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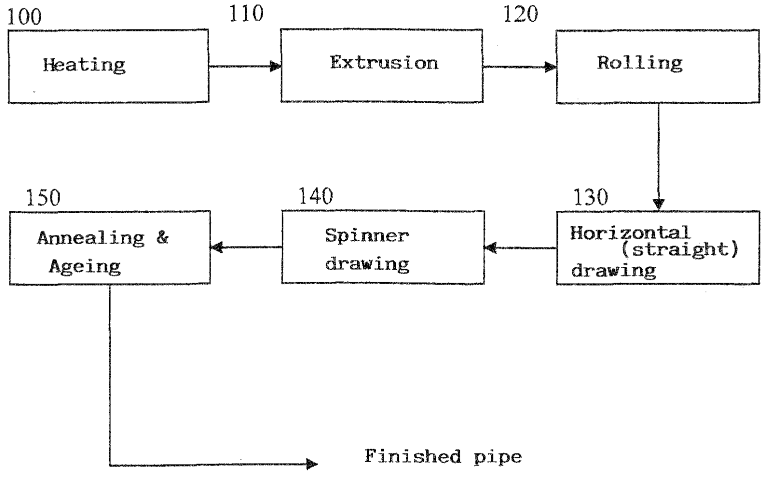
(54) Method for the production of alloy pipes for heat exchangers using precipitation hardening through underwater extrusion

(57) Production method for heat exchanger pipes comprising the following stages:
a) production of a billet in an alloy suitable for hardening through precipitation;
b) direct hot extrusion under hydrostatic head in a water bath, of the billet previously heated to a temperature equal to or higher than the solution heat treatment of the alloy, in order to construct an extruded pipe blank of a pre-determined size;
c) cold rolling of the extruded pipe blank to obtain a rolled blank having a reduced transversal measurement and consequently having an increased length;
d) subjecting the rolled blank to a straight drawing process to obtain a semi-finished pipe;
e) subjecting the semi-finished pipe to spinner drawing to reduce the transversal measurement and consequently, to obtain a pipe having its definitive size;
f) subjecting the pipe to annealing in a tunnel furnace in a manner to determine the hardening of the pipe through precipitation.

FIG. 3



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Description

Technical field

[0001] The present invention relates to a production method for heat exchanger pipes, in particular for application in air conditioning and refrigeration sectors, or more in general, for applications that require high thermo-mechanical properties.

Background

[0002] Generally, piping used in ACR (Air Conditioning and Refrigeration) sectors are produced from Cu-DHP (Deoxidized High residual Phosphorous) alloys, without oxygen, wherein, in order to guarantee deoxidation a relatively high residual phosphorous content must be maintained, normally between 0.015 and 0.04%. The presence of phosphorous is able to eliminate any effects of fragility in reducing environments, and improve cold plastic deformability and above all increase the aptitude for brazing. Cu-DHP alloys have therefore proved as being particularly suitable for metal working applications, where seams must be mechanically stable. In fact, in brazing processes, deoxidizers are often used precisely in order to prevent the surface from becoming covered with oxides (the formation of which is induced by the heat) which hinder correct copenetration of the added alloy material. In a similar manner, if the copper contains oxygen before processing, the strength of the seam will be compromised. For this reason, the type of copper used for rolled products for roofing and metalworking, but also for the production of pipes for fluid distribution installations, is Cu-DHP. In particular, these alloys are used regularly for cooling fluid piping, which currently use HFC, having almost totally replaced CFC.

[0003] However, current trends in global environmental policies (such as the regulations set out in the Kyoto protocol) wish to encourage the market in the direction of other less damaging cooling fluids for the environment, above all in relation to the repercussions at global level due to greenhouse effects. However, from an operational viewpoint, these cooling fluids require higher working pressure.

[0004] The use of common ACR pipes in heat exchangers which operate under these working pressure levels would also necessarily provoke a considerable increase in the pipe thickness, with the relative increase in production costs, especially considering the constant increase in raw material prices in recent years. Furthermore, greater pipe thickness results in a reduction in exchange coefficients, thus penalising the overall refrigeration process efficiency.

[0005] This drawback remains, although to a lesser degree, even when producing pipes in a suitable manner to increase thermal exchange efficiency, such as providing a suitable corrugated internal surface on pipes, by applying profiles with relatively complex geometries, which increase fluid turbulence inside the pipes thus provoking higher exchange coefficients. In particular, it is possible to produce profiles that guarantee excellent thermal exchange efficiency, by impressing the flat surface of a strip with one or more ribbed rollers. This solution is able to also provide criss-crossed ribbing.

[0006] Beginning with this type of ribbed strip, it is possible to then produce a pipe using suitable lengthwise welding.

[0007] As an alternative, it is possible to improve the mechanical characteristics of the pipe, while at the same time limiting to a considerable degree the pipe thickness required because of higher working pressure, by using alloys having stronger mechanical characteristics.

[0008] Among the copper alloys (or in any case, those having high thermal and electrical conductivity), and possessing relatively high mechanical resistance characteristics, are the alloys susceptible for precipitation hardening, such as those described in the patent EP-B-0399070.

[0009] Precipitation hardened alloys are processed using a specific heat treatment including a first heating stage at a temperature high enough to provoke complete solution heat treatment in the base metal of the constituent that makes the alloy susceptible to hardening (forming of a solid solution); a second cooling stage which may be shorter or longer, (quench hardening) wherein the solid solution is brought to oversaturation conditions and therefore thermodynamically metastable; and a last stage, for ageing, which creates the segregation of a precipitate, accompanied by a distortion of the base lattice which provokes a considerable increase in the hardening properties. Among the alloys that react in this manner are the Cu-Fe-P and Cu-Fe-Ni-P systems, which can undergo suitable heat treatment to create a great improvement in the mechanical properties in relation to those of pure copper, while maintaining their electrical and thermal conductivity properties practically unchanged.

[0010] The mechanical properties of the precipitation hardened alloys of Cu-Fe-P and Cu-Fe-Ni-P systems depend on the specific heat treatment which they undergo during their preparation, and that is conceived to optimise the development of the mechanical resistance and the electrical and thermal conductivity. Their hardness and mechanical resistance depend on the quench hardening stage as well as the ageing and precipitation treatment. Furthermore, the electrical conductivity grows during the course of the treatment until it reaches a maximum, normally when it reaches the precipitate status.

[0011] The use of these alloys to replace Cu-DHP alloys for producing pipes using longitudinal welding, such as those beginning from a ribbed strip, does have certain drawbacks. Because of the concentrated high heat levels developed with traditional welding techniques, this leads to a worsening in the thermo-mechanical characteristics of the alloy along the weld seam, where a new solution heat treatment would occur on the precipitate. For this reason, such as that described in the Japanese patent application n°. JP 2002-108180, according to prior art a process exists to obtain welded pipes produced using an alloy susceptible to precipitation hardening wherein the pipe is first formed and welded using a flat strip, and only following this process are solution heat treatment, quench hardening and ageing processes applied, in other words, operating on pipes that are substantially finished (or possibly only subjected to one or more cold-drawing processes). However, this method consumes very high amounts of energy which increases the cost of the finished pipe even further.

[0012] Moreover, it is obvious that direct pipe forming from alloys susceptible to precipitation hardening, such as through extrusion as described in the Japanese patent application n°. JP 2003-089378, also involves a range of practical problems that need to be resolved. In particular, the solution heat treatment is especially costly and complex to perform at high temperatures, followed by the quench hardening process in order to maintain iron and phosphorous in solid solution with the copper in the correct conditions from the viewpoint of thermodynamic equilibrium, in order to induce precipitation.

[0013] The ageing stage too, essential in order to provide the material with the required electrical conductivity, and above all, thermal properties, also in this case, lead to consuming a large amount of energy, and prolonging the production times.

[0014] Therefore one aim of the present invention is to provide a production method for heat exchanger pipes conceived to work under the high pressure levels dictated by the use of new thermal fluids, and which is free of the drawbacks described above, and in particular, that results as relatively simple and economical to perform, while also providing pipes with a relatively reduced thickness (in order to prevent a negative influence on the thermal exchange coefficiency), but having high mechanical resistance. Another aim of the invention is to provide a method having the aforesaid characteristics, able to use alloys which are already readily available and that do not require the creation of a specific alloy for the purpose.

Summary of the invention

[0015] According to the present invention, therefore, a production method is provided for pipes having high mechanical resistance and high thermal exchange capacity, in particular for application on heat exchangers, as defined in Claim 1.

[0016] In particular, according to the invention, said pipes are produced using any type of metal alloy having high thermal and electrical conductivity properties, susceptible to being subjected to a precipitation hardening process (ageing) based on blanks obtained through hot extrusion of billets performed with the exit of the hot blank transferred directly under hydrostatic head in a water bath in order to guarantee extremely rapid cooling speed, totally comparable with traditional quench hardening processes.

[0017] In particular, the billets are extruded after they have been heated to a relatively high temperature, equal to, or preferably higher than the temperature of the solution heat treatment of the metal alloy which is used each time (for example approximately 900°C for a copper alloy of the KFC type, in other words, alloyed with Fe, P and, possibly, Ni), thus enabling the alloying elements responsible for precipitation hardening, such as phosphorous and iron, to be bought completely to solution in the billet. The rapid cooling of the external wall of the extruded product, which is the direct result of performing extrusion under hydrostatic water head, guarantees not only the billet cooling, but also a cooling process strong enough to determine "solution heat treatment" quench hardening, in other words, performed with a cooling speed such that it is able to maintain the solid solution of alloying elements in the base matrix of the alloy (normally Cu) even at room temperature, in oversaturation conditions. In this manner the solution heat treatment and quench hardening processes are performed without the need for a separate heat treatment stage ad hoc, but performed at the same time as the extrusion stage, thus providing considerable energy saving.

[0018] After this stage, the extruded pipe blank obtained in this manner, undergoes a range of traditional cold processing stages according to prior art, such as rolling and drawing, in such a manner so that the transversal measurements (wall diameter and thickness) are gradually reduced and consequently the length is also increased, until the definitive measurements for the finished pipes have been reached as required.

[0019] Naturally, during these cold-processing stages the material is subject to work hardening, which can even be quite considerable. Therefore, at the end (or towards the end) of the cold mechanical process, the extruded, rolled and drawn pipes must undergo distension heat treatment (annealing or crystallization).

[0020] According to a further characteristic of the method according to the invention, said "inevitable" final heat treatment stage is performed at the end of the production cycle, choosing the temperature and length of the crystallization operation in the most suitable manner, in order to also perform the ageing process of the material at the same time, with the consequential precipitation of intermetallic compounds on the edge of the grains of the metal matrix as a result of the "mobilisation" of the alloying elements previously brought into solid solution in oversaturation conditions, caused by the heat treatment and the following slow cooling .

[0021] More precisely, the production method for pipes for heat exchangers according to the present invention comprises the following stages:

a) production of a billet in an alloy susceptible to precipitation hardening and having suitable thermal conductivity;
b) hot extrusion directly under hydrostatic head in a water bath of said billet previously heated to a temperature equal to or higher than that of the solution heat treatment of the alloy, to construct an extruded pipe blank having a predetermined size;
c) cold rolling of the extruded pipe blank in such a manner to obtain a rolled blank having a reduced transversal measurement, and consequently an increased length;
d) subjecting the rolled blank to straight drawing in order to obtain a semi-finished pipe;
e) subjecting the semi-finished pipe to spinner drawing to reduce the transversal measurement and consequently to obtain a pipe having substantially definitive measurements;
f) subjecting the pipe to annealing in a tunnel furnace performed in such a manner to determine the hardening of the pipe through the precipitation of at least part of the alloying elements contained in said alloy and previously brought to solid solution during the extrusion stage.

[0022] In this manner, with the same thermal conductivity, which is determined by the choice of the chemical composition of the alloy each time it is used, pipes can be produced which are mechanically very resistant, in particular, to the application of strong internal pressure, thanks to the fact that the material results as having a greater basic mechanical resistance caused by the precipitation of intermetallic compounds (ageing), as well as the fact that the pipes obtained in this manner have no seams (seamless), unlike welded pipes commonly used for thermal exchange applications.

[0023] Preferably, the billets are produced using an alloy chosen within Cu-Fe-P and Cu-Fe-Ni-P systems. More preferably, according to the method of the present invention, the billets are produced using an alloy from the Cu-Fe-P and Cu-Fe-Ni-P systems wherein the Fe is between 800 and 1500 ppm, the P is between 250 and 500 ppm and the Ni is in the interval between 100 and 20000 ppm with a Fe/P weight ratio between 2,5 and 5, preferably 4. Furthermore other precipitation system alloys can also be used, wherein the Cu is present with one or more elements chosen from among Ni , Co, Mg, Zr, Si, Cr, B, Sb, Zn, Be, Sn, Al, Ag, Ti and Mn.

Brief description of the figures

[0024] A preferred embodiment of the invention is now described, provided simply as a non-limiting example with reference to the figures in the appended drawings wherein:

- figure 1 schematically shows a cross-section of a tank wherein under hydrostatic head in a water bath, the stage b) of extrusion of a preheated billet is performed according to the method of the present invention;
- figure 2 shows a further cross-section of the tank shown in figure 1 illustrating how a section of the extruded and quench hardened blank is moved away from the tank to undergo the successive operations according to the method of the present invention;
- figure 3 is a block diagram that schematically shows sequence of the successive processing stages that comprise the method according to the present invention.

Detailed description

[0025] The production method of pipes for heat exchangers according to the present invention foresees, first of all, the melting of bars of any type of metal alloy possessing high thermal and electrical conductivity properties, and which is susceptible to undergoing a precipitation hardening process (ageing), preferably being an alloy chosen from within Cu-Fe-P and Cu-Fe-Ni-P systems. More preferably, the bars are melted using an alloy within Cu-Fe-P and Cu-Fe-Ni-P systems having a Fe/P ratio between 2,5 and 5.

[0026] Successively, the bars are cut into billets for the following extrusion operation (for example, performed at approximately 900°C for a copper alloy of the KFC type, in other words alloyed with Fe, P and, possibly, Ni), which enables the alloying elements (successively) responsible for the precipitation hardening, such as phosphorous and iron, to be brought completely to solution in the billet.

[0027] The extrusion is performed using a heating furnace inside which the temperature is increased progressively between the entrance and the exit to provide a plurality of zones having different temperatures, preferably between 600 and 1200°C, more preferably between 700 and 1100°C. The period of time the billet remains inside the furnace is approximately an hour and a half. In this manner, the billets are heated (block 100 in Figure 3) to a temperature equal to, or preferably higher than, the temperature of the solution heat treatment of the metal alloy which is used each time.

The temperature of the billets on exit from the furnace is therefore between 900 and 950°C, preferably between 910 and 930°C, while that of the shell, (in other words the temperature at which the container is maintained to prevent excessive thermal amplitude during the extrusion campaign) is equal to approximately 430°C. This heating process permits the alloying elements responsible for the precipitation hardening, such as phosphorous and iron to be brought completely to solution in the billet.

[0028] According to one aspect of the present invention the extrusion (block 110 in Figure 3) is performed with the exit of the hot extruded blank, having predetermined measurements, directly under hydrostatic head in a water bath (Figure 1), in a manner to guarantee extremely rapid cooling speed, totally comparable to that obtained using traditional quench hardening processes. Since the extruded pipe blank exits from the drawplate at a temperature over 900°C, at a speed of approximately 450 mm/s, the water bath is maintained suitably at a temperature no higher than 50°C, thus guaranteeing a cooling speed no lower than approximately 40°C/s.

[0029] The homogeneous cooling of the pipe is ensured by maintaining an effective hydrostatic head of at least 300mm above the pipe, guaranteed not only by the geometry of the tank itself and its position in relation to the extrusion drawplate, but also through the use of a high pressure water jet system that hits the extruded pipe at a tangent lapping the entire surface.

[0030] In this way, thanks to its high thermal inertia, the water bath cools the external wall of the extruded piece rapidly, blocking in conditions of thermodynamic non-equilibrium, the iron and phosphorous previous solubilized during the heating of the billet. This substantially represents "solution heat treatment" quench hardening, in other words performed by the cooling speed that is such that it provokes the maintaining in solid solution of the alloying elements in the base matrix of the alloy (normally, Cu) even at room temperature, in conditions of oversaturation. In this stage of the process, segregation can occur in part of the alloying elements through intermediate metastable stages, and therefore, during the first moments in the solid solution certain zones are formed which are richer in solute atoms that tend to move to positions of greater symmetry, inserting themselves into the gaps of the base lattice. This provokes lattice distortion, which is accompanied by a considerable increase in the hardening, but on the other hand, also accompanied by a reduction in the thermal and electrical conductivity.

[0031] Extrusion performed under water does not require a specific solution heat treatment process ad hoc followed by a separate quench hardening process; performing both operations simultaneously contributes towards considerable energy saving, and at the same time, permits monitoring of the characteristics of the produced material.

[0032] Following this stage in the production process, the extruded pipe blanks thus obtained and moved out of the tank (Figure 2) then undergo a range of traditional cold processes such as rolling and drawing (blocks 120 to 140 in Figure 3), in a manner to gradually reduce the transversal measurements (wall diameter and thickness) and therefore, also to increase the length, until the definitive required finished pipe measurements have been obtained.

[0033] These operations involve very strong plastic deforming, and therefore, together with the considerable reduction in the external diameter and thickness of the pipe, from a metallographic point of view, this leads to a strong hardening effect which can be noted in an increased hardness of the material.

[0034] After the cold rolling stage (block 120), the rolled blanks undergo a straight drawing stage (straight drawing, block 130 in Figure 3), with further reduction of the external diameter and thickness, however, not accompanied by further increase in hardness. The rolling, considered as the most difficult stage in the process, hardens the material to such a point that the successive plastic deforming caused by drawing does not confer substantial increases to the hardness levels reached at the end of the previous processing stage.

[0035] The last stage of the cold plastic deforming process for the production of industrial pipes includes multiple steps of spinner drawing (drawing by spinners, block 140 of Figure 3) wherein the drawn semi-finished products are brought to the final pre-established measurements (diameter and thickness). This processing stage also provokes an increase in material hardness, although generally this increase is insignificant.

[0036] According to the method of the present invention, the rolled and drawn pipe, which has now reached its substantially definitive measurements, now undergoes distension heat treatment, which not only involves recrystallization, but also the so-called "ageing" process. According to one characteristic of the method according to the invention, this "inevitable" final heat treatment stage is therefore performed at the end of the production cycle, choosing the temperature and duration of the crystallization operation appropriately, in order to provoke the material ageing process at the same time, with the consequential precipitation of intermetallic compounds on the edges of the matrix grains as a result of the "mobilisation", caused by this heat treatment and successive slow cooling of the alloying elements previously brought into solid solution in conditions of oversaturation. This last heat treatment therefore facilitates the precipitation in a semicoherent form with the matrix of the particles FeP_2 and Fe_2P and therefore starts up the actual precipitation hardening action.

[0037] This ageing process also determines above all, at the same time, an increase in the electrical and thermal conductivity of the alloy, a property that is clearly desirable in a pipe destined for use in heat exchangers, and at the same time it induces an improvement of approximately 25% in the mechanical properties.

[0038] Preferably, according to the method of the present invention, the recrystallization and ageing process is performed, for example, in a furnace (tunnel furnace), at a temperature between 500 and 650°C for a period of time between 1.5 and 3 hours. More preferably, this process is performed at a temperature of 575°C for 2.5 hours.

[0039] Further characteristics of the invention will be made clearer from the description of the practical example of realisation.

EXAMPLE 1

2 bars weighing approximately 4000 kg each, in KFC alloy were prepared.

[0040] Table 1 shows the data relative to the composition percentage (alloying elements Fe and P, and impurities) of the alloys used for CO_2 realisation of the heat exchanger pipes according to the method of the present invention.

Table 1 - composition percentage of the alloys used for CO_2 realisation of heat exchanger pipes according to the method of the present invention.

Alloy	Fe % $^p/_p$	P % $^p/_p$	Ni % $^p/_p$	Cu % $^p/_p$	Pb % $^p/_p$	SN % $^p/_p$
Billet A	0.1521	0.0391	0.0048	remainder	0.0042	0.0042
	0.1459	0.0361	0.0048	remainder	0.0038	0.0033
	0.1392	0.0317	0.0046	remainder	0.0031	0.0032
Billet B	0.1636	0.0386	0.0051	remainder	0.0036	0.0034
	0.1479	0.0372	0.0047	remainder	0.0035	0.0031
	0.1454	0.0324	0.0049	remainder	0.0032	0,0033

[0041] The bars were then cut into billets measuring 305 mm in diameter and 680 mm in length, for the successive extrusion operation. 3 disks approximately 10 mm thick were cut from the bars in order to perform the so called "Calotte test" at the beginning, centre and end of the bar. The material resisted all tests without showing signs of fracture or sagging, even in the central area which is the part placed under major stress during testing.

[0042] The heating furnace used for extrusion is composed of 11 zones wherein the temperature is set according to the diagram shown in table 2. The standard period of time inside the furnace is approximately 1.5 hours.

Table 2 - Schematic diagram of the tunnel furnace zones used for billet heating for extrusion, and the relative zone temperatures.

Zone	1	2	3	4	5	6	7	8	9	10	11
Temp. [°C]	700	700	734	843	887	921	955	1000	1020	1020	1020

[0043] Each billet on exit from the furnace was measured for the main extrusion parameters, and in particular, the billet temperature, the shell temperature (in other words the temperature at which the container must be maintained constant to prevent excessive thermal amplitude during the extrusion campaign) the pressure of the perforating chuck, the extrusion thrust pressure (in other words the maximum pressure reached during the single extrusion) and the final pressure in relation to the working pressure during the extrusion operation.

Table 3 - Main extrusion parameters of billets taken from KFC alloy bars, according to the method of the present invention.

N° estruded piece	T billet [°C]	T shell [°C]	P chuck [bar]	P thrust [bar]	P final [bar]
1	930	429	90	277	233
2	930	429	91	255	233
3	925	429	91	267	230
4	925	429	91	276	236
5	918	429	95	299	230

(continued)

N° estruded piece	T billet [°C]	T shell [°C]	P chuck [bar]	P thrust [bar]	P final [bar]
6	917	429	96	299	242
7	912	429	104	290	240
8	916	429	97	294	241
9	918	429	98	301	243
10	917	430	94	299	235
11	917	429	96	305	228
12	915	429	103	291	240
13	916	429	96	308	239
14	922	431	95	299	234
15	920	431	102	287	222
16	920	431	95	305	230

[0044] From the results shown in Table 3, it was seen that the temperature of the billet is generally between 910 and 930°C, while that of the shell remains practically constant and equal to about 430°C. The figures recorded are generally comparable to those normally found during the extrusion of billets in Cu DHP. Chemical analysis was performed again on extruded rings taken from the end of each extruded piece. The results are shown in Table 4.

Table 4 - Chemical analysis performed on each extruded piece.

N° estruded piece	Fe	P	Zn	Ni	Pb	Sn	Ag	Fe/P
	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	[ppm]	-
1	1480	346	5	41	8	<1	71	4.28
2	1403	332	2	43	10	<1	75	4.22
3	1332	318	6	42	14	2	73	4.19
4	1452	360	4	40	15	<1	69	4.03
5	1363	325	8	43	16	2.8	72	4.49
6	1474	367	9	45	21	<1	71	4.02
7	1376	333	1	42	14	<1	70	4.13
8	1428	352	8	42	14	<1	75	4.06
9	1450	356	4	43	18	<1	72	4.07
10	1380	337	<1	42	14	<1	71	4.09
11	1372	333	<1	40	8	<1	76	4.12
12	1459	368	8	44	10	<1	72	3.96
13	1282	310	8	43	15	<1	73	4.14
14	1445	369	11	41	7	<1	70	3.92
15	1451	368	3	42	14	<1	72	3.94
16	1334	306	4	43	15	<1	73	4.36

[0045] Extrusion was performed under water: the extruded pipe blank on exit from the drawplate runs over a graphite bench at a speed of 450 mm per second and reaches a water tank with a volume of 55 m^3 which is maintained at a constant temperature of 45 °C. This permits the extruded pipe to pass from a temperature of approximately 900 °C to that of 80 °C in about 20 seconds (cooling speed approximately 40°C/sec). The homogenous cooling of the pipe, which remains constantly 300 mm under the surface of the water, is guaranteed even further by a high pressure water jet system that hits the pipe at a tangent lapping the entire surface. With this system, rapid cooling occurs (quench hardening) blocking in thermodynamically metastable conditions the iron and the phosphorous dissolved during the heating action. In this manner, a specific solution heat treatment ad hoc, followed by a separate quench hardening stage, is not necessary. The efficacy of the extrusion under water in order to obtain the solution heat treatment of the KFC alloy was monitored indirectly through the measurement of the electrical conductivity. In fact, because of the induced lattice distortion, the presence of solutes inside the crystal lattice of the copper strongly reduces the electrical conductivity of the alloy. However, it would be expected that the same electrical conductivity would begin to increase again following the successive precipitation process (ageing) during which the iron and phosphorous combine to form semi-coherent precipitates with the matrix. The crystal lattice, therefore, would be no longer distorted and the expected conductivity should result as close to those levels of the Cu DHP (around the level expected equal to 85% IACS).

[0046] Table 5 summarizes the average IACS% levels of electrical conductivity measured using Sigmatest D 2.068 (Foerster). These ranged between 47 and 51% IACS, thus confirming the efficacy of underwater extrusion to obtain the solution heat treatment of iron and phosphorous in the copper matrix. In particular, it is worth noting that the lowest levels of electrical conductivity occur where the highest concentrations of iron and phosphorous are present. The same table also shows the hardness levels at reduced load HV 500g/15" measured on the polished cross-section of the same samples.

Table 5 - Electrical conductivity and hardness at reduced load HV 500g/15" measured on the extruded pieces.

N° extruded piece	Fe [ppm]	P [ppm]	Fe/P	IACS%	HV 500g/15’’
1	1480	346	4.28	48.6	54.7
2	1403	332	4.22	48.29	54.9
3	1332	318	4.19	49.98	55.4
4	1452	360	4.03	47.28	51.8
5	1363	325	4.49	49.84	54.9
6	1474	367	4.02	48.09	55.35
7	1376	333	4.13	49.41	61.7
8	1428	352	4.06	48.86	56.2
9	1450	356	4.07	48.52	61.2
10	1380	337	4.09	48.66	56.1
11	1372	333	4.12	49.24	51.1
12	1459	368	3.96	48.72	62.7
13	1282	310	4.14	50.59	58.3
14	1445	369	3.92	48.57	63.6
15	1451	368	3.94	48.48	52.95
16	1334	306	4.36	50.05	49.3

Cross-section metallographic test specimens were taken from the samples of the extruded pipe blank taken from the end of the piece, for metallographic testing after chemical attack using a solution of ammonia and hydrogen peroxide. As is known in prior art, when copper containing phosphorous is heated to a high temperature (900°C) in an oxidizing environment, the oxygen is diffused from the exterior towards the interior of the matrix, and the diffusion of the phosphorous occurs in the opposite direction. The result is the forming of particles composed of $Cu_2O \cdot P_2O_5$ which are distributed in a uniform manner in the copper matrix. The depth of the forming of this layer depends proportionally on the temperature and the length of time it is maintained.

[0047] Furthermore, while the layer of copper protoxide and oxide formed on the surface of the billet is easy to eliminate through "descaling" performed using high pressure water, the diffusion layer of the oxygen and the consequential dispersion of the $Cu_2O \cdot P_2O_5$ precipitates cannot be eliminated using the same method, because it is intrinsically connected with the metal matrix. On the other hand, if the elimination of the jacket is performed under optimal conditions, it is able to eliminate the oxidized layer completely, since it removes a uniform thickness of material. The average diameter of the extruded pipe grains was measured using metallographic analysis on the extruded piece sections. The levels, ranging between 120 and 150 µm, correspond with those generally found in Cu DHP samples.

[0048] The production cycle was continued with the cold rolling stage, performed only on a part of the extruded pipe blanks, selected in a manner to create a sample representing the total interval of the levels of the available Fe/P ratios, and in particular on the extruded pieces at the end of this interval (Fe/P=3.92 and Fe/P=4.36). The rolling mill was set at 70 strokes a minute with a travel step of 11,11 mm and a rotation of 60° for each stroke. On exit from the rolling mill the pipe had an internal diameter of 40.5 mm, an external diameter of 45 mm, a thickness of 2.25 mm, and a weight of 2693 g/m.

[0049] The rolling provoked considerable hardening from a metallographic point of view, with a hardness variation that for the extruded piece n° 14 measured from 63.6 HV 500g/15'' (refer to Table 5) to 127.7 HV 500g/15", and the extruded piece n°16 from 49.3 HV 500g/15" (Table 5) to 126.6 HV 500g/15".

[0050] After the cold rolling stage, the rolled pieces were caterpillar drawn to obtain semi-finished pipes with the following characteristics: Internal diameter 31.4 mm, external diameter 35.26 mm, thickness 1.93 mm and weight of 1801 g/m.

Table 6 - Load cell levels measured during the straight drawing performed on KFC pipes according to the invention and on Cu DHP pipes(for comparison).

N° estruded piece	**Load cell [kg]**
9	6650
11	6580
12	6650
13	6590
14	6540
15	6590
16	6580
Cu DHP (1)	6340
Cu DHP (2)	6300

[0051] Table 6 shows the levels measured by the load cell for each drawn semi-finished pipe, together with certain levels measured for Cu DHP pipes drawn using the same operating settings as those used for the KFC pipes. As can be seen, the strength required for drawing the copper DHP is about 300 kg lower than that required for drawing KFC pipes. This is a further confirmation of the hardening obtained through the solution of the iron and phosphorous in the copper matrix, which increases the plastic deforming resistance of the alloy. However, the differences are small and are within the standard working interval on the installation.

[0052] The last stage of the process for the production of industrial pipes involves 7 spinner-drawing steps in order to obtain the final pre-established diameter of 9.52 X 0.45 mm. After the spinner drawing a further increase in hardness was recorded, although slight, and measured at about 5-10 HV 500g/15''.

[0053] Once the geometrical measurements have reached the predetermined levels, the heat treatment of the drawn pipe must also perform the function of precipitating the FeP_2 and Fe_2P particles in semi-coherent form with the matrix, provoking hardening. Therefore, in order to identify the conditions that are able to guarantee obtaining a well-recrystallised metallic matrix and reaching the ageing conditions as required, isochrone tests were performed in a muffle furnace for a period of 2.5 hours at increasing temperatures beginning from 525°C (in other words the temperature generally used for copper DHP annealing).

[0054] The samples subjected to isochrone tests at different temperatures also underwent metallographic analysis in order to evaluate the morphology of the crystalline structure obtained and to compare it with that of a Cu DHP pipe aged under the same conditions. The results of these analyses are shown in table 7.

Table 7 - Results concerning the morphology (metallographic analysis) of KFC pipe samples according to the invention and Cu DHP pipes following isochrone tests for annealing/recrystallization.

T [°C]	**Morphology : Cu DHP**	**Morphology: Cu KFC**
525	Grain well recrystallized, grain size~ 35 µm	Extremely fine structure, grain size ~ 12.5 µm

(continued)

T [°C]	Morphology : Cu DHP	Morphology: Cu KFC
550	Recrystallized structure, grain size 37.5 μm	Recrystallized structure, grain size 12.5 μm
575	Recrystallized structure, grain size 40 μm	Recrystallized structure, grain size 15 μm
600	Recrystallized structure, grain size 45 μm	Recrystallized structure, grain size 17 μm
625	Recrystallized structure, grain size 60 μm	Recrystallized structure, grain size 20 μm

[0055] The different behaviour of a KFC alloy in relation to that of Cu DHP can be explained by both the hardening particles that create an obstacle, not only for the dislocation movement, but also for that of the edge of the grain, and by the presence of the iron still dissolved in the metallic matrix which, as is known, increases the temperature of recrystallization. This means that in order to obtain a grain with a size that is comparable to that of the Cu DHP the recrystallization temperature must be increased.

Table 8 - synoptic layout of the results of the annealing tests on the KFC pipes according to the invention and the Cu DHP pipes(comparison) f 9.52 x 0.45 mm.

Alloy	Heat treatment	Average grain diameter [μm]	HV/300/15’’	IACS%
KFC (estruded piece 14)	hardened	-	142.4	n.d.
	2.5 h a 525°C	12.5	74.7	n.d.
	2.5 h a 550°C	12.5	71.9	n.d.
	2.5 h a 575°C	15	68.1	n.d.
	2.5 h a 600°C	17.5	64.8	n.d.
	2.5 h a 625°C	20	63.7	n.d.
KFC (estruded piece 16)	hardened	-	135.95	49.6
	2.5 h a 525°C	12.5	71.7	88,8
	2.5 h a 550°C	12.5	68.6	86.7
	2.5 h a 575°C	15	64	83.7
	2.5 h a 600°C	17.5	63.9	81.2
	2.5 h a 625°C	20	63.05	78.5
Cu DHP	Hardened	-	127.2	85
	2.5 h a 525°C	35	51.3	88
	2.5 h a 550°C	37.5	47.6	n.d.
	2.5 h a 575°C	40	42.8	n.d.
	2.5 h a 600°C	45	n.d.	n.d.
	2.5 h a 625°C	60	n.d.	n.d.

[0056] These tests demonstrated that it is possible to perform both recrystallization, and ageing of the KFC alloy at the same time. In fact, the electrical conductivity, rises by about 50% IACS of the hardened sample as far as a level of approximately 80% IACS, thus indicating the exit of the iron and of the phosphorous from the solid solution with the copper to form semicoherent precipitates of Fe_2P and FeP_2. Examination of the figures in Table 8 shows that the best compromise seems to be a heat treatment at 575°C for 2.5 hours (electrical conductivity 83.7% IACS and size of the crystalline grain equal to 15 μm).

Claims

1. Production method for a pipe having strong mechanical resistance and high thermal exchange capacity, in particular for application in heat exchangers, comprising the following stages:

    a) production of a billet in an alloy susceptible to precipitation hardening and presenting suitable thermal conductivity;
    b) hot extrusion directly under hydrostatic head in a water bath of said billet, previously heated to form an extruded pipe blank having predetermined measurements;
    c) subjecting the extruded pipe blank to a range of cold mechanical deforming processes to reduce the transversal measurements and consequently, to obtain a pipe having substantially definitive measurements; and
    d) subjecting the pipe to an annealing process performed in a manner to determine the hardening of the pipe through the precipitation of at least part of the alloying elements contained in said alloy and previously brought to solid solution during the extrusion stage.

2. Method according to claim 1, **characterised in that** said stage c) of subjecting the extruded pipe blank to a range of cold mechanical deforming processes comprises the following stages:

    e) cold rolling of the extruded pipe blank in a manner to obtain a rolled blank having reduced transversal measurements and consequently having an increased length;
    f) subjecting the rolled blank to straight drawing to obtain a semi-finished pipe;
    g) subjecting the semi-finished pipe to spinner drawing to reduce the transversal measurements and consequently to obtain said pipe having substantially definitive measurements.

3. Method according to claim 1 or 2, **characterised in that** said stage of subjecting the pipe to an annealing process is performed inside a tunnel furnace.

4. Method according to any one of the previous claims, **characterised in that** said metal alloy susceptible to precipitation hardening is an alloy preferably chosen from the group composed of Cu-Fe-P and Cu-Fe-Ni-P systems.

5. Method according to claim 1, **characterised in that** in order to perform stage a) a metal alloy is chosen that is susceptible to precipitation hardening wherein the Fe weight content is between 800 and 1500 ppm, P weight content is between 250 and 500 ppm and the Ni weight content is between 100 and 20000 ppm.

6. Method according to claim 1, **characterised in that** in order to perform stage a) a metal alloy is chosen that belongs to a precipitation system wherein the Cu is present with one or more elements chosen from among Ni , Co, Mg, Zr, Si, Cr, B, Sb, Zn, Be, Sn, Al, Ag, Ti and Mn.

7. Method according to claim 4 or 5, **characterised in that** said metal alloy susceptible to precipitation hardening is an alloy preferably of Cu-Fe-P and Cu-Fe-Ni-P systems, wherein the Fe/P weight ratio is between 2.5 and 5.

8. Method according to claim 7, **characterised in that** said metal alloy is an alloy preferably of Cu-Fe-P and Cu-Fe-Ni-P systems, wherein the Fe/P weight ratio is equal to 4.

9. Method according to one of the previous claims, **characterised in that** said extrusion stage b) is performed at a temperature equal to or higher than the temperature of the solution heat treatment of said metal alloy whereof the billet is formed.

10. Method according to any one of the previous claims, **characterised in that** said billet is preheated using a heating furnace inside which the temperature increases progressively from an entrance to an exit of said furnace, forming inside said furnace a plurality of zones each one having a temperature between 600 and 1200°C.

11. Method according to claim 10, **characterised in that** said zones of said plurality of zones each have a temperature between 700 and 1100°C.

12. Method according to one of the claims 10 or 11, **characterised in that** the temperature of said billet on exit from the said heating furnace and immediately preceding said hot extrusion stage b) is between 900 and 950°C.

13. Method according to claim 12, **characterised in that** the temperature of said billet on exit from the said heating furnace and immediately preceding said hot extrusion stage b) is between 910 and 930°C.

14. Method according to any one of the previous claims, **characterised in that** the cooling speed of the extruded pipe is equivalent to that obtained during the quench hardening of solution heat treatment for the same alloy as that used for the billet and substantially not lower than 40°C/s.

15. Method according to any one of the previous claims, **characterised in that** the temperature of said water bath is no higher than 50°C and that the effective hydrostatic head of said water bath is at least 300mm.

16. Method according to any one of the previous claims, **characterised in that** said annealing stage d) is performed at a temperature between 500 and 650°C for a period of time between 1.5 and 3 hours.

17. Method according to claim 16, **characterised in that** said annealing stage d) is performed at a temperature of approximately 575°C for 2.5 hours.

FIG. 1

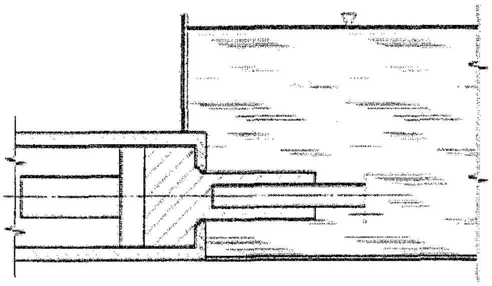


FIG. 2

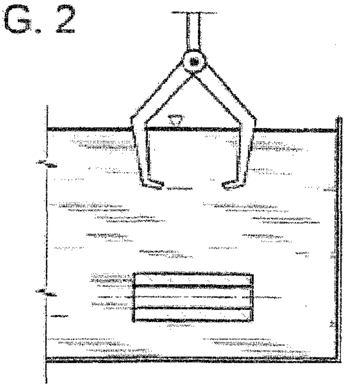
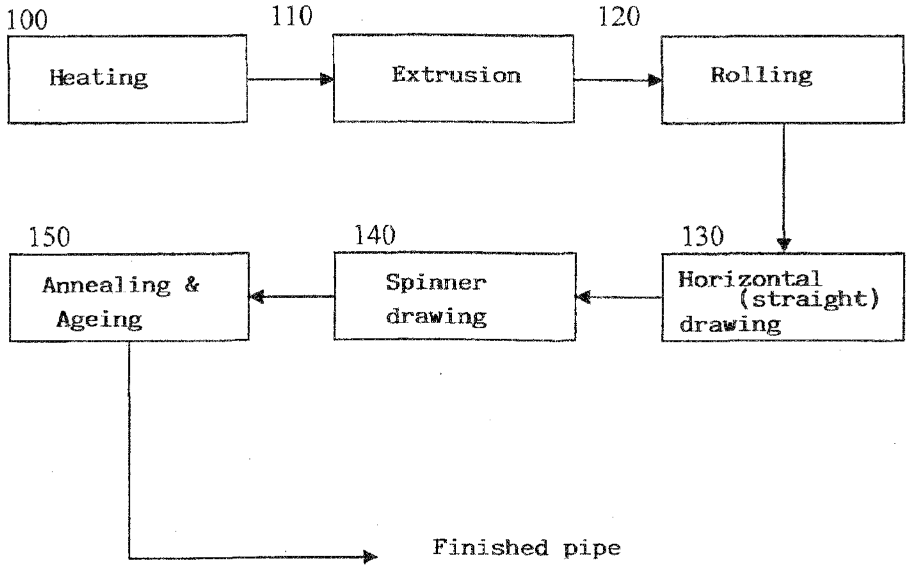


FIG. 3



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EUROPEAN SEARCH REPORT

Application Number
EP 07 42 5533

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The present search report has been drawn up for all claims

Place of search	Date of completion of the search	Examiner
Munich	17 December 2007	Ritter, Florian

CATEGORY OF CITED DOCUMENTS

X : particularly relevant if taken alone
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