cr and Al and having good protective properties. Even when an oxide scale is not previously formed, in the environment of use, an oxide scale comprising predominantly Cr and Al is formed, thereby making it possible to greatly increase the resistance to metal dusting and resistance to carburization of a metal tube. For this purpose, it is effective for the Al content to be at least 1.5%. On the other hand, if Al is present in an amount exceeding 10%, precipitation of hardening precipitates occurs in the alloy, resulting in a marked decrease in toughness and creep elongation of the alloy. A preferred range for the A1 content when forming an oxide scale comprising predominantly Cr and Al is 2 - 8%, a more preferred range is 2 - 4%, and the most preferred range is 2.2 - 3.5%.

[0075] However, in order to form oxide scale (B) comprising predominantly Si, the Al content is preferably less than 1.5%. A more preferred range for the Al content in this case is 0.01 - 1.2%, and the most preferred range is 0.01 - 0.5%.

Oxygen (O): at most 0.02%

[0076] Oxygen is present as an impurity. If the oxygen content exceeds 0.02%, a large amount of oxide inclusions are present in the alloy, and they cause workability to decrease and flaws to form on the surface of a metal tube. Thus, the upper limit on the oxygen content is made 0.02%.

[0077] In addition to the above-described alloying elements, if desired, at least one of the elements described below can be added.

Co: 0.01 - 5%

[0078] Co has the effect of stabilizing an austenite phase, and a portion of Ni may be replaced by at least 0.01% of Co . However, if Co is added in excess of 5%, the hot workability of the alloy is markedly decreased. A preferred range for the Co content is 0.01 - 3%.

One or two of Mo: 0.01 - 10% and W: 0.01 - 10%

[0079] Mo and W are both solid-solution strengthening elements and are effective at increasing the high-temperature strength of an alloy. In order to exhibit this effect, at least 0.01 % of either one can be added. However, excessive addition of these elements worsens workability and impairs the stability of alloy structure, and hence the content of Mo and W are both made at most 10%. A preferred range for each of Mo and W is 0.01 - 8% and a more preferred range is 0.1 - 5%.

One or two of Ti: 0.01 - 2% and Nb: 0.01 - 2%

[0080] Addition of even a minute amount of Ti or Nb has a great effect on improving high-temperature strength, ductility, and toughness. However, these effects are not obtained with addition of less than 0.01% of each, while addition of over 2% causes a decrease in workability and weldability. A preferred range for either Ti or Nb is 0.01 - 1.5% and a more preferred range is 0.02 - 1.2%.

[0081] One or more of B: 0.001 - 0.1%, Zr: 0.001 - 0.1%, and Hf: 0.001 - 0.5%

[0082] Each of B, Zr, and Hf is an element which strengthens grain boundaries and is effective at improving hot workability and high-temperature strength. However, for each of these elements, these effects cannot be obtained by addition of less than 0.001%, while excessive addition (greater than 0.1% for B and Zr, and greater than 0.5% for Hf) worsens weldability.

One or two of Mg: 0.0005 - 0.1% and Ca: 0.0005 - 0.1%

[0083] Each of Mg and Ca is an element which is effective at improving hot workability. This effect is marked with addition of at least 0.0005% for each. However, excessive addition of these elements worsens weldability, so the upper limit for each is made 0.1 %.

One or more of Y, La, Ce, and Nd: 0.0005 - 0.15% each

[0084] Y, La, Ce, and Nd are elements which are effective at improving resistance to oxidation, but this effect is not obtained with addition of less than 0.0005% for each, while excessive addition worsens workability, so the upper limit is made 0.15% for each. A preferred lower limit for each of these elements is 0.005%.

[0085] A metal tube according to the present invention having the ability to protect against a carburizing gas can be formed into a required tube shape such as a seamless tube or a welded tube by a combination of methods selected from melting, casting, hot working, cold working, welding, and the like. Alternatively, a required tube shape can be formed by techniques such as powder metallurgy and centrifugal casting.

[0086] The surface of a metal tube which has undergone final heat treatment may be subjected to surface treatment such as pickling, shot blasting, machining, grinding, or electrolytic polishing. It is possible to apply a plurality of these techniques sequentially. A Cu-enriched layer is then formed by the above-described method or methods. Oxide scale (A) and oxide scale (B) may be formed at the time of final heat treatment, or they may be formed by carrying out heat treatment after surface treatment or after treatment to form the Cu-enriched layer.

[0087] A metal tube according to the present invention may have one or more bosses formed on the inner surface and/or the outer surface of the tube without in any way damaging the ability to protect against a carburizing gas. Examples of such bosses can be seen in finned tubes and the like used in tubes for pyrolysis furnaces for ethylene production. The bosses may be formed at the time of hot working or by welding, for example.

[0088] The following examples illustrate the present invention, but the present invention is not limited to these examples. In the examples, unless otherwise specified, percent means mass percent.

Example 1

[0089] This example illustrates the case in which the Al content of a base metal is less than 1.5%, and an oxide scale comprising predominantly Cr is formed when forming an oxide scale.

[0090] Each of the metal materials having the chemical compositions shown in Table 1 was melted in a high frequency heating vacuum furnace and formed into a billet. From the billet, a metal tube having an outer diameter of 56 mm and a wall thickness of 6 mm was prepared by hot forging and cold rolling. Each metal tube was subjected to solid-solution heat treatment at 1200° C in air for 10 minutes. Thereafter, the metal tube was cut into circular pieces approximately 30 mm long, and some of the cut metal tubes were subjected to surface processing treatment selected from shot blasting (outer surface only) (abbreviated as SB), pickling (abbreviated as Pic), pickling descaling (abbreviated as PiD), machining (outer surface only) (abbreviated as Mac), grinding (abbreviated as Grd), and combinations thereof. Then, each cut metal tube was subjected to alternating current electrolysis (abbreviated as ACEl) or controlled atmospheric heat treatment (abbreviated as ACHT) to form a Cu-enriched layer on the inner and outer surfaces of the tube. In addition, some of the metal tubes were subjected to shot peening (abbreviated as SP) on the outer surface of the tube in order to impart strains to the metal surface. In this example, oxide scale (A) comprising predominantly Cr and oxide scale (B) comprising predominantly Si were formed at the time of controlled atmospheric heat treatment. As a result of the controlled atmospheric heat treatment, these oxide layers were formed, and at the same time, a Cu-enriched layer was also formed on the inner side of the oxide layers. In this example, in order to demonstrate that a Cu-enriched layer could be formed by controlled atmospheric heat treatment alone, surface processing treatment and alternating current electrolysis were not applied to those metal tubes which were subjected to this heat treatment.

[0091] Alternating current electrolysis was carried out in a sulfuric acid bath with a pH of 3 by repeated alternating application of a noble potential of +1.1 volts and a base potential of -0.6 volts (each vs SCE) for 0.15 seconds each. The application of these alternating potentials were continued for a total of 120 seconds. In Comparative Examples 4-B and 17-A in Table 2, the noble potential was changed to -0.25 volts. The atmospheric heat treatment was carried out in a low oxygen atmosphere with an oxygen partial pressure of 10^{-1} - 10^{-8} MPa (remainder was hydrogen gas and water vapor) at 1120 - 1220° C for 3 minutes.

[0092] A square test piece measuring 20 mm on a side was cut from each of the above-described metal tubes, and the Cu concentration at the surface of the test piece was measured in the depth direction by AES to determine the presence of a Cu-enriched layer based on the Cu content of the base metal as well as the thickness and Cu concentration of the Cu-enriched layer.

[0093] The metal tubes which underwent controlled atmospheric heat treatment were subjected to measurement of an oxide scale formed on its surface in the following manner, in addition to the above-described measurement of the Cu-enriched layer by AES. Thus, a sectional specimen for microscopic observation was prepared, and the thickness of each surface oxide scale was measured by observation under a microscope. Using the same test piece, the Cr content of oxide scale (A) comprising predominantly Cr and the Si content of oxide scale (B) comprising predominantly Si were measured by EDX analysis. These contents were measured at three locations selected at random for each scale layer. The contents of Cr, Al, and Si were determined relative to the total amount of metal elements, and the average values thereof were calculated.

[Evaluation of resistance to metal dusting]

[0094] A test piece measuring 20 mm wide x 25 mm long was cut from the above-described metal tubes. The test piece was kept at 650° C for 1000 hours in a carburizing gas atmosphere containing, in volume percent, 60% CO-26% H_2-11.5% CO_2-2.5% H_2O. During this period, the test piece was removed at prescribed intervals, its surface was visually observed for the presence or absence of pitting, and the time until the occurrence of pitting was recorded. The results are shown in Table 2. In Table 2, a time until the occurrence of pitting of 1000 hours, for example, means that pitting occurred when 1000 hours had elapsed.

[Evaluation of resistance to carburization]

[0095] A test piece measuring 20 mm wide x 30 mm long was cut from the above-described metal tubes. The test piece was kept for 300 hours at 1050° C in a carburizing gas atmosphere containing, in volume percent, 15% CH_4-3%

CO_2-82% H_2, and the amount of C (mass percent) which penetrated into the base metal was measured in the following manner.

[0096] After an oxide scale which formed on the surface of the test piece after it was kept in the carburizing gas atmosphere was removed, metal chips were peeled at a pitch of 0.5 mm in the depth direction from the surface. The amount of C in the chips at a depth of 0.5 - 1.0 mm and the amount of C in the chips at a depth of 1.0 - 1.5 mm were then determined by chemical analysis. The average of these two values for the amount of C from which the amount of C contained in the base metal prior to the test had been subtracted was made the amount of penetrated C at a depth of 1 mm. The results are shown in Table 2.

Table 1

Alloy No.	Chemical composition of base metal (mass%), Bal.:Fe+impurities										
	C	Si	Mn	P	S	Cr	Ni	Cu	N	Al	Oxygen	Others
1	0.06	0.05	0.25	0.021	0.001	27.5	45.2	1.9	0.05	0.02	0.008	-
2	0.13	0.23	0.15	0.011	0.001	28.4	56.8	1.5	0.03	0.03	0.007	0.12 Ti
3	0.05	0.94	0.15	0.005	0.002	28.9	60.3	0.05	0.02	0.02	0.009	1.2 Co
4	0.02	0.25	0.11	0.004	0.002	30.8	63.5	0.02	0.03	0.03	0.008	3.5 Mo
5	0.25	0.45	0.24	0.016	0.001	25.6	42.1	0.5	0.02	0.04	0.007	0.003 B
6	0.11	0.42	0.16	0.028	0.001	24.9	35.9	0.8	0.02	0.03	0.007	0.06 Ti, 0.005 Ca
7	0.08	0.35	0.18	0.015	<0.001	27.9	46.5	1.4	0.01	0.02	0.005	0.05Nb
8	0.02	0.67	0.18	0.011	<0.001	29.8	54.6	1.0	0.03	0.04	0.015	0.02 Zr, 0.003 Mg
9	0.16	0.50	0.15	0.005	0.001	20.6	60.2	0.2	0.02	0.03	0.014	0.5 Mo, 0.003 Ca
10	0.15	0.48	0.22	0.054	0.002	29.5	57.5	0.08	0.02	0.02	0.013	0.005 Ca
11	0.08	0.26	0.24	0.009	0.002	26.5	56.9	1.1	0.02	0.02	0.005	0.03 Nd, 1.4 Ti
12	0.11	0.45	0.21	0.011	0.008	23.1	62.1	0.9	0.02	0.03	0.006	4.2 Mo,0.05 Y
13	0.04	0.67	0.05	0.016	0.003	20.8	65.8	1.9	0.01	0.02	0.015	0.04 Hf
14	0.06	0.37	3.21	0.015	0.001	24.5	60.5	1.5	0.01	0.02	0.012	0.6 Co, 0.4 Ti, 0.04 Ce
15	0.07	0.31	1.45	0.021	0.002	26.8	47.6	0.97	0.02	0.03	0.004	0.05 La
16	0.02	1.95	0.21	0.003	<0.001	29.5	62.6	1.5	0.02	0.02	0.006	2.0 Mo, 0.8 Ti, 0.003 B,
17	0.11	0.01	0.45	0.011	0.002	30.7	58.7	0.01	0.12	0.03	0.011	0.02 Zr, 0.004 Ca
18	0.08	0.45	0.42	0.015	0.002	16.8	73.1	3.8	0.04	1.15	0.015	-
19	0.07	0.44	0.32	0.011	0.001	19.9	70.2	0.67	0.01	0.02	0.007	0.004 Mg, 2.1 Co
20	0.06	0.65	0.79	0.008	0.001	24.5	64.2	0.65	0.02	0.03	0.004	0.2 Co, 2.5 W
21	0.12	0.74	0.12	0.009	0.003	27.9	60.5	1.25	0.04	0.04	0.006	3.1 Mo, 0.05 Ti
22	0.45	0.45	0.19	0.005	0.001	29.5	57.8	1.6	0.01	0.05	0.008	2.5 Mo, 0.002 B
23	0.11	0.44	0.24	0.002	0.002	30.6	60.2	2.5	0.01	0.01	0.008	0.01 Zr, 0.02 Y
24	0.04	0.30	0.11	0.006	<0.001	27.8	57.4	1.1	0.07	0.02	0.008	1.2 W

(continued)

Alloy No.	Chemical composition of base metal (mass%), Bal.:Fe+impurities											
	C	Si	Mn	P	S	Cr	Ni	Cu	N	Al	Oxygen	Others
25	0.11	0.38	0.16	0.007	0.001	29.0	56.8	1.4	0.05	0.02	0.007	0.05 Ti, 0.01 La, 0.03 Ce
26	0.09	0.37	0.60	0.005	0.003	21.9	60.0	0.90	0.04	0.04	0.007	0.03 Zr
27	0.51	0.48	0.71	0.002	<0.001	28.3	583	0.98	0.08	0.05	0.008	0.02 Mg
28	0.23	0.89	0.39	0.003	0.002	27.4	56.3	1.3	0.09	0.04	0.004	0.02 Y
29	0.33	0.21	0.19	0.005	<0.001	29.2	49.9	1.5	0.04	0.04	0.005	0.03 Ce
30	0.43	0.43	0.73	0.002	0.001	24.3	52.5	0.88	0.04	0.03	0.007	0.01 Nd
31	0.32	0.74	0.43	0.007	0.003	26.4	60.4	1.7	0.06	0.02	0.004	-
32	0.35	0.01	0.50	0.003	0.002	18.4	64.3	2.1	0.03	0.04	0.003	-
33	0.06	1.38	0.25	0.009	0.001	27.9	60.2	0	0.02	0.02	0.007	-
34	0.08	0.75	0.14	0.021	0.002	29.4	57.9	6.3	0.02	0.06	0.004	2 Mo, 0,2 Ti
35	0.07	1.47	0.21	0.013	0.001	27.8	54.5	8.9	0.01	0.03	0.006	0.005 Ca, 0.04 La
The underlined value is outside the range defined herein.												

Table 2

Alloy No.	Test piece No.	Processing of metal tube after solid solution heat treatment1)	Cu-enriched layer		Oxide scale2)		Resistance to metal dusting3)	Resistance to carburization4)
			Cu concentration (at. %)	Thickness (nm)	(A) Cr content (mass %)	(B) Si content (mass %)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass %)
1	1-A	SB→ACEI	1.71	>1	-	-	1000	0.7
2	2-A	SB→ACEI	1.22	>1	-	-	>1000	0.5
3	3-A	SB→ACEI	0.21	0.6	-	-	1000	0.6
	3-B	SB→Pic→ACEI	0.12	03	-	-	800	0.8
	3-C	PiD→ACEI	0.37	0.6	-	-	>1000	0.6
	3-D	PiD→Pic→ACEI	0.25	0.3	-	-	1000	0.7
	3-E	Mac→ACEI	0.35	0.6	-	-	>1000	0.6
	3-F	Mac→Pic→ACEI	0.24	0.6	-	-	1000	0.7
	3-G	ACHT	0.59	1	85	80	>1000	0.4
4	4-A	SB→ACEI	0.33	0.45	-	-	1000	0.6
	4-B	SB→ACEI	0.22	0.15	-	-	200	1.9
5	5-A	SB→Pic→ACEI	0.41	0.4	-	-	>1000	0.4
6	6-A	PiD→Pic→ACEI→SP	0.44	0.4	-	-	>1000	0.8
7	7-A	SB→ACEI	1.32	>1	-	-	>1000	0.5
8	8-A	PiD→ACEI	0.94	1	-	-	>1000	0.4
9	9-A	Mac→ACEI→SP	0.36	0.3	-	-	800	0.9
10	10-A	Mac→ACEI	0.13	0.3	-	-	900	0.7

(continued)

Alloy No.	Test piece No.	Processing of metal tube after solid solution heat treatment[1]	Cu-enriched layer		Oxide scale[2]		Resistance to metal dusting[3]	Resistance to carburization[4]
			Cu concentration (at. %)	Thickness (nm)	(A) Cr content (mass %)	(B) Si content (mass %)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass %)
11	11-A	Pic→ACEI→SP	0.95	>1	-	-	>1000	0.5
12	12-A	ACEI	0.79	0.6	-	-	>1000	0.5
13	13-A	PiD→ACEI	2.13	0.8	-	-	>1000	0.5
14	14-A	PiD→ACEI	1.63	1	-	-	>1000	0.5
15	15-A	PiD→ACEI	1.21	1	-	-	>1000	0.5
16	16-A	SB→Pic→ACEI	1.33	0.5	-	-	>1000	0.2
17	17-A	SB→ACEI	0.05	>1	-	-	200	1.7
	17-B	SB→ACEI	0.15	0.5	-	-	800	0.9
	17-C	PiD→Pic→ACEI	0.13	0.3	-	-	800	0.9
	17-D	ACHT	0.18	>1	85	-	800	0.7
18	18-A	ACHT	4.24	>1	60	73	1000	0.6
19	19-A	PiD→ACEI	0.48	0.6	-	-	1000	0.5
20	20-A	PiD→Pic→ACEI	0.40	0.4	-	-	1000	0.6
21	21-A	Mac→ACEI	1.03	>1	-	-	>1000	0.5
22	22-A	Grd→ACEI	1.37	>1	-	-	>1000	0.3
23	23-A	SB→Pic→ACEI	2.58	0.6	-	-	>1000	0.2

(continued)

Alloy No.	Test piece No.	Processing of metal tube after solid solution heat treatment 1)	Cu-enriched layer		Oxide scale2)		Resistance to Resistance to metal dusting3) carburization4)	
			Cu concentration (at. %)	Thickness (nm)	(A) Cr content (mass %)	(B) Si content (mass %)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass %)
24	24-A	PiD→ACEl	1.21	0.6	-	-	>1000	03
25	25-A	SB→ACEl	1.27	>1	-	-	>1000	0.3
26	26-A	SB→ACEl	1.02	0.5	-	-	>1000	0.5
27	27-A	PiD→ACEl	132	0.4	-	-	1000	0.6
28	28-A	SB→ACEl	0.40	>1	-	-	>1000	0.3
29	29-A	PiD→ACEl	039	0.4	-	-	>1000	0.2
30	30-A	SB→ACEl	1.11	0.5	-	-	1000	0.4
31	31-A	PiD→ACEl	0.53	0.6	-	-	>1000	0.4
32	32-A	ACHT	0.43	0.5	71	-	>1000	0.3
33	33-A	SB→ACEl	not detected	0	-	-	<100	1.9
34	34-A	PiD→ACEl→SP	15.5	0.2	-	-	>1000	<0.1
35	35-A	SB→ACEl	32.1	0.3	-	-	>1000	<0.1

1) SB: Shot blasting; ACEl: Alternating current electrolysis; Pic: Pickling; FiD : Pickling descaling; Mac: Machining;ACHT: Controlled atmospheric heat treatment; SP: Shot peening; Grd: Grinding;

2) Oxide scale: (A) = Oxide scale comprising predominantly Cr, (B) = Oxide scale comprising predominantly Si;

3) Resistance to metal dusting: 60%CO-26%H_2-11.5%CO_2-2.5%H_2O gas (650°C);

4) Resistance to carburization: 15%CH_4-3%CO_2-82%H_2 gas, 1050°C×300 hours.

The underlined value is outside the range defined herein.

[0097] As can be seen from Table 2, the metal tube of Alloy No. 33 for which the chemical composition did not meet the conditions prescribed for the present invention was inferior in resistance to metal dusting as indicated by the short time until the occurrence of pitting which was less than 100 hours. In addition, the metal tube was also inferior with respect to resistance to carburization as indicated by the large penetrated amount of C which was 1.9%.

[0098] In contrast, among metal tubes of Alloys Nos. 1 - 32 and 34 - 35 which had a chemical composition satisfying the conditions prescribed by the present invention, the tested metal tubes for which the Cu concentration and thickness of the Cu-enriched layer satisfied the conditions prescribed by the present invention had a long time until the occurrence of pitting indicating that their resistance to metal dusting was excellent, and the amount of penetrated C was less than 1 % indicating that they had improved resistance to carburization. However, the tested metal tubes for which at least one of the Cu concentration and the thickness of the Cu-enriched layer did not satisfy the conditions prescribed by the present invention had a short time until the occurrence of pitting, so their resistance to metal dusting was inferior, and they had a large amount of penetration of C, so their resistance to carburization was also inferior.

[0099] From Table 2, it can be seen that even if only controlled atmospheric heat treatment (ACHT) is carried out on a metal tube, a Cu-enriched layer can be formed immediately beneath an oxide scale which is produced by this heat treatment. Regarding the oxide scale, when the base metal has an Si content which is as low as 0.01%, only oxide scale (A) comprising predominantly Cr is formed. Under the heat treatment conditions used in this example, when the base metal has an Si content of approximately 0.4% or greater, oxide scale (B) comprising predominantly Si seems to form as an appreciable continuous layer between oxide scale (A) and the Cu-enriched layer.

Example 2

[0100] This example illustrates the case in which the Al content of the base metal is at least 1.5% so that when an oxide scale is formed, an oxide scale comprising predominantly Cr and Al is formed. In view of the high Al content of at least 1.5%, the Si content of the base metal was made at most 1% for the reason described above.

[0101] Using metal materials having the chemical compositions shown in Table 3, metal tubes for testing were prepared in the same manner as described in Example 1 except that in Comparative Examples 2-B and 6-C of Table 4, the noble potential was changed to -0.25 volts during alternating current electrolysis.

[0102] The metal tubes which were prepared were measured for the composition of the oxide scale and the thickness and Cu concentration (atomic percent) of the Cu-enriched layer and tested to evaluate resistance to metal dusting and resistance to carburization in the same manner as in Example 1. However, since the metal tubes prepared in this example had a high Al content of at least 1.5%, they were superior with respect to resistance to metal dusting and resistance to carburization to the metal tubes prepared in Example 1. Therefore, the test conditions were made more severe by lengthening the test time from the 1000 hours of Example 1 to 3000 hours in the test for evaluating resistance to metal dusting, and by increasing the test temperature from 1050° C to 1100° C in the test for evaluating resistance to carburization.

[0103] In this example, since the Al content of the base metal was a high value of at least 1.5%, oxide scale (A) which was formed by controlled atmospheric heat treatment (ACHT) comprised predominantly Cr and Al. Therefore, the total content of Cr + Al in that layer was measured by EDX analysis. Each of the tested metal tubes on which controlled atmospheric heat treatment was carried out had an Si content of less than 0.3%, and oxide scale (B) comprising predominantly Si did not form as a continuous layer, so measurement of oxide scale (B) was not performed.

[0104] Results of the above measurements are shown in Table 4.

Table 3

Alloy No.	Chemical composition of base metal (mass%), Bal.: Fe + impurities											
	C	Si	Mn	P	S	Cr	Ni	Al	Cu	N	Oxygen	Others
1	0.06	0.08	0.22	0.007	<0.001	20.5	67.2	3.1	1.5	0.011	0.006	0.004 B, 0.003 Ca, 2.0 Mo
2	0.01	0.11	0.19	0.005	<0.001	19.9	68.1	2.9	0.1	0.012	0.003	0.003 Ca, 0.04 La
3	0.02	0.33	0.15	0.021	<0.001	25.5	65.5	2.9	0.1	0.007	0.004	0.004 Hf, 0.11 Ti
4	0.03	0.21	0.11	0.011	0.001	21.1	68.1	2.6	1.5	0.005	0.003	0.04 Ce, 1.1 W
5	0.06	0.01	0.02	0.014	0.011	26.6	63.5	2.5	1.5	0.001	0.008	0.08 Nb
6	0.06	0.03	0.11	0.011	0.005	30.1	60.2	2.9	0.2	0.011	0.005	0.002 Mg
7	0.01	0.09	0.19	0.002	0.001	16.4	62.5	1.6	1.1	0.008	0.003	0.05Y
8	0.09	0.33	0.45	0.017	0.003	22.1	64.2	3.2	0.7	0.005	0.004	0.03 Zr
9	0.02	0.87	0.25	0.018	0.007	24.3	56.3	1.8	0.2	0.006	0.006	7.1 Mo
10	0.02	0.33	0.22	0.022	0.003	22.1	57.3	3.1	0.2	0.006	0.006	-
11	0.03	0.54	0.29	0.025	0.002	19.8	37.1	2.9	0.3	0.001	0.015	1.2 Co, 0.01 La
12	0.03	0.14	0.19	0.016	0.009	21.1	63.2	2.6	0.5	0.005	0.009	1.15 Ti, 0.002 Mg
13	0.03	0.22	0.18	0.012	0.022	20.4	67.4	2.9	0.1	0.004	0.006	2.1 Mo, 0.11 Nb
14	0.02	0.18	2.50	0.011	0.021	25.4	66.4	3.1	0.8	0.187	0.006	-
15	0.06	0.08	0.02	0.054	0.011	26.5	63.2	3.6	1.2	0.014	0.004	0.5 W, 0.05 Nb, 0.003 B
16	0.03	0.11	0.44	0.028	0.007	25.3	60.1	3.1	0.2	0.028	0.004	0.02 Ce, 0.004 Ca
17	0.08	0.06	1.06	0.002	0.001	20.3	73.4	2.8	0.2	0.015	0.006	0.11 Ti, 0.005 Ca, 0.04 Nd
18	0.05	0.15	0.26	0.004	0.032	18.7	66.3	8.5	3.9	0.001	0.005	0.23 Co, 0.003 Mg
19	0.01	0.21	0.29	0.007	0.002	20.4	45.0	2.8	1.4	0.004	0.004	0.81 Co
20	0.33	0.28	3.34	0.008	<0.001	22.1	58.4	2.6	1.1	0.011	0.004	0.05 Co, 1.9 Mo
21	0.07	0.16	0.15	0.002	<0.001	24.7	65.0	2.9	0.2	0.023	0.004	0.1 Hf, 0.03 Co
22	0.06	0.06	0.08	0.013	0.002	26.0	63.3	3.2	2.8	0.009	0.005	1.8 Mo, 0.03 Zr
23	0.09	0.19	0.15	0.019	0.004	19.1	53.5	4.3	1.4	0.019	0.003	0.86 W, 0.004 Ca
24	0.03	0.29	0.18	0.023	0.005	24.3	60.2	2.6	1.3	0.008	0.005	0.32 Nb, 0.04 Nd

(continued)

Alloy No.	Chemical composition of base metal (mass%), Bal.: Fe + impurities										
	C	Si	Mn	P	S	Cr	Ni	Al	Cu	N	Oxygen	Others
25	0.01	0.20	0.04	0.029	0.003	22.0	58.3	2.6	1.5	0.007	0.005	0.007 B, 0.002 Mg
26	0.07	0.25	0.15	0.012	<0.001	24.4	63.0	2.9	0.4	0.021	0.005	0.26 W
27	0.07	0.12	0.20	0.015	0.005	23.2	66.2	3.1	2.4	0.010	0.005	0.43 Ti
28	0.04	0.11	0.15	0.014	<0.001	19.9	57.6	3.6	2.4	0.021	0.004	0.031 B
29	0.03	0.04	0.13	0.021	0.005	22.1	59.2	3.1	1.2	0.011	0.003	0.03 Hf
30	0.03	0.22	0.11	0.026	0.003	23.0	58.3	2.9	1.8	0.007	0.004	0.015 Ca
31	0.04	0.25	0.13	0.008	<0.001	21.9	63.2	3.4	1.2	0.008	0.004	0.05 La
32	0.06	0.12	0.09	0.012	<0.001	25.9	62.9	3.1	0.8	0.019	0.003	0.03 Ce
33	0.09	0.07	0.13	0.019	0.002	20.0	56.3	4.1	1.4	0.019	0.004	0.05 Nd
34	0.04	0.15	0.08	0.020	0.003	23.1	58.4	3.6	1.2	0.013	0.004	-
35	0.05	0.24	0.14	0.024	0.003	22.1	58.2	3.1	1.8	0.016	0.004	-
36	0.07	0.35	0.21	0.011	0.002	24.9	59.1	2.6	0	0.030	0.009	-
37	0.09	0.11	0.15	0.017	0.001	203.4	57.9	2.8	7.9	0.007	0.004	0.05 La, 6.5 Mo. 0.02 Zr
The underlined value is outside the range defined herein.												

Table 4

Alloy No.	Test piece No.	Processing of metal tube after solid solution heat treatment1)	Cu-enriched layer		Oxide scale2)	Resistance to metal dusting3)	Resistance to carburization4)
			Cu concentration (at. %)	Thickness (nm)	(A) Total content of Cr+Al (mass%)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass%)
1	1-A	SB→Pic→ACEI	0.9	0.6	-	>3000	0.4
2	2-A	SB→ACEI	03	0.3	-	2500	0.6
	2-B	SB→Pic→ACEI	<0.1	03	-	200	1.6
	2-C	PiD→ACEI	035	0.5	-	3000	0.6
	2-D	PiD→Pic→ACEI	0.35	0.5	-	3000	0.6
	2-E	Mac→ACEI	03	03	-	3000	0.6
	2-F	Mac→Pic→ACEI	0.25	03	-	2500	0.7
	2-G	ACHT	0.2	0.8	90	2500	0.7
3	3-A	Mac→ACEI	0.1	03	-	2000	0.6
4	4-A	SB→Pic→ACEI	1.1	0.4	-	3000	0.4
5	5-A	ACHT	1.3	03	80	>3000	0.4
6	6-A	PiD→ACEI	0.3	0.4	-	3000	0.4
	6-B	SB→ACEI	03	0.4	-	3000	0.4
	6-C	SB→ACEI	0.3	0.1	-	200	1.5
7	7-A	SB→Pic→ACEI	0.7	0.5	-	2500	0.7
8	8-A	SB→Pic→ACEI	0.55	0.6	-	>3000	03
9	9-A	PiD→ACEI	03	03	-	2500	0.6
10	10-A	PiD→ACE I	0.45	0.4	-	3000	0.5
11	11-A	Mac→ACEI	0.4	0.3	-	2500	0.7
12	12-A	Mac→ACEI	0.6	0.4	-	>3000	0.4
13	13-A	Mac→ACEI	0.4	0.7	-	3000	0.6

(continued)

Alloy No.	Test piece No.	Processing of metal tube after solid solution heat treatment[1]	Cu-enriched layer		Oxide scale[2]	Resistance to metal dusting[3]	Resistance to carburization[4]
			Cu concentration (at. %)	Thickness (nm)	(A) Total content of Cr+Al (mass%)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass%)
14	14-A	PiD→ACEI	0.8	0.5	-	>3000	0.4
15	15-A	SB→ACEI	1.2	>1	-	>3000	0.3
16	16-A	Mac→Pic→ACEI	035	09	-	3000	0.5
17	17-A	PiD→ACEI	0.3	0.6	-	2500	0.7
18	18-A	ACHT	4.2	1	>95	>3000	0.2
19	19-A	SB→Pic→ACEI	1.1	0.6	-	>3000	0.4
20	20-A	ACHT	1.3	0.6	70	>3000	0.4
21	21-A	Mac→ACEI	0.2	>1	-	2500	0.5
22	22-A	SB→ACEI	3.0	0.6	-	>3000	0.3
23	23-A	PiD→ACEI	13	0.3	-	>3000	02
24	24-A	PiD→ACEI	1.2	0.3	-	>3000	0.3
25	25-A	Grd→ACEI	1.0	>1	-	>3000	0.3
			Cu concentration (at. %)	Thickness (nm)	(A) Total content of Cr+Al (mass %)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass %)
26	26-A	Mac→ACEI	0.4	0.6	-	>3000	0.5
27	27-A	ACEI	2.1	0.7	-	>3000	0.3
28	28-A	ACEI	13	0.9	-	>3000	02
29	29-A	PiD→ACEI	1.4	0.6	-	>3000	03
30	30-A	Grd→ACEI	0.9	0.4	-	>3000	0.5
31	31-A	ACEI	0.5	>1	-	>3000	03

(continued)

			Cu concentration (at. %)	Thickness (nm)	(A) Total content of Cr+Al (mass %)	Time unitil ccurrence of pitting (h)	Amount of penetrated C (mass %)
32	32-A	PiD→ACEl	2.1	0.7	-	>3000	0.4
33	33-A	SB→ACEl	1.2	0.4	-	>3000	0.3
34	34-A	ACEl	1.7	03	-	2500	0.2
35	35-A	ACHT	1.0	0.9	75	>3000	03
36	36-A	SB→ACEl	not detected	0	-	200	2.0
37	37-A	ACEl	12.4	0.8	-	>3000	0.1

[1] SB: Shot blasting; ACEl: Alternating current electrolysis; Pic: Pickling; PiD: Pickling descaling;
Mac: Machining; ACHT: Controlled atmospheric heat treatment; SP: Shot peening; Grd: Grinding;

[2] Oxide scale: (A) = Oxide scale comprising predominantly Cr and Al;

[3] Resistance to metal dusting: 60%CO-26%H_2-11.5%CO_2-2.5%H_2O gas (650°C);

[4] Resistance to carburization: 15%CH_4-3%CO_2-82%H_2 gas, 1100°C×300 hours.

The underlined value is outside the range defined herein.

[0105] As can be seen from Table 4, the metal tube of Alloy No. 36 for which the chemical composition did not satisfy the conditions prescribed by the present invention had a time until the occurrence of pitting which was a low value of 200 hours, so it was inferior with respect to resistance to metal dusting. In addition, the amount of penetrated C in this metal tube was a large value of 2.0%, so it was inferior with respect to resistance to carburization.

[0106] In contrast, of metal tubes of Alloys Nos. 1 - 35 and 37 which had a chemical composition which satisfied the conditions prescribed by present invention, the tested metal tubes for which the Cu concentration and the thickness of the Cu-enriched layer satisfied the conditions prescribed by the present invention had a long time until the occurrence of pitting and were superior with respect to resistance to metal dusting, and the amount of penetrated C was less than 1%, so they were superior with respect to resistance to carburization. However, tested metal tubes for which at least one of the Cu concentration and the thickness of the Cu-enriched layer did not satisfy the conditions prescribed by the present invention had a short time until the occurrence of pitting, so their resistance to metal dusting was inferior, and the amount of penetration of C was large, so they were inferior with respect to resistance to carburization.

[0107] From a comparison with Example 1, it can be seen that by increasing the Al content of the base metal, both the resistance to metal dusting and the resistance to carburization can be increased.

Claims

1. A metal tube for use in a carburizing gas atmosphere formed from a base metal containing, in mass percent, Cr: 15 - 35%, Ni: 30 - 75%, Al: 0.001 - 10%, and Cu: 0.01 - 10%, **characterized in that** the metal tube has a Cu-enriched layer in its surface region, and the Cu-enriched layer has a Cu concentration of at least 0.1 atomic percent and a thickness of at least 0.3 nm.

2. A metal tube as set forth in claim 1 further having an oxide scale having a Cr content of at least 50 mass percent or having a total content of Cr + Al of at least 50 mass percent on the outer side of the Cu-enriched layer.

3. A metal tube as set forth in claim 2 having, between the oxide scale and the Cu-enriched layer, a second oxide scale having an Si content of at least 50 mass percent.

4. A metal tube as set forth in any of claims 1 to 3 wherein the inner surface and/or the outer surface of the tube has an irregular shape.

5. A metal tube as set forth in any of claims 1 to 4 wherein the base metal has a chemical composition comprising, in mass percent, C: 0.01 - 0.6%, Si: 0.01 - 5%, Mn: 0.01 - 10%, P: at most 0.08%, S: at most 0.05%, Cr: 15 - 35%, Ni: 30 - 75%, Cu: 0.01 - 10%, N: 0.001 - 0.25%, Al: 0.001 - 10%, O (oxygen): at most 0.02%, and a remainder of Fe and impurities.

6. A metal tube as set forth in claim 5 wherein the chemical composition further contains, in mass percent, at least one element selected from the following (i) through (vi):

(i) Co: 0.01 - 5%,
(ii) One or both of Mo: 0.01 - 10% and W: 0.01 - 10%,
(iii) One or both of Ti: 0.01 - 2% and Nb: 0.01 - 2%,
(iv) One or more of B: 0.001 - 0.1%, Zr: 0.001 - 0.1 %, and Hf: 0.001-0.5%,
(v) One or both of Mg: 0.0005 - 0.1% and Ca: 0.0005 - 0.1%, and
(vi) One or more of Y: 0.0005 - 0.15%, La: 0.0005 - 0.15%, Ce: 0.0005 - 0.15%, and Nd: 0.0005 - 0.15%.

Fig. 1

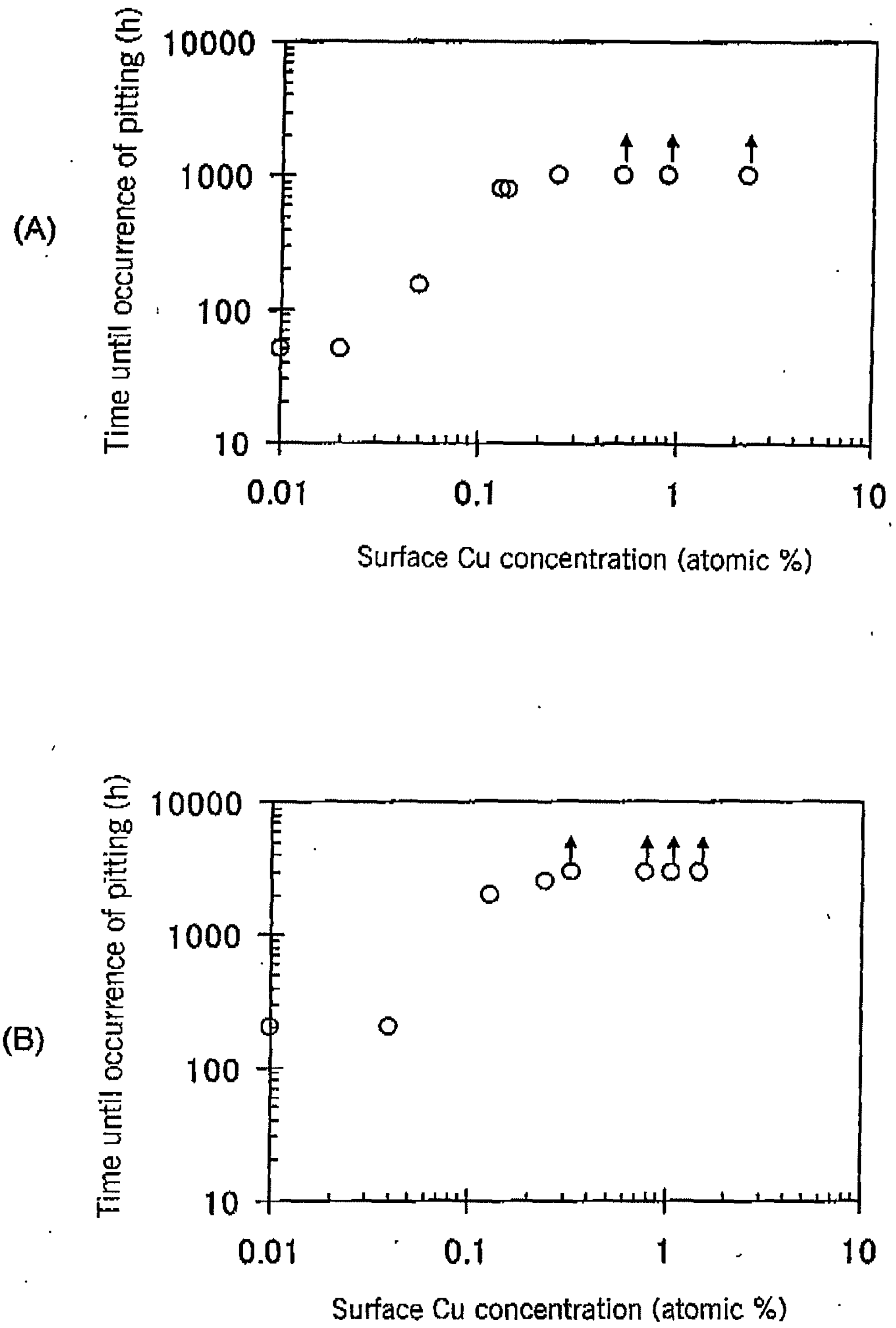

(A)
Time until occurrence of pitting (h)
10000
1000
100
10
0.01
0.1
1
10
Surface Cu concentration (atomic %)
(B)
Time until occurrence of pitting (h)
10000
1000
100
10
0.01
0.1
1
10
Surface Cu concentration (atomic %)

Fig. 2

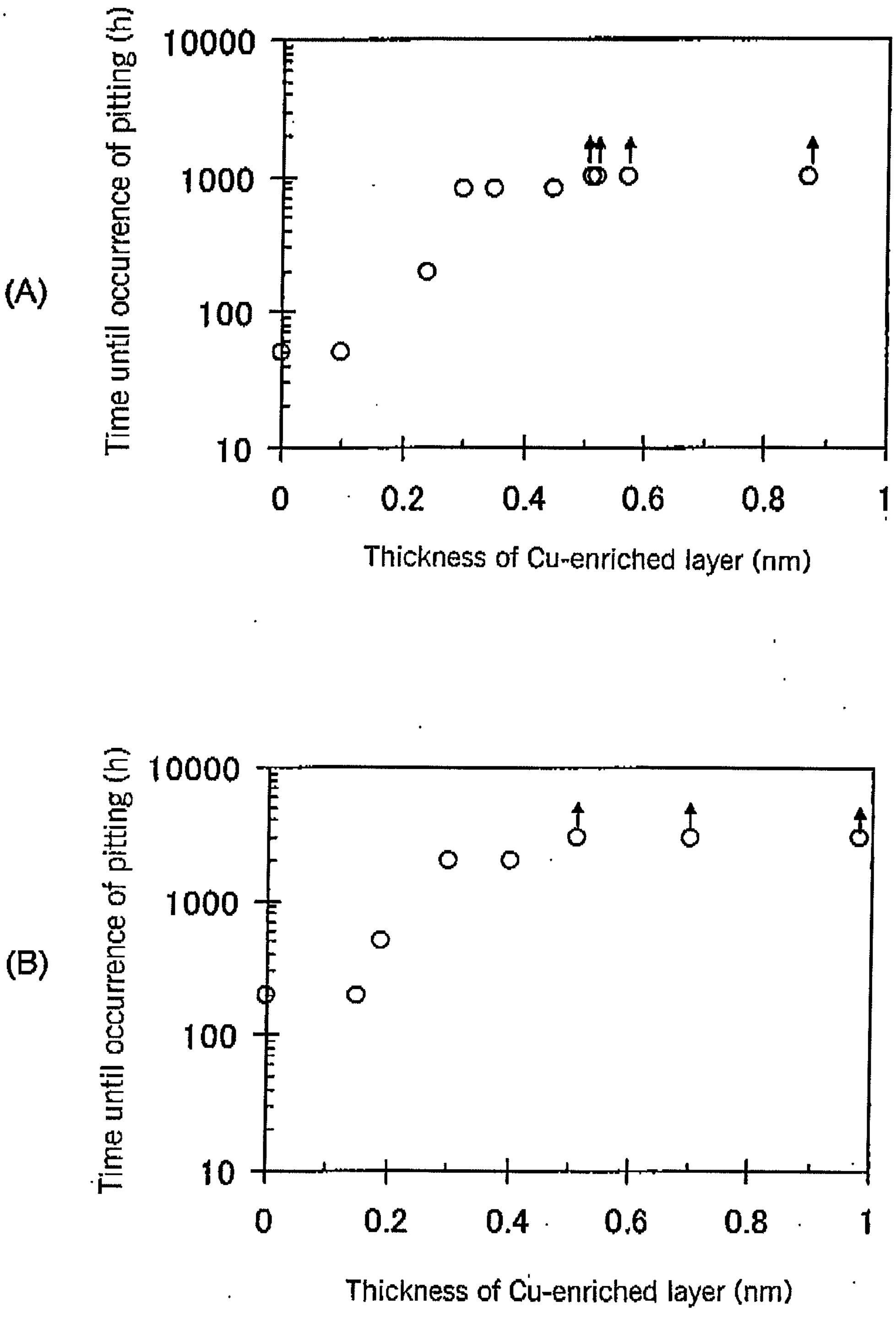
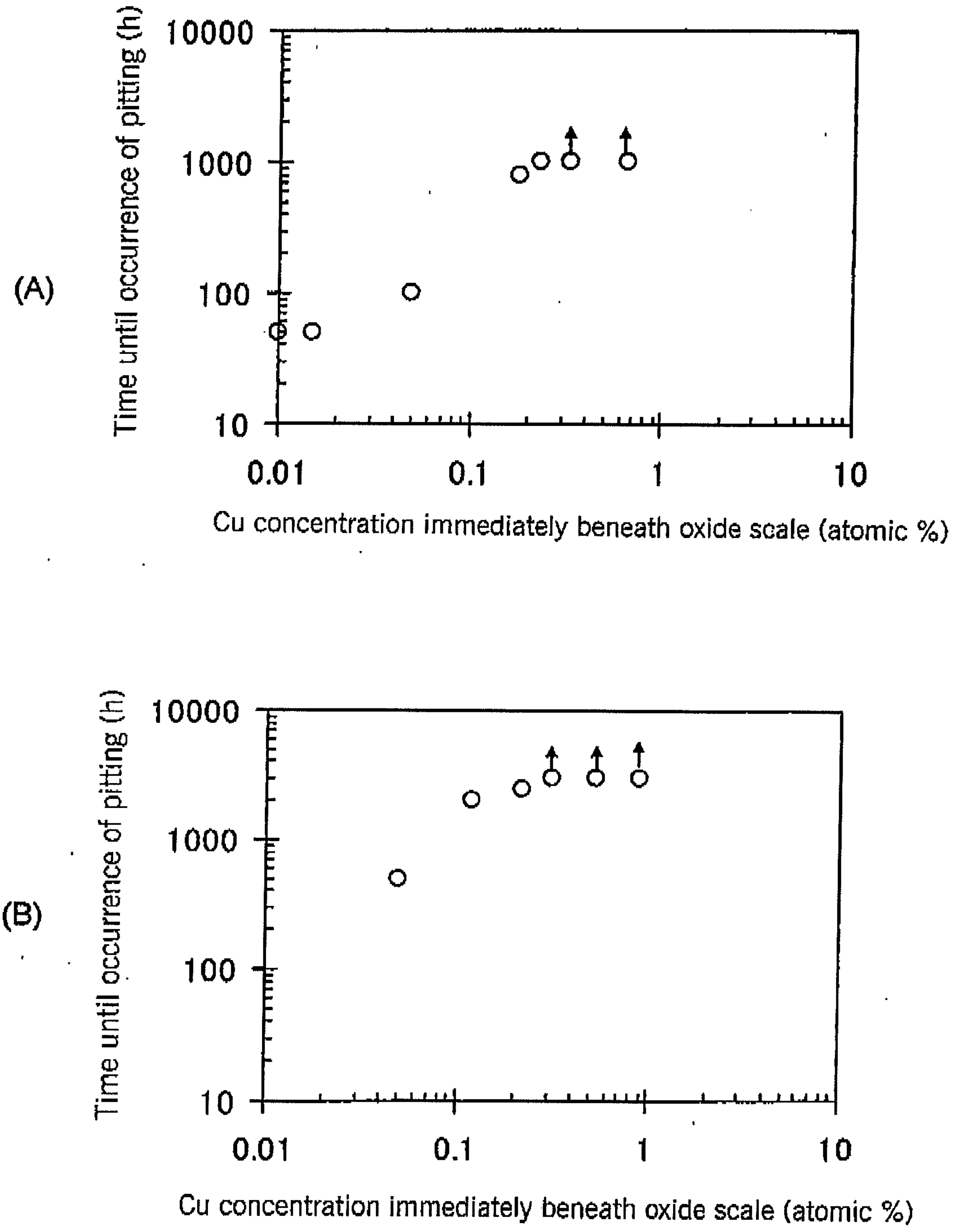

(A)
Time until occurrence of pitting (h)
10000
1000
100
10
0
0.2
0.4
0.6
0.8
1
Thickness of Cu-enriched layer (nm)
(B)
Time until occurrence of pitting (h)
10000
1000
100
10
0
0.2
0.4
0.6
0.8
1
Thickness of Cu-enriched layer (nm)

Fig. 3


(A)
Time until occurrence of pitting (h)
10000
1000
100
10
0.01
0.1
1
10
Cu concentration immediately beneath oxide scale (atomic %)
(B)
Time until occurrence of pitting (h)
10000
1000
100
10
0.01
0.1
1
10
Cu concentration immediately beneath oxide scale (atomic %)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/000892

A. CLASSIFICATION OF SUBJECT MATTER
Int.Cl^7 C22C38/00, C21D9/08, C22C19/05, 38/16, 38/58, C23F15/00

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)
Int.Cl^7 C22C38/00, C21D9/08, C22C19/05, 38/16, 38/58, C23F15/00

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	1996-2005
Kokai Jitsuyo Shinan Koho	1971-2005	Toroku Jitsuyo Shinan Koho	1994-2005

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	JP 2003-73763 A (Sumitomo Metal Industries, Ltd.), 12 March, 2003 (12.03.03), Full text & US 6623869 B1 & EP 1403392 A1 & WO 02/103072 A1	1-6
X	JP 7-29129 B2 (Nippon Steel Corp.), 05 April, 1995 (05.04.95), Full text (Family: none)	1-4,6
X	JP 3355510 B2 (Bayer AG.), 09 December, 2002 (09.12.02), Full text & US 5695716 A & EP 657556 A1	1-4,6

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

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Date of the actual completion of the international search 15 April, 2005 (15.04.05)	Date of mailing of the international search report 10 May, 2005 (10.05.05)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (January 2004)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2005/000892

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-302796 A (Nippon Steel Corp.), 02 November, 1999 (02.11.99), Full text (Family: none)	1-6

Form PCT/ISA/210 (continuation of second sheet) (January 2004)

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- JP H1129776 A **[0014]**
- JP 2000509105 A **[0014]**