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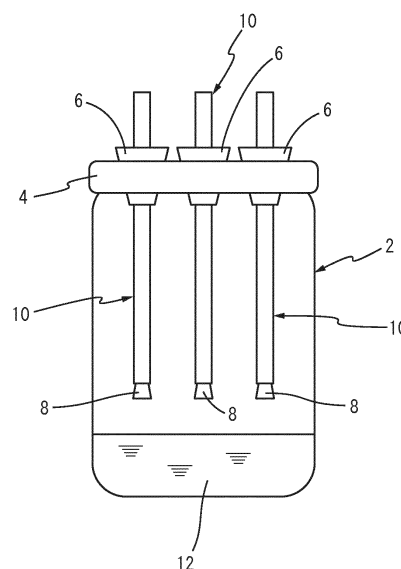
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(54) **HIGHLY CORROSION-RESISTANT COPPER PIPE**

(57) Provided is a corrosion resistant copper tube which can exhibit a further improved resistance to ant nest corrosion, and which is suitably usable as a heat transfer tube and refrigerant tube in air-conditioning equipment and refrigerating equipment. The copper tube is formed of a copper material consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities, and has electric conductivity (Y1 or Y2: %IACS) which satisfies $50-75X \leq Y1 \leq 60-75X$ in the case where the tube includes a recrystallized structure, or $47-75X \leq Y2 \leq 57-75X$ in the case where the tube includes a deformation structure, wherein X (% by weight) represents a content of phosphorus.

FIG. 3



Description

TECHNICAL FIELD

[0001] The present invention relates to a highly corrosion-resistant copper tube, and more particularly relates to a copper tube suitably usable as a heat transfer tube and a refrigerant tube in air-conditioning equipment and refrigerating equipment, for example. The present invention also relates to a technique of improving resistance of the copper tube against ant nest corrosion (or formicary corrosion).

BACKGROUND ART

[0002] A seamless copper tube has been generally employed as the heat transfer tube, the refrigerant tube and the like (tubes arranged inside desired equipment), which are used, for example, in the refrigerating equipment as well as the air-conditioning equipment such as a room air conditioner and a packaged air conditioner. Among others, a tube made of a phosphorous deoxidized copper (JIS-H3300-C1220) having excellent properties in terms of corrosion resistance, brazability, heat conductivity and bending workability, for example, has been mainly used as the seamless copper tube.

[0003] However, it is recognized that the above-described phosphorous deoxidized copper tube used in the air-conditioning equipment and the refrigerating equipment suffers from generation of so-called "ant nest corrosion" (or "formicary corrosion") which is an unusual corrosion that progresses in the form of an ants' nest from a surface of the tube in a direction of the wall thickness. The ant nest corrosion is considered to be generated in a damp environment by a corrosive medium in the form of a lower carboxylic acid such as a formic acid and an acetic acid. Further, it is recognized that such corrosion is also generated in the presence of a chlorine-based organic solvent such as 1,1,1-trichloroethane, particular kinds of lubricating oil, and formaldehyde, for example. It is known that generation of the ant nest corrosion is particularly remarkable where the phosphorous deoxidized copper tube is used as a conduit in the air-conditioning equipment and the refrigerating equipment, which conduit is liable to dewing. Once the ant nest corrosion is generated, it progresses rapidly and penetrates through the wall of the copper tube in a short time, giving rise to a problem that the equipment becomes unworkable.

[0004] To solve the above-described problems, WO2014/148127 (Patent Document 1) proposes a highly corrosion-resistant copper tube formed of a copper material comprising 0.05-1.0% by weight of P (phosphorus) and the balance consisting of Cu (copper) and inevitable impurities, and discloses that the copper tube enjoys resistance to the ant nest corrosion. More particularly, it indicates that a copper tube having a higher resistance to the ant nest corrosion than that of the conventional tube material made of the phosphorous deoxidized copper in an area with a larger P content can be practically advantageously obtained.

[0005] However, even the copper tube obtained with an increased P content may suffer from generation of the ant nest corrosion under a severer corrosive environment. Therefore, it is desired to develop a copper tube which can exhibit an even higher resistance to the ant nest corrosion than the conventional copper tube.

PRIOR ART DOCUMENT

PATENT DOCUMENT

[0006] Patent Document 1: WO2014/148127

SUMMARY OF THE INVENTION

TECHNICAL PROBLEM

[0007] The present invention was made in view of the background art described above. It is therefore an object of the invention to provide a copper tube which can exhibit a higher resistance to the ant nest corrosion, and which has an excellent anti-corrosion property and is suitably usable as the heat transfer tube and the refrigerant tube in the air-conditioning equipment and the refrigerating equipment. It is another object of the invention to provide a process for advantageously producing such a copper tube. It is a further object of the invention to advantageously extend a service life of equipment produced by using such a copper tube.

SOLUTION TO PROBLEM

[0008] The inventors of the present invention made further intensive studies on the ant nest corrosion generated in

the copper tube used in the air-conditioning equipment, the refrigerating equipment and the like, and found that the corrosion resistance of the copper tube can be further improved not only by setting the P content within a predetermined range but also by controlling a value of electric conductivity of the copper tube after plastic working for tube-making. The present invention was completed based on this finding.

[0009] Based on the above-described finding, the invention provides a highly corrosion-resistant copper tube formed of a copper material consisting of 0.15-0.6% by weight of P (phosphorus) and the balance being Cu (copper) and impurities, characterized in that the tube is subjected to final annealing so as to include a recrystallized structure, and has electric conductivity (Y1: %IACS) which satisfies the following formula (1):

$$50-75X \leq Y1 \leq 60-75X \quad \dots(1)$$

wherein X (% by weight) represents a content of P.

[0010] The invention also provides a highly corrosion-resistant copper tube formed of a Cu material consisting of 0.15-0.6% by weight of P and the balance being Cu and impurities, characterized in that the tube is not subjected to final annealing and includes a deformation structure, and has electric conductivity (Y2: %IACS) which satisfies the following formula (2):

$$47-75X \leq Y2 \leq 57-75X \quad \dots(2)$$

wherein X (% by weight) represents a content of P.

[0011] In a preferable form of the highly corrosion-resistant copper tube according to the invention, a content of a group of specific impurity elements consisting of Cr (chromium), Mn (manganese), Fe (iron), Co (cobalt), Zr (zirconium) and Mo (molybdenum) among the impurities is controlled so as to be not higher than 0.01% by weight in total.

[0012] In further preferable form of the highly corrosion-resistant copper tube according to the invention, a content of inevitable impurity elements other than the group of the specific impurity elements among the impurities is controlled so as to be not higher than 0.005% by weight in total.

[0013] In still other preferable form of the highly corrosion-resistant copper tube according to the invention, the tube is arranged in a damp environment and subjected to corrosion that progresses in the form of an ants' nest from a surface of the tube in a direction of a wall thickness of the tube by a corrosive medium in the form of a lower carboxylic acid.

[0014] The present invention also provides a process for producing a highly corrosion-resistant copper tube comprising: a step of providing a Cu ingot consisting of 0.15-0.6% by weight of P and the balance being Cu and impurities; a step of heat-treating the Cu ingot at a temperature of 750-950°C; a step of hot-extruding the heat-treated Cu ingot at a temperature of 750-950°C so as to obtain a Cu blank tube; a step of cold-working the Cu blank tube by a drawing process and further a grooving process as necessary to form a desired size of Cu tube; and a step of subjecting the Cu tube obtained by the cold working to final annealing so as to obtain the Cu tube including a recrystallized structure and having electric conductivity (Y1: %IACS) which satisfies the following formula (1):

$$50-75X \leq Y1 \leq 60-75X \quad \dots(1)$$

wherein X (% by weight) represents a content of P.

[0015] In a preferable form of the process for producing a highly corrosion-resistant copper tube according to the invention, the final annealing is performed at a temperature of 300-600°C.

[0016] The present invention also provides a process for producing a highly corrosion-resistant copper tube comprising: a step of providing a Cu ingot consisting of 0.15-0.6% by weight of P and the balance being Cu and impurities; a step of heat-treating the Cu ingot at a temperature of 750-950°C; a step of hot-extruding the heat-treated Cu ingot at a temperature of 750-950°C so as to obtain a Cu blank tube; and a step of cold-working the Cu blank tube by a drawing process and further a grooving process as necessary to form a desired size of Cu tube including a deformation structure and having electric conductivity (Y2: %IACS) which satisfies the following formula (2):

$$47-75X \leq Y2 \leq 57-75X \quad \dots(2)$$

wherein X (% by weight) represents a content of P.

[0017] In further preferable form of the process for producing a highly corrosion-resistant copper tube according to

the invention, the heat-treating step of the Cu ingot is a homogenization process.

[0018] In still other preferable form of the process for producing a highly corrosion-resistant copper tube according to the invention, the heat-treating of the Cu ingot is a preliminary heat treatment performed in advance of the extrusion.

[0019] The present invention also provides a heat transfer tube and a refrigerant tube (tubes arranged inside desired equipment) which are used in air-conditioning equipment or refrigerating equipment, each of which consists of the highly corrosion-resistant copper tube that is excellent in the resistance to the ant nest corrosion, as described above.

[0020] Furthermore, the present invention provides a method of improving a corrosion-resistance of a copper tube against the ant nest corrosion which is generated by a corrosive medium in the form of a lower carboxylic acid in a damp environment and progresses from the surface of the copper tube used for air-conditioning equipment or refrigerating equipment in the damp environment, wherein the copper tube is formed of a Cu material consisting of 0.15-0.6% by weight of P and the balance being Cu and impurities, and includes a recrystallized structure, and the copper tube has electric conductivity (Y1: %IACS) which satisfies the following formula (1):

$$50-75X \leq Y1 \leq 60-75X \quad \dots(1)$$

wherein X (% by weight) represents a content of P.

[0021] In addition, the present invention also provides a method of improving a corrosion resistance of a copper tube against the ant nest corrosion which is generated by a corrosive medium in the form of a lower carboxylic acid in a damp environment and progresses from the surface of a copper tube used for air-conditioning equipment or refrigerating equipment in the damp environment, wherein the copper tube is formed of a Cu material consisting of 0.15-0.6% by weight of P and the balance being Cu and impurities, and includes a deformation structure, and the copper tube has electric conductivity (Y2: %IACS) which satisfies the following formula (2):

$$47-75X \leq Y2 \leq 57-75X \quad \dots(2)$$

wherein X (% by weight) represents a content of P.

ADVANTAGEOUS EFFECTS OF THE INVENTION

[0022] By making a copper tube which is formed of a Cu material comprising a predetermined amount of P and includes a recrystallized structure or a deformation structure so as to have electric conductivity which satisfies the above-described formula (1) or (2) according to the invention, the obtained copper tube has a concentration of a solid-solubilized or dissolved P in a matrix phase of Cu within an optimum range of 0.15-0.50% by weight. For this reason, even when corrosion is generated in the obtained copper tube under an environment vulnerable to the ant nest corrosion, the corrosion effectively shifts not to the form of the ant nest corrosion, but to the form of general corrosion or pitting corrosion, so that the resistance of the copper tube against the ant nest corrosion is further improved. Thus, a practically useful copper tube which exhibits a more excellent corrosion resistance than that of the conventional copper tube with respect to the resistance to ant nest corrosion can be provided.

[0023] According to the process for producing the copper tube according to the invention, the copper tube having the above-described properties can be industrially advantageously and easily produced.

[0024] Furthermore, by using the copper tube according to the invention as the heat transfer tube, the refrigerant tube (tubes arranged inside desired equipment) and the like in the air-conditioning equipment and the refrigerating equipment, the service life of the equipment can be further effectively extended.

BRIEF DESCRIPTION OF THE DRAWINGS

[0025]

Fig. 1 is a schematic fragmentary enlarged view showing, in transverse cross section, a part of an internally grooved tube produced in one embodiment of the invention.

Fig. 2 is a schematic fragmentary view showing the internally grooved tube of Fig. 1 in longitudinal cross section including the tube axis.

Fig. 3 is a schematic cross sectional view showing an apparatus used for a corrosion resistance test of the tube in the illustrated embodiments.

MODE FOR CARRYING OUT THE INVENTION

[0026] A highly corrosion-resistant copper tube according to the invention is formed of a copper tube which is made of a copper material or alloy (molten metal, ingot or the like) having a P content held within a range of 0.15-0.6% by weight and comprising the balance of Cu and impurities. In the case where the copper tube is subjected to cold working and then final annealing so as to include a recrystallized structure as a material structure, electric conductivity (Y1) of the copper tube is set to satisfy the above-described formula (1), while in the case where the copper tube is not subjected to the final annealing and a deformation structure remains, electric conductivity (Y2) of the copper tube is set to satisfy the above-described formula (2). Owing to these characteristics, even under a severer corrosive environment, the type of corrosion generated in the copper tube shifts from a selective corrosion in the form of the ants' nest which progresses in a direction perpendicular to an axial direction of the copper tube (i.e., in a direction of a wall thickness of the copper tube) to a surface corrosion which progresses in a direction parallel to the axial direction of the copper tube (i.e., in a direction along the surface of the copper tube) so that the ant nest corrosion is effectively suppressed or prevented, whereby the copper tube can exhibit a corrosion resistance which is considerably higher than that of the conventional copper tube.

[0027] With respect to the Cu material to provide the above-described copper tube according to the invention, the P content is set so as to be not lower than 0.15% by weight, because where the P content of the copper tube is lower than 0.15% by weight, the selective corrosion which progresses in the form of the ants' nest is likely to be generated under a severer corrosive environment. On the other hand, an excessive amount of the P content does not permit substantially effective improvement in the resistance of the copper tube against the ant nest corrosion, and even causes deterioration of workability of the copper tube during production, giving rise to a problem of cracking of the copper tube, for example. For this reason, the upper limit of the P content needs to be 0.6% by weight to optimize the amount of the solid-solubilized P with respect to Cu, as described later.

[0028] The highly corrosion-resistant copper tube according to the invention is formed of the material comprising the balance of Cu and impurities in addition to the above-described amount of P. In the invention, a content of a group of specific impurity elements consisting of Cr, Mn, Fe, Co, Zr and Mo, among the impurities, is controlled so as to be not higher than 0.01% by weight in total, so that the corrosion resistance of the copper tube is further improved. It is because the group of the specific impurity elements is likely to form a compound with P by annealing or other heat treatments, resulting in deterioration of the corrosion resistance of the copper tube due to a generated P-based precipitation.

[0029] Furthermore, as inevitable impurities contained with Cu in the copper tube material, there are S, Si, Ti, Ag, Pb, Se, Te, Bi, Sn, Sb, As and the like in addition to the above-described group of the specific impurity elements. The total amount of such inevitable impurities is preferably controlled so as to be not higher than 0.005% by weight.

[0030] As the Cu material in which a content of the above-described group of the specific impurity elements and other inevitable impurity elements is reduced, a commercially pure copper whose purity is increased by a conventional smelting technique, such as an electrolytic copper obtained by increasing the purity so as to include not lower than 99.99% by weight of Cu, is advantageously used.

[0031] In the copper tube obtained by forming the Cu material controlled to have the above-described P content, the electric conductivity, which relates to the amount of solid-solubilized P, is held within a predetermined range in accordance with the amount of deformation by working of the copper tube, so that a remarkable resistance to the ant nest corrosion is exhibited. Namely, in the case where the tube-making step comprises an annealing (final) step after hot extrusion of the Cu material to form a Cu blank tube and plastic working (cold working) processes of the blank tube such as rolling and drawing, and a grooving process such as inner grooving, whereby a crystal structure of the copper tube takes the form of a recrystallized structure, the electric conductivity (Y1: %IACS) of the tube satisfies the above-described formula (1). On the other hand, in the case where the annealing is not performed and the crystal structure of the copper tube remains to be the deformation structure which is formed during the cold working (including a case where the annealing (intermediate annealing) is performed during the drawing process, and a case where the annealing is performed after the drawing and then the cold working like the grooving is further performed), the electric conductivity (Y2: %IACS) of the tube satisfies the above-described formula (2). By controlling the electric conductivity as described above, a sufficient amount of solid-solubilized P required for the resistance to the ant nest corrosion is assured, so that a high degree of corrosion resistance can be stably achieved. It is noted that tubes having the deformation structure also include ones which have a mixture of the deformation structure and the recrystallized structure wherein the recrystallized structure formed by annealing is lightly processed so that the surface portion is the deformation structure while the inner portion remains to be the recrystallized structure.

[0032] In summary, the most vital point of the invention is to control the electric conductivity so as to satisfy either the above-described formula (1) or formula (2) depending upon whether the copper tube is subjected to the final annealing or not, that is, whether the microstructure of the copper tube is the recrystallized structure or the microstructure which includes the deformation structure, so that even under a severer corrosive environment, the type of corrosion generated in the copper tube shifts from the selective corrosion which progresses in the direction perpendicular to the axial direction

of the copper tube (i.e., in the direction of the wall thickness of the copper tube) to the surface corrosion which progresses in the direction parallel to the axial direction of the copper tube (i.e., in the direction along the surface of the copper tube), whereby the copper tube can exhibit a corrosion resistance which is considerably higher than that of the conventional copper tube.

[0033] When the electric conductivity (Y1) of the copper tube subjected to the final annealing so as to include the recrystallized structure is lower than (50-75X), or the electric conductivity (Y2) of the copper tube including the deformation structure is lower than (47-75X), the form of the generated corrosion shifts from the surface corrosion to the selective corrosion, namely the ant nest corrosion, causing deterioration of the corrosion resistance. On the other hand, when the electric conductivities (Y1, Y2) have higher values than those of the right member of the above-described formulae (1) and (2), namely (60-75X) and (57-75X) respectively, the corrosion resistance becomes saturated, and rather the workability of the tubes may be deteriorated when they are fixed to equipment as a heat transfer tube or a refrigerant tube.

[0034] By setting the electric conductivities (Y1 or Y2) as described above, the copper tube formed of the material wherein the concentration of the solid-solubilized P in the matrix phase of Cu is held within an optimum range of 0.15-0.50% by weight is realized, so that even when the corrosion is generated under an environment vulnerable to the ant nest corrosion, the corrosion progresses in the form of the general corrosion or the pitting corrosion, not in the ant nest corrosion, so that the corrosion resistance to the ant nest corrosion is further improved.

[0035] As described above, in the invention, the concentration of the solid-solubilized P in the matrix phase of Cu is defined depending on the electric conductivity, whereby an excellent resistance to the ant nest corrosion is achieved. Generally, the electric conductivity can be easily measured by an eddy current conductivity meter, which is easy to carry and permits stable measurement of the concentration of the solid-solubilized P. To calculate the amount of solid-solution of additive elements in a metal, a method wherein the amount of the additive elements in a compound including the additive elements is subtracted from a component value of the additive elements is generally employed. The amount of the compound is determined by a method wherein the amount is calculated referring to a metal photograph by a transmission electron microscope and the like, a method wherein constituents other than the compound are dissolved by an acidic solution so as to calculate the amount from the weight of the residue, and the like. However, each of these methods requires considerable time and labor, so that the calculation is difficult to perform.

[0036] In production of the copper tube according to the invention described above, usually a cast body such as an ingot or a billet formed of the Cu material having the above-described P content (concentration) is subjected to conventional processes such as casting, homogenization treatment, hot extrusion, rolling, drawing and grooving of the tube, so as to obtain a desired copper tube. In order that the conductivity (Y1) of the copper tube subjected to annealing so as to include the recrystallized structure and the conductivity (Y2) of the copper tube not subjected to the final annealing so as to include the deformation structure satisfy the above-described formula (1) and formula (2) respectively, a method wherein a preliminary heating in the hot extrusion step, which is a hot plastic working, serves also as the homogenization treatment is preferably employed. The preliminary heating is performed at a temperature of 750-950°C and held for at least 30 minutes, and subsequently the hot extrusion is performed at a temperature of 750-950°C. However, where the homogenization treatment is performed in a separate step, the heating is performed at a temperature of 750-950°C for at least 30 minutes, whereby a P segregation layer is effectively removed. Furthermore, by performing the subsequent hot extrusion at a temperature of at least 750°C, the structure of cast metal is effectively destroyed so that the added P is uniformly solid-solubilized in the material. In this respect, it is noted that the upper limit of the length of time for which the above-described heating temperature is kept is generally set to be 12 hours from the economical viewpoint. If the heating is performed at a temperature higher than 950°C, the material may suffer from cracking during the hot extrusion, giving rise to a problem of difficulty in assuring safe working.

[0037] It is also possible to employ methods such as a casting-and-rolling process and an upcasting (continuous casting) process, which have been proposed in recent years, to produce the highly corrosion-resistant copper tube according to the invention. In these methods, a Cu molten metal which is controlled to have the above-described P content is formed into the copper tube directly by casting, while conditions at the time of casting such as speeds of stirring of the components and cooling are appropriately controlled and steps such as subsequent drawing and annealing are employed as necessary, whereby the desired highly corrosion-resistant copper tube can be obtained.

[0038] Furthermore, in the above-described production process, a desired size of copper tube formed by the drawing, which is cold working, is used without or after subjection to the predetermined final annealing, for a desired purpose. Alternatively, the copper tube obtained in the drawing step is further subjected to the cold working such as a grooving step, for example an internal grooving, external grooving and the like, as necessary, so as to obtain a desired size of copper tube. The copper tube is then used without or after subjection to the predetermined final annealing, for a desired purpose.

[0039] The final annealing to the copper tube as described above is performed for changing the microstructure from the deformation structure to the recrystallized structure so as to enhance the workability of the tube during a bending process, for example. In general, the final annealing is performed at an annealing temperature of 300-600°C, and an annealing time is suitably set within a range of around 5-120 minutes. The annealing temperature lower than 300°C

causes difficulty to achieve sufficient effects of annealing, while the annealing temperature higher than 600°C has a risk of deterioration of the corrosion resistance of the copper tube. Furthermore, the annealing time shorter than 5 minutes provides almost no effect of annealing, while the effect of annealing is saturated and the economy of production is deteriorated where the annealing time exceeds 120 minutes.

[0040] Sizes such as an outside diameter and a thickness (wall thickness of the tube) of the copper tube obtained according to the invention as described above are suitably set according to the use of the copper tube. In the case where the copper tube according to the invention is used as the heat transfer tube, the copper tube may have smooth (or non-grooved) inner and outer surfaces which are formed by the tube extrusion. Alternatively, the heat transfer tube may advantageously have internal or external grooves of various shapes formed by various known internal or external working.

[0041] As described above, the copper tube according to the invention is obtained by tube-making the Cu material whose P content is 0.15-0.6% by weight, and is formed to have the electric conductivity (Y1 or Y2) which satisfies the above-described formula (1) or formula (2) depending upon whether it has been subjected to the final annealing or not (namely, the form of the microstructure), so that the tube advantageously exhibits a high degree of resistance to the ant nest corrosion.

[0042] By utilizing such characteristics according to the invention, the copper tube is advantageously used as a tube which is disposed in a damp environment and subjected to corrosion that progresses in the form of an ants' nest from the surface of the tube in the direction of the wall thickness due to a corrosive medium in the form of the lower carboxylic acid.

[0043] The above-described copper tube according to the invention is advantageously used as a heat transfer tube or refrigerant tube in air-conditioning equipment, and also as a heat transfer tube or refrigerant tube (tubes arranged inside desired equipment) in refrigerating equipment.

EXAMPLES

[0044] To clarify the present invention more specifically, some examples according to the present invention will be described. It is to be understood that the invention is by no means limited by details of the illustrated examples, but may be embodied with various changes, modifications and improvements which are not described herein, and which may occur to those skilled in the art, without departing from the spirit of the invention.

[0045] Initially, billets Nos. 1-15 corresponding to respective copper tubes Nos. 1-15 were cast by adding P in ratios shown in Table 1 to an highly pure electrolytic copper whose Cu content is not lower than 99.999% by weight, while billets Nos. 20-31 corresponding to respective copper tubes Nos. 20-31 were cast by adding, in addition to P in ratios shown in Table 1, any one of Cr, Mn, Fe Co, Zr and Mo constituting a group of specific impurity elements in ratios shown in Table 1, so as to examine effects of inclusion of the group of the specific impurity elements. Further, billets Nos. 16-19 corresponding to respective copper tubes Nos. 16-19 were cast by adding Si or Ti, which are inevitable impurity elements other than the group of the specific impurity elements, in ratios shown in Table 1.

Table 1

Billet No.	Content of chemical components (% by weight)									
	P	Si	Ti	Cr	Mn	Fe	Co	Zr	Mo	Cu
1	0.20	-	-	-	-	-	-	-	-	balance
2	0.20	-	-	-	-	-	-	-	-	balance
3	0.22	-	-	-	-	-	-	-	-	balance
4	0.22	-	-	-	-	-	-	-	-	balance
5	0.50	-	-	-	-	-	-	-	-	balance
6	0.50	-	-	-	-	-	-	-	-	balance
7	0.23	-	-	-	-	-	-	-	-	balance
8	0.23	-	-	-	-	-	-	-	-	balance
9	0.38	-	-	-	-	-	-	-	-	balance
10	0.38	-	-	-	-	-	-	-	-	balance
11	0.13	-	-	-	-	-	-	-	-	balance

(continued)

Billet No.	Content of chemical components (% by weight)									
	P	Si	Ti	Cr	Mn	Fe	Co	Zr	Mo	Cu
12	0.13	-	-	-	-	-	-	-	-	balance
13	0.22	-	-	-	-	-	-	-	-	balance
14	0.22	-	-	-	-	-	-	-	-	balance
15	0.65	-	-	-	-	-	-	-	-	balance
16	0.30	0.08	-	-	-	-	-	-	-	balance
17	0.30	0.08	-	-	-	-	-	-	-	balance
18	0.31	-	0.08	-	-	-	-	-	-	balance
19	0.31	-	0.08	-	-	-	-	-	-	balance
20	0.28	-	-	0.07	-	-	-	-	-	balance
21	0.28	-	-	0.07	-	-	-	-	-	balance
22	0.29	-	-	-	0.10	-	-	-	-	balance
23	0.29	-	-	-	0.10	-	-	-	-	balance
24	0.30	-	-	-	-	0.05	-	-	-	balance
25	0.30	-	-	-	-	0.05	-	-	-	balance
26	0.31	-	-	-	-	-	0.10	-	-	balance
27	0.31	-	-	-	-	-	0.10	-	-	balance
28	0.29	-	-	-	-	-	-	0.05	-	balance
29	0.29	-	-	-	-	-	-	0.05	-	balance
30	0.29	-	-	-	-	-	-	-	0.08	balance
31	0.29	-	-	-	-	-	-	-	0.08	balance

[0046] Next, the billets nos. 1-31 were heated to a temperature of 700, 820 or 825°C respectively, as shown in Table 2, held at the temperature for 1 hour, and then subjected to hot extrusion at a temperature of 700, 820 or 825°C so as to obtain various extruded blank tubes with an outside diameter of 102mm and an inside diameter of 75mm. Further, the obtained extruded blank tubes were subjected to cold rolling by a Pilger mill rolling machine so as to obtain rolled blank tubes with an outside diameter of 46mm and an inside diameter of 39.8mm. A working ratio (reduction of area) at the time of the cold rolling was 88.9%. The reduction of area is calculated according to the following formula:

$$\text{Reduction of area (\%)} = [(\text{cross-sectional area before working} - \text{cross-sectional area after working}) / \text{cross-sectional area before working}] \times 100$$

[0047] Then, the various rolled blank tubes obtained as described above were subjected to cold drawing for a plurality of times so as to obtain drawn blank tubes having an outside diameter of 7.8-10.0mm and a thickness of 0.25-0.30mm. The working ratio in the entire cold drawing is 95.1-97.0% based on the reduction of area. The total working ratio in the cold rolling and cold drawing, namely the total working ratio in the cold working is 98.9-99.3% based on the reduction of area. Furthermore, during the above-described drawing process, one or a plurality of intermediate annealing processes was/were performed. After the final drawing, the intermediate annealing was performed to produce a base tube prepared for component rolling. The intermediate annealing was performed at a temperature of 600°C.

[0048] Each of the obtained various base tubes was subjected to conventional ball-rolling (cold working) process, so that internally grooved tubes (copper tubes Nos. 1-31) which have a plurality of spiral grooves formed in an inner circumferential surface were prepared as seamless tubes used as heat transfer tubes to be used in a cross-fin tube type heat exchanger. These internally grooved tubes have the following specifications: outside diameter of 7.0mm; groove-bottom wall thickness (t) of 0.23mm; fin height (h) of 0.22mm; fin apical angle (γ) of 13°; 44 spiral grooves; and lead

angle (α) of 28°.

[0049] Among the obtained internally grooved tubes, each of the copper tubes Nos. 1, 3, 5, 7, 9, 11, 13, 16, 18, 20, 22, 24, 26, 28 and 30 was formed into a level wound coil (LWC) wherein the tube is multiply and regularly wound in a cylindrical coil and uncoiled from the inner circumference of the coil. Then, each level wound coil was subjected to the final annealing in a roller-hearth continuous annealing furnace at a temperature of 500°C for 20 minutes.

[0050] It is noted that, in production of the above-described internally grooved tubes (copper tubes), the copper tube No. 15 was made of a Cu material containing an excessive amount of P, so that the tube suffered from deficiencies such as a crack during tube-making, and the working could not be finished so as to obtain a copper tube to be subjected to the corrosion test.

[0051] To calculate a content of impurities in the copper tubes Nos. 1-14, each copper tube was dissolved into an acid (aqua regia) and analyzed by a high-frequency inductively coupled plasma emission spectrometric analysis method (ICP-OES) with respect to contents of elements included as the impurities in the tube. As a result, it was confirmed with respect to all of the copper tubes that the total content of the group of the specific impurity elements (Cr, Mn, Fe, Co, Zr and Mo) was less than 0.010% by weight, and also the total content of the inevitable impurities other than the group of the specific impurity elements (S, Si, Ti, Ag, Pb, Se, Te, Bi, Sn, Sb and As) was less than 0.005% by weight.

[0052] With respect to each of the obtained internally grooved tubes (copper tubes) subjected to the final annealing and those not subjected to the final annealing, the electric conductivity was measured with an eddy current conductivity meter. Results are shown in Table 2 given below.

Table 2

Copper tube No.	Hot extrusion			Annealing temperature (°C)	Electric conductivity (%IACS)
	Heating temperature (°C)	Holding time (min)	Extruding temperature (°C)		
1	820	60	820	500	37
2	820	60	820	No annealing	36
3	820	60	700	500	40
4	820	60	700	No annealing	38
5	820	60	820	500	13
6	820	60	820	No annealing	12
7	825	60	825	500	40
8	825	60	825	No annealing	38
9	825	60	825	500	26
10	825	60	825	No annealing	25
11	820	60	820	500	40
12	820	60	820	No annealing	38
13	700	60	700	500	48
14	700	60	700	No annealing	46
15	820	60	820	-	-
16	820	60	820	500	42
17	820	60	820	No annealing	41
18	820	60	820	500	41
19	820	60	820	No annealing	40
20	820	60	820	500	43
21	820	60	820	No annealing	42
22	820	60	820	500	40

(continued)

Copper tube No.	Hot extrusion			Annealing temperature (°C)	Electric conductivity (%IACS)
	Heating temperature (°C)	Holding time (min)	Extruding temperature (°C)		
23	820	60	820	No annealing	39
24	820	60	820	500	46
25	820	60	820	No annealing	45
26	820	60	820	500	43
27	820	60	820	No annealing	41
28	820	60	820	500	46
29	820	60	820	No annealing	45
30	820	60	820	500	49
31	820	60	820	No annealing	48

[0053] Subsequently, each of the thus prepared internally grooved tubes (copper tubes Nos. 1-31) was subjected to an ant nest corrosion test by using a test apparatus shown in Fig. 3. In Fig. 3, 2 represents a plastic container which has a capacity of 2L and which can be hermetically sealed with a cap 4. Silicone plugs 6 are attached to the cap 4 such that the plugs 6 extend through the cap 4. Copper tubes 10 are inserted into the plastic container 2 by a predetermined length, such that the copper tubes 10 extend through the respective silicone plugs 6. Lower open ends of the copper tubes 10 are closed with silicone plugs 8. In this case, the length of the copper tubes is 18cm, and the length of the portion exposed to the inside of the plastic container is 15cm. Furthermore, 100mL of a formic acid aqueous solution having a predetermined concentration is accommodated in the plastic container 2, such that the copper tubes 10 do not contact with the aqueous solution.

[0054] In the ant nest corrosion test, the concentration of the formic acid aqueous solution 12 was set to be 0.1%. The copper tubes 10 were set in the plastic container 2 in which the formic acid aqueous solution 12 was accommodated, and the plastic container 2 was left within a constant temperature bath at a temperature of 40°C. The plastic container 2 with the copper tubes 10 was taken out of the bath and left for two hours at room temperature (15°C) each day, to cause dewing on surfaces of the copper tubes 10 due to a difference between the temperature of the constant temperature bath and the room temperature. The copper tubes 10 were subjected to the corrosion test under the above-described conditions for 80 days.

[0055] Each of the copper tubes subjected to the corrosion test was examined in the cross section of its part which was exposed to the inside of the plastic container 2, and measured the maximum corrosion depth from the outer surface of the tube. Results of the measurement are indicated in Table 3 given below.

Table 3

Copper tube No.	Characteristics of ant nest corrosion	
	Maximum corrosion depth (mm)	Evaluation
1	0.08	Good
2	0.09	Good
3	0.06	Good
4	0.06	Good
5	0.02	Good
6	0.03	Good
7	0.07	Good
8	0.07	Good
9	0.04	Good

(continued)

Copper tube No.	Characteristics of ant nest corrosion	
	Maximum corrosion depth (mm)	Evaluation
10	0.03	Good
11	0.14	Poor
12	0.14	Poor
13	0.13	Poor
14	0.14	Poor
15	-	-
16	≥ 0.3 (penetrated)	Poor
17	≥ 0.3 (penetrated)	Poor
18	≥ 0.3 (penetrated)	Poor
19	≥ 0.3 (penetrated)	Poor
20	≥ 0.3 (penetrated)	Poor
21	≥ 0.3 (penetrated)	Poor
22	≥ 0.3 (penetrated)	Poor
23	≥ 0.3 (penetrated)	Poor
24	≥ 0.3 (penetrated)	Poor
25	≥ 0.3 (penetrated)	Poor
26	≥ 0.3 (penetrated)	Poor
27	≥ 0.3 (penetrated)	Poor
28	≥ 0.3 (penetrated)	Poor
29	≥ 0.3 (penetrated)	Poor
30	≥ 0.3 (penetrated)	Poor
31	≥ 0.3 (penetrated)	Poor

[0056] As is apparent from the results indicated in Table 3, in the corrosion test using the aqueous formic acid solution having the concentration of 0.1 %, any of the copper tubes Nos. 1-10 formed of the Cu billet comprising P within the range of 0.15-0.6% by weight according to the invention wherein the electric conductivity (Y1) satisfies the above-described formula (1) for the tube subjected to the final annealing, and the electric conductivity (Y2) satisfies the above-described formula (2) for the tube not subjected to the final annealing, did not suffer from the ant nest corrosion, and merely had a slight corrosion generated on the outer surface of the tube.

[0057] On the contrary, although the copper tubes Nos. 11 and 12, which were the comparative examples, had the electric conductivity satisfying the formula (1) or (2), their content of P was less than 0.15% by weight, so that a remarkable ant nest corrosion was recognized in the tubes. Furthermore, the copper tubes Nos. 13, 14 and 16-31 had a content of P within the range of the invention, but their value of the electric conductivity was outside the range of the invention, so that a remarkable ant nest corrosion was recognized in each of the tubes. In particular, the copper tubes Nos. 16-31 suffered from the corrosion penetrating the tube walls. It is noted that the copper tube No. 15 was made of the Cu material (billet) containing an excessive amount of P, so that the tube could not be subjected to the entire tube-making process so as to obtain a valid copper tube to be subjected to the corrosion test. Thus, the intended corrosion test could not be performed with respect to the copper tube No. 15.

NOMENCLATURE OF REFERENCE SIGNS

- | | |
|----------------------|----------------------------------|
| 2: Plastic container | 4: Cap |
| 6: Silicone plugs | 8: Silicone plugs |
| 10: Copper tubes | 12: Formic acid aqueous solution |

Claims

1. A highly corrosion-resistant copper tube formed of a copper material consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities, **characterized in that** the tube includes a recrystallized structure and has electric conductivity (Y1: %IACS) which satisfies the following formula:

$$50-75X \leq Y1 \leq 60-75X$$

wherein X (% by weight) represents a content of phosphorus.

2. A highly corrosion-resistant copper tube formed of a copper material consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities, **characterized in that** the tube includes a deformation structure and has electric conductivity (Y2: %IACS) which satisfies the following formula:

$$47-75X \leq Y2 \leq 57-75X$$

wherein X (% by weight) represents a content of phosphorus.

3. The highly corrosion-resistant copper tube according to claim 1 or 2, wherein a content of a group of specific impurity elements consisting of Cr, Mn, Fe, Co, Zr and Mo among the impurities is not higher than 0.01 % by weight in total.
4. The highly corrosion-resistant copper tube according to claim 3, wherein a content of inevitable impurity elements other than the group of the specific impurity elements among said impurities is not higher than 0.005% by weight in total.
5. The highly corrosion-resistant copper tube according to any one of claims 1 to 4, wherein the tube is arranged in a damp environment and subjected to corrosion that progresses in the form of an ants' nest from a surface of the tube in a direction of a wall thickness of the tube by a corrosive medium in the form of a lower carboxylic acid.

6. A process for producing a highly corrosion-resistant copper tube comprising:

a step of providing a copper ingot consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities;
 a step of heat-treating the copper ingot at a temperature of 750-950°C;
 a step of hot-extruding the heat-treated copper ingot at a temperature of 750-950°C so as to obtain a copper blank tube;
 a step of cold-working the copper blank tube by a drawing process and further a grooving process as necessary to form a desired size of copper tube; and
 a step of subjecting the copper tube obtained by the cold working to final annealing so as to obtain the copper tube including a recrystallized structure and having electric conductivity (Y1: %IACS) which satisfies the following formula:

$$50-75X \leq Y1 \leq 60-75X$$

wherein X (% by weight) represents a content of phosphorus.

7. The process for producing a highly corrosion-resistant copper tube according to claim 6, wherein the final annealing is performed at a temperature of 300-600°C.
8. A process for producing a highly corrosion-resistant copper tube comprising:

a step of providing a copper ingot consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities;
 a step of heat-treating the copper ingot at a temperature of 750-950°C;

a step of hot-extruding the heat-treated copper ingot at a temperature of 750-950°C so as to obtain a copper blank tube; and

a step of cold-working the copper blank tube by a drawing process and further a grooving process as necessary to form a desired size of copper tube including a deformation structure and having electric conductivity (Y2: %IACS) which satisfies the following formula:

$$47-75X \leq Y2 \leq 57-75X$$

wherein X (% by weight) represents a content of phosphorus.

9. The process for producing a highly corrosion-resistant copper tube according to any one of claims 6 to 8, wherein the heat-treating step of the copper ingot is a homogenization process.

10. The process for producing a highly corrosion-resistant copper tube according to any one of claims 6 to 8, wherein the heat-treating of the copper ingot is a preliminary heat treatment performed in advance of the extrusion.

11. A heat transfer tube for air-conditioning equipment or refrigerating equipment, consisting of the highly corrosion-resistant copper tube according to any one of claims 1 to 5.

12. A refrigerant tube for air-conditioning equipment or refrigerating equipment, consisting of the highly corrosion-resistant copper tube according to any one of claims 1 to 5.

13. A method of improving a corrosion resistance of a copper tube against ant nest corrosion which is generated by a corrosive medium in the form of a lower carboxylic acid in a damp environment and progresses from a surface of the copper tube used for air-conditioning equipment or refrigerating equipment in the damp environment, wherein:

the copper tube is formed of a copper material consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities, and includes a recrystallized structure, and the copper tube has electric conductivity (Y1: %IACS) which satisfies the following formula:

$$50-75X \leq Y1 \leq 60-75X$$

wherein X (% by weight) represents a content of phosphorus.

14. A method of improving a corrosion resistance of a copper tube against ant nest corrosion which is generated by a corrosive medium in the form of a lower carboxylic acid in a damp environment and progresses from a surface of the copper tube used for air-conditioning equipment or refrigerating equipment in the damp environment, wherein:

the copper tube is formed of a copper material consisting of 0.15-0.6% by weight of phosphorus and the balance being copper and impurities, and includes a deformation structure, and the copper tube has electric conductivity (Y2: %IACS) which satisfies the following formula:

$$47-75X \leq Y2 \leq 57-75X$$

wherein X (% by weight) represents a content of phosphorus.

FIG. 1

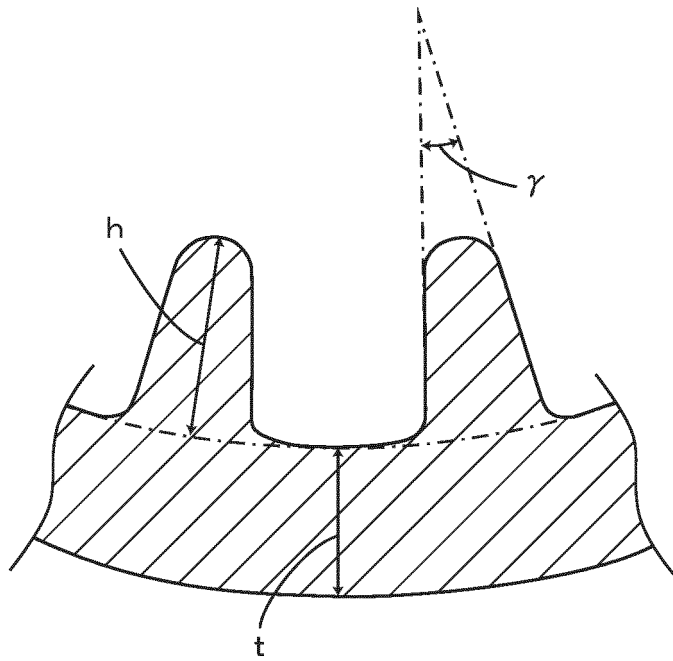


FIG. 2

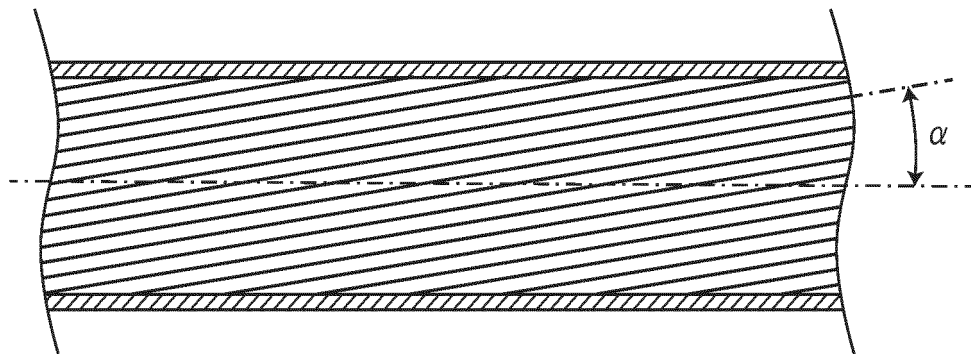
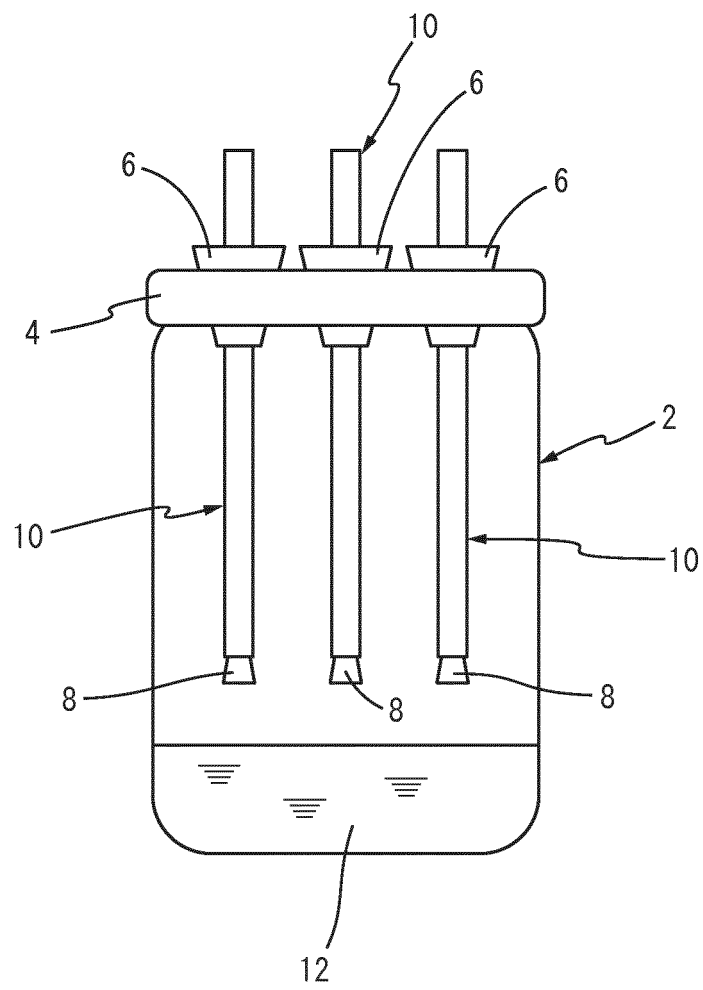


FIG. 3



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2017/016194

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/00(2006.01)i, F28F21/08(2006.01)i, C22F1/00(2006.01)n, C22F1/08(2006.01)n

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)

C22C1/00-49/14, C22F1/00-3/02, F28F21/08

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 1996-2017

Kokai Jitsuyo Shinan Koho 1971-2017 Toroku Jitsuyo Shinan Koho 1994-2017

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2001-247923 A (Sambo Copper Alloy Co., Ltd.), 14 September 2001 (14.09.2001), (Family: none)	1-14
A	JP 2008-304170 A (Kobe Steel, Ltd.), 18 December 2008 (18.12.2008), (Family: none)	1-14
A	JP 2009-235428 A (Kobelco & Materials Copper Tube, Ltd.), 15 October 2009 (15.10.2009), (Family: none)	1-14
A	WO 2014/148127 A1 (UACJ Corp.), 25 September 2014 (25.09.2014), & US 2015/0377568 A1 & CN 105143478 A	1-14

☐ 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
05 July 2017 (05.07.17)Date of mailing of the international search report
18 July 2017 (18.07.17)Name and mailing address of the ISA/
Japan Patent Office
3-4-3, Kasumigaseki, Chiyoda-ku,
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- WO 2014148127 A [0004] [0006]