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(54) **Copper alloy having excellent corrosion cracking resistance and dezincing resistance, and method for producing same**

Kupferlegierung, die exzellente Korrosionsbeständigkeit und Entzinkungsbeständigkeit aufweist, und eine Methode zu deren Herstellung

Alliage de cuivre, qui a une excellente résistance à la corrosion et au dézincage, et procédure de fabrication

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- **"Copper and Copper Alloys" 2001 , ASM INTERNATIONAL , MATERIALS PARK, OHIO, USA XP002264346 * page 23 * * page 249; table 2 ***
- **PATENT ABSTRACTS OF JAPAN vol. 2002, no. 02, 2 April 2002 (2002-04-02) & JP 2001 294956 A (SUMITOMO LIGHT METAL IND LTD;SHINNITTO KINZOKU KK), 26 October 2001 (2001-10-26)**
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Description

BACKGROUND OF THE INVENTION

Field of the Invention

[0001] The present invention generally relates to a copper alloy and a method for producing the same. More specifically, the invention relates to a copper alloy having an excellent corrosion cracking resistance and an excellent dezincing resistance, in addition to characteristics of conventional brasses having an excellent machinability or cutting workability and an excellent recyclability, and a method for producing the same.

Description of the Prior Art

[0002] Conventional brasses, such as free-cutting brass rods/bars (JISC3604) and forging brass rods/bars (JISC3771), which are copper-zinc alloys containing lead (Pb), are widely used for metal parts for water lines and valve parts due to their excellent malleability, hot workability and cutting workability. In addition, the scraps of brasses can be easily provided due to the large amount of distribution, so that brasses have an excellent recyclability and are low in costs.

[0003] In recent years, in order to improve the dezincing corrosion resistance of brass materials for use in water contact parts and so forth, various proposals have been made. For example, Japanese Patent Laid-Open No. 10-183275 discloses that tin (Sn) is added to a copper-zinc alloy to be extruded to control the concentration of Sn in a gamma phase through various heat treatments to improve the dezincing resistance of the alloy. In addition, Japanese Patent Laid-Open No. 6-108184 proposes that Sn is added to a copper-zinc alloy to be extruded to form a single alpha phase to enhance the dezincing corrosion resistance of the alloy. That is, the above described alloys are characterized in that a larger amount of Sn than that in conventional brasses is added.

[0004] Moreover, Japanese Patent Laid-Open No. 2001-294956 proposes that very small amounts of phosphorus (P) and tin (Sn) are added to a copper-zinc alloy to be extruded and reduced to be heat-treated to form a structure wherein a beta phase is separated by an alpha phase, to improve the dezincing resistance of the alloy.

[0005] EP 1 008 664 A1 discloses a copper-based alloy comprising 58 to 63 % of copper, 0.5 to 4.0 % of lead, 0.05 to 0.25 % of phosphorus, 0.5 to 3.0 % of tin and 0.05 to 0.3 % of nickel, with the balance being zinc and unavoidable impurities.

[0006] Several copper alloys comprising Cu, Sn, Pb, Zn, Fe and Si are disclosed in ASM Speciality Handbook - Copper and Copper Alloys.

[0007] However, if conventional copper-zinc alloys are used in warm water in a corrosive water quality environment, the ionization tendency of zinc in a beta phase is strong to give the elution of zinc priority, so that they have a very low dezincing corrosion resistance. In addition, the stress corrosion cracking sensing resistance of copper-zinc alloys increases as the amount of zinc increases. In particular, brasses of an alpha-plus-beta phase, such as forging brass rods/bars (JIS C3771) and free-cutting brass rods/bars (JIS C3604), have an inferior stress corrosion cracking resistance.

[0008] In the method for adding the large amount of Sn to improve the dezincing resistance, the local coagulation time of brass increases with the increase of the amount of Sn, so that the inverse segregation of Sn occurs during forging to cause surface detects on an ingot and to damage hot workability in extrusion and so forth. Therefore, there is a problem in that the yields of products are remarkably deteriorated. In addition, Sn is more expensive than copper-zinc scraps, so that there is a problem in that the costs increase if the amount of Sn to be added is large.

[0009] Moreover, the method for adding the very small amounts of Sn and P to carry out heat treatments can be inexpensively carried out to improve the dezincing resistance due to the small amount of additives. However, there is a problem in that this method can not improve the stress corrosion cracking resistance of the alloy.

SUMMARY OF THE INVENTION

[0010] It is therefore an object of the present invention to eliminate the aforementioned problems and to provide a copper alloy having an excellent corrosion cracking resistance and an excellent dezincing resistance while maintaining excellent characteristics of conventional brasses, and a method for producing the same.

[0011] In order to accomplish the aforementioned and other objects, the inventors have diligently studied and found that it is possible to provide a copper alloy having an excellent corrosion cracking resistance and an excellent dezincing resistance while maintaining excellent characteristics of conventional brasses, by adding appropriate amounts of tin (Sn), silicon (Si), phosphorus (P), and at least one of bismuth (Bi) and lead (Pb), and optionally at least one of nickel (Ni) and iron (Fe) to a conventional brass material and by carrying out a heat treatment on appropriate conditions to control the structure of the alloy. Thus, the inventors have made the present invention.

[0012] According to one aspect of the present invention, a copper alloy comprises 58 to 66 wt% of copper, 0.3 to 0.5

wt% of tin, 0.01 to 0.5 wt% of silicon 0.02 to 0.15 wt% of phosphorus at least one of 0.3 to 3.0 wt% of bismuth and 0.3 to 3.5 wt% of lead, and optionally at least one of 0.02 to 3.0 wt% of nickel and 0.02 to 0.6 wt% of iron, with the balance being zinc and unavoidable impurities, wherein a proportion of an alpha phase is 80 vol% or more.

[0013] The total amount of phosphorus, nickel and iron may be in the range of from 0.02 to 3.0 wt%.

[0014] In this case, an apparent content B' of zinc in the copper alloy may be in the range of from 34 to 39 wt%, the apparent content B' of zinc being expressed by the following expression: $B' = [(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$, wherein A denotes the content (wt%) of copper and B denotes the content (wt%) of zinc, t_1, t_2, t_3 and t_4 denoting zinc equivalents of tin, silicon, nickel and iron, respectively ($t_1 = 2.0$, $t_2 = 10.0$, $t_3 = -1.3$, $t_4 = 0.9$), and q_1, q_2, q_3 and q_4 denoting the contents (wt%) of tin, silicon, nickel and iron, respectively.

[0015] According to another aspect of the present invention, there is provided a method for producing a copper alloy, the method comprising the steps of: preparing raw materials of a copper alloy comprising 58 to 66 wt% of copper, 0.3 to 0.5 wt% of tin, 0.01 to 0.5 wt% of silicon, 0.02 to 0.15 wt% of phosphorus at least one of 0.3 to 3.0 wt% of bismuth and 0.3 to 3.5 wt% of lead, and optionally at least one of 0.02 to 3.0 wt% of nickel and 0.02 to 0.6 wt% of iron, with the balance being zinc and unavoidable impurities; casting the raw materials to form an ingot; hot working the ingot; cold or hot working the hot worked ingot; annealing the cold or hot worked ingot at a temperature of 300 to 600 °C for two minutes to five hours; and cooling the annealed ingot at a cooling rate of 0.2 to 10 °C/sec.

[0016] The total amount of phosphorus, nickel and iron may be in the range of from 0.02 to 3.0 wt%.

[0017] In this case, an apparent content B' of zinc in the copper alloy may be in the range of from 34 to 39 wt%, the apparent content B' of zinc being expressed by the following expression: $B' = [(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A+B+t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$, wherein A denotes the content (wt%) of copper and B denotes the content (wt%) of zinc, t_1, t_2, t_3 and t_4 denoting zinc equivalents of tin, silicon, nickel and iron, respectively ($t_1 = 2.0$, $t_2 = 10.0$, $t_3 = -1.3$, $t_4 = 0.9$), and q_1, q_2, q_3 and q_4 denoting the contents (wt%) of tin, silicon, nickel and iron, respectively.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0018] The preferred embodiments of a copper alloy having an excellent corrosion cracking resistance and an excellent dezincing resistance according to the present invention will be described below.

[0019] According to the present invention, a copper alloy having an excellent corrosion cracking resistance and an excellent dezincing resistance consists of 58 to 66 wt% of copper (Cu), 0.3 to 0.5 wt% of Sn, 0.01 to 0.5 wt% of Si, 0.02 to 0.15 wt% of P, at least one of 0.3 to 3.0 wt% of Bi and 0.3 to 3.5 wt% of Pb, and optionally at least one of 0.02 to 3.0 wt% of Ni and 0.02 to 0.6 wt% of FE, with the balance being zinc (Zn) and unavoidable impurities, wherein the proportion of an alpha phase is 80 vol% or more.

[0020] If the amount of Cu is less than 58 wt%, a beta phase increases, so that it is not possible to improve the dezincing resistance of the alloy even if a heat treatment is subsequently carried out. On the other hand, if the amount of Cu exceeds 66 wt%, a beta phase does not sufficiently deposit even in a high temperature range, so that the hot workability of the alloy deteriorates. Therefore, the amount of Cu is preferably in the range of from 58 to 66 wt%, more preferably in the range of from 60 to 62 wt%.

[0021] Tin (Sn) has the function of improving the dezincing resistance of an alpha phase and a beta phase. If the amount of Sn is less than 0.3 wt%, it is not possible to obtain a satisfied dezincing resistance. If the amount of Sn exceeds 0.5 wt%, a hard, friable gamma phase is easy to deposit, so that the extension of mechanical characteristics deteriorates. Therefore, the amount of Sn is in the range of from 0.3 to 0.5 wt%.

[0022] Silicon (Si) remarkably has the functions of improving the dezincing resistance of a beta phase and of improving the stress corrosion cracking resistance of the whole alloy if a predetermined proportion of Si is solid-dissolved in beta and alpha phases. If the amount of Si is less than 0.01 wt%, these functions can not be obtained. Since the zinc equivalent of Si is a high value of 10, if the amount of Si to be added exceeds 0.5 wt%, the proportion of a beta phase increases, and the extension of mechanical characteristics deteriorates. Therefore, the amount of Si is preferably in the range of 0.01 to 0.5 wt%, more preferably in the range of 0.1 to 0.2 wt%.

[0023] Furthermore, if a small amount of a third element, such as Sn, Si or Ni, is added to a copper-zinc alloy, it is often solid-dissolved in alpha and beta phases without forming a specific phase. In that case, such a structure that the amount of Zn increases or decreases is produced in the copper-zinc alloy, so that the alloy has properties corresponding thereto. Guillet has proposed a method for expressing this relationship by using the zinc equivalent of an additional element. That is, the apparent zinc content B' of the third element is expressed by $B' = [(B+tq)/(A+B+tq)]x100$, wherein A denotes the content of Cu (wt%), and B denotes the content of Zn (wt%), t denoting the zinc equivalent of an additional element, and q denoting the content of the additional element (wt%) (see "Fundamentals and Technologies of Copper and Copper Alloys (Revised Edition), pp225-226" (Japan Wrought Copper Association)).

[0024] If the proportion of an alpha phase is 80 vol% or more, advantageous effects will be described below. In brasses of an alpha-plus-beta phase, the beta phase is inferior to the alpha phase with respect to both of stress corrosion cracking resistance and dezincing resistance. The zinc equivalents of Sn and Si are 2 and 10, respectively, and the solid solutions

of Sn and Si are preferentially formed in a beta phase. If the amount of these elements to be added increases, the proportion of the beta phase increases, and the hardness of the whole material increases to decrease the elongation thereof. If the proportion of the alpha phase is set to be 80 vol% or more, the residual beta phase can be reinforced by adding a very small amount of elements without damaging the elongation of the whole material, and the stress corrosion cracking resistance of the alpha phase can be improved by the solid solution of Si. Therefore, the proportion of the alpha phase is preferably 80 vol% or more, and more preferably 90 vol% or more.

[0025] According to the present invention, a copper alloy having an excellent stress corrosion cracking resistance and dezincing resistance contains at least one of 0.3 to 3.5 wt% of Pb and 0.3 to 3.0 wt% of Bi.

[0026] Lead (Pb) and bismuth (Bi) serve to improve the machinability or cutting workability of brasses, respectively. If the amount of Pb is 0.3 wt% or more, it is possible to obtain a good free-cutting workability. However, if the amount of Pb exceeds 3.5 wt%, the mechanical properties of brasses deteriorate to tend to cause embrittlement. Therefore, the amount of Pb is preferably in the range of from 0.3 to 3.5 wt%. In addition, since the material cost of Pb is low, the amount of Pb is more preferably in the range of 2.5 to 3.5 wt%. For the same reasons, if the amount of Bi is in the range of from 0.3 to 3.0 wt%, preferably in the range of from 1.4 to 2.5 wt%, it is possible to obtain a good free-cutting workability. Since Pb is harmful to the human body although Bi is more expensive than Pb, Bi can be substituted for Pb.

[0027] In a preferred embodiment of the present invention, a copper alloy having an excellent stress corrosion cracking resistance and dezincing resistance preferably contains at least one of 0.02 to 0.15 wt% of P, 0.02 to 3.0 wt% of Ni, and 0.02 to 0.6 wt% of Fe, the total amount of these elements being in the range of from 0.02 to 3.0 wt%.

[0028] Nickel (Ni) has the function of decreasing the size of crystal grains, and also has the function of increasing the proportion of the alpha phase since the zinc equivalent of Ni is negative. If the amount of Ni is less than 0.02 wt%, it is not sufficiently obtain these functions. On the other hand, if the amount of Ni exceeds 3.0 wt%, there are problems on mechanical characteristics and adding costs. Therefore, the amount of Ni is preferably in the range of 0.02 to 3.0 wt%, and more preferably in the range of 0.1 to 0.4 wt%.

[0029] Phosphorus (P) has the function of improving the dezincing resistance of the alpha phase without damaging mechanical characteristics. However, if the amount of P is less than 0.02 wt%, it is not possible to obtain such a function, and if the amount of P exceeds 0.15 wt%, intergranular segregation is caused to deteriorate the ductility and stress corrosion cracking resistance of the alloy. Therefore, the amount of P to be added is in the range of from 0.02 to 0.15 wt%.

[0030] Iron (Fe) has the functions of inhibiting the size of the alpha phase from being increased and of stabilizing mechanical characteristics. Since most of scrap materials include Fe, costs increase if the amount of Fe is less than 0.02 wt%, and the elongation of the alloy deteriorates if the amount of Fe exceeds 0.6 wt%. Therefore, the amount of Fe to be added is preferably in the range of from 0.02 to 0.6 wt%.

[0031] If the total amount of Ni, Fe and P is less than 0.02 wt%, the use of scraps is restricted to increase costs. On the other hand, if the total amount exceeds 3.0 wt%, intergranular segregation is caused to deteriorate the ductility of the alloy. Therefore, the total amount of Ni, Fe and P is preferably in the range of from 0.02 to 3.0 wt%, and more preferably in the range of from 0.05 to 0.5 wt%.

[0032] A preferred embodiment of a method for producing a copper alloy having an excellent stress corrosion cracking resistance and dezincing resistance according to the present invention will be described below.

[0033] First, raw materials having the above described compositions are mixed so that an apparent content B' of Zn is in the range of from 34 to 39 wt%, the apparent content B' being equal to $[(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$, wherein A denotes the content (wt%) of Cu and B denotes the content (wt%) of Zn, t_1, t_2, t_3 and t_4 denoting zinc equivalents of Sn, Si, Ni and Fe, respectively ($t_1 = 2.0$, $t_2 = 10.0$, $t_3 = -1.3$, $t_4 = 0.9$), and q_1, q_2, q_3 and q_4 denoting the contents (wt%) of Sn, Si, Ni and Fe, respectively.

[0034] Then, after the mixture is cast to form an ingot, it is extruded in a temperature range of from 600 to 850 °C. By the mixing, it is possible to obtain an alpha-plus-beta phase structure having a good hot workability in a high temperature region. After the hot forging or cold reduction of a bar thus obtained is carried out, the bar is heat-treated at a temperature of 300 to 600 °C for two minutes to five hours, and then cooled at a cooling rate of 0.2 to 10 °C/sec to control the structure.

[0035] By carrying out the heat treatment, the beta phase portion after extruding is changed to an alpha or gamma phase except for a part of the beta phase portion. At this time, the concentration of additives in the residual beta phase increases, and the solid solution of Si is formed in the alpha phase, so that the stress corrosion cracking resistance and dezincing resistance of the bar are improved. If the heat treatment temperature is lower than 300 °C, phase transformation is not sufficiently carried out. If the heat treatment temperature is higher than 600 °C, the beta phase is stable, so that no alpha-plus-gamma phase is deposited. Therefore, the heat treatment temperature is preferably in the range of from 300 to 600 °C. If the cooling rate is higher than 10 °C/sec, there is the possibility that distortion may be caused by cooling. If the cooling rate is lower than 0.2 °C /sec, there are some cases where the size of crystal grains increases to have an influence on dezincing resistance. Therefore, the cooling temperature is preferably in the range of from 0.2 to 10 °C/sec.

[0036] Examples of copper alloys having an excellent stress corrosion cracking resistance and dezincing resistance and methods thereof according to the present invention will be described below in detail.

[Examples 1 through 19]

[0037] Raw materials of components in each of Examples 1 through 19 shown in Table 1 were mixed to be melted in an induction furnace to be semi-continuously cast to form a bar having a diameter of 80 mm. Then, the bar was hot-extruded so as to have a diameter of 30 mm, and cold-drawn so as to have a diameter of 29.5 mm. Thereafter, in each example, the bar was heat-treated on heat treatment conditions shown in Table 2, and the cooling rate was in the range of from 0.2 to 10 °C/sec.

[0038] Table 1 shows the compositions of samples thus obtained, and the apparent content B' of Zn, which is equal to $[(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$, wherein A denotes the content (wt%) of Cu and B denotes the content (wt%) of Zn, t_1, t_2, t_3 and t_4 denoting zinc equivalents of Sn, Si, Ni and Fe, respectively (t_1 = 2.0, t_2 = 10. 0, t_3 = -1.3, t_4 = 0.9), and q_1, q_2, q_3 and q_4 denoting the contents (wt%) of Sn, Si, Ni and Fe, respectively.

Table 1

Ex.	Cu	Zn	Sn	Si	Pb	Bi	P	Ni	Fe	Apparent Content of Zn
1	60.9	35.44	0.39	0.02	2.93	0.00	0.06	0.00	0.23	37.5
2	61.8	34.83	0.39	0.12	2.60	0.00	0.04	0.02	0.21	37.4
3	62.8	33.72	0.37	0.03	2.93	0.00	0.09	0.00	0.11	35.7
4	59.9	36.54	0.38	0.05	2.90	0.00	0.05	0.03	0.15	38.8
5	61.0	35.39	0.38	0.11	2.67	0.00	0.08	0.08	0.29	38.0
6	62.1	34.38	0.42	0.04	2.65	0.00	0.05	0.10	0.26	36.5
7	61.1	35.40	0.42	0.05	2.65	0.00	0.05	0.18	0.15	37.5
8	62.9	33.07	0.60	0.10	3.00	0.00	0.05	0.21	0.12	35.8
9	61.9	33.93	0.71	0.10	3.00	0.00	0.05	0.30	0.03	36.8
10	63.1	32.33	0.77	0.20	3.00	0.00	0.05	0.51	0.08	35.9
11	62.2	33.40	0.65	0.10	3.00	0.00	0.05	0.48	0.16	36.2
12	63.0	33.06	0.40	0.20	3.00	0.00	0.05	0.11	0.17	36.3
13	60.4	35.68	0.41	0.11	2.00	0.00	0.10	1.30	0.00	37.3
14	59.2	36.99	0.32	0.05	2.30	0.00	0.04	0.87	0.23	38.6
15	65.7	30.41	0.65	0.34	2.60	0.00	0.08	0.12	0.10	34.8
16	63.4	34.21	0.51	0.09	1.41	0.00	0.11	0.15	0.12	36.2
17	61.3	36.02	0.63	0.02	1.20	0.50	0.06	0.17	0.10	37.9
18	62.1	35.21	0.39	0.10	0.20	1.80	0.05	0.04	0.11	37.4
19	60.9	35.68	0.45	0.12	0.00	2.60	0.06	0.06	0.13	38.3
										(wt%)

[0039] The proportion of the alpha phase, hardness, dezincing resistance and stress corrosion cracking resistance of each of the obtained samples were evaluated.

[0040] The proportion of the alpha phase was obtained by the point calculating method on a microphotograph of a cross section (see "Handbook of Metals" (edited by Japan Society for Metals, the revised fifth edition, Maruzen), p 289). Furthermore, 23 x 30 points were measured at intervals of 10 μm in a lattice.

[0041] The dezincing resistance was evaluated on the basis of ISO 6509 by observing the depth of dezincing resistance after the sample was dipped in a solution containing 12.7 g/L of $CuCl_2 \cdot 2H_2O$ at a temperature of 75±3 °C for 24 hours. The sample was tested so that the direction of extruding was coincident with the direction of dezincing corrosion. After the region of 10 mm x 10 mm was measured, the dezincing resistance was evaluated as "good" when the maximum dezincing depth was 100 μm or less, and the dezincing resistance was evaluated as "not bad" when the maximum dezincing depth exceeds 100 μm.

[0042] In order to evaluate the stress corrosion cracking resistance, each of the samples before cold drawing was cut into pieces having a thickness of 1.5 mm to be hot-rolled so as to have a thickness of about 0.5 mm, and the surface thereof was cold-rolled by about 0.03 mm. Thereafter, a heat treatment was carried out, so that a sample having a thickness of 0. 5 mm, a width of 10 mm and a length of 140 mm was prepared. Then, a stress being 50 % of the proof stress was applied to each of the samples by the two-point load method based on JIS H8711, and each of the samples was held in a desiccator including 14 % NH_3. In this state, the time required to cause corrosion cracking was measured. The stress corrosion cracking resistance was evaluated by "bad" when cracks were produced within 5 hours, "not bad" when cracks are produced in 5 to 15 hours, and "good" when no cracks are produced after 15 hours or more.

[0043] Table 2 shows the proportions of the alpha phase and the results of dezincing tests and stress corrosion

cracking tests in Examples 1 through 19. As can be seen from this table, in all examples, the proportions of the alpha phase were 80 vol% or more, and the stress corrosion cracking resistance and dezincing resistance were good.

Table 2

Ex.	Heat Treatment Conditions	Proportion of α Phase (vol%)	Hardness (Hv)	Dezincing Resistance	Stress Corrosion Cracking Resistance
1	400°C×2hr	83	89.2	good	good
2	550°C×1hr	89	84.1	good	good
3	600°C×3hr	90	80.2	good	good
4	550°C×2hr	95	90.6	good	good
5	600°C×2hr	92	91.2	good	good
6	450°C×2hr	92	94.1	good	good
7	600°C×1hr	81	90.4	good	good
8	550°C×3hr	97	101.3	good	good
9	450°C×2hr	86	108.6	good	good
10	500°C×2hr	98	116.7	good	good
11	550°C×1hr	95	106.8	good	good
12	550°C×2hr	96	98.6	good	good
13	500°C×3hr	95	92.6	good	good
14	550°C×2hr	94	103.1	good	good
15	550°C×1hr	82	107.5	good	good
16	450°C×2hr	93	93.7	good	good
17	500°C×2hr	86	102.4	good	good
18	450°C×3hr	87	88.7	good	good
19	400°C×3hr	84	88.3	good	good

[Comparative Examples 1 through 5]

[0044] Raw materials containing elements in each of Comparative Examples 1 through 5 shown in Table 3 were mixed to prepare samples by the same method as that in the above described Examples. By the same method as that in the above described Examples, the compositions of the respective samples thus obtained were analyzed, and their apparent contents of Zn were calculated. Table 3 shows the results of analysis and the apparent contents of Zn.

Table 3

Comp.	Cu	Zn	Sn	Si	Pb	Bi	P	Ni	Fe	Apparent Content of Zn
1	58.3	38.16	0.28	0.00	2.08	0.00	0.01	0.11	0.18	39.9
2	60.7	35.98	0.35	0.00	2.55	0.00	0.03	0.20	0.19	37.6
3	59.8	37.44	0.26	0.00	0.00	2.30	0.00	0.11	0.09	38.8
4	60.9	35.44	0.39	0.02	2.93	0.00	0.06	0.00	0.23	37.5
5	62.1	34.38	0.42	0.04	2.65	0.00	0.05	0.10	0.26	36.5
										(wt%)

[0045] With respect to each of the samples obtained in Comparative Examples 1 through 5, the proportion of the alpha phase, hardness, dezincing resistance and stress corrosion cracking resistance were evaluated. The results thereof are shown in Table 4. As can be seen from this table, in the case of Comparative Example 1, the amount of Si to be added was zero, and the zinc equivalent was greater than 39, so that the proportion of the alpha phase was not sufficient and the stress corrosion cracking resistance and dezincing resistance were inferior. Also in Comparative Examples 2 and 3, the amount of Si to be added was zero, so that the stress corrosion cracking resistance was inferior. In Comparative Examples 4 and 5, the heat treatment conditions are not appropriate, so that the proportion of the alpha phase was not sufficient. Therefore, both of the dezincing resistance and stress corrosion cracking resistance were inferior.

Table 4

Comp.	Heat Treatment Conditions	Proportion of α Phase (vol%)	Hardness (Hv)	Dezincing Resistance	Stress Corrosion Cracking Resistance
1	400°C × 2hr	71	93.3	not bad	bad
2	550°C × 2hr	85	101.6	good	bad
3	500°C×3hr	74	87.6	not bad	bad
4	none	78	90.3	not bad	not bad
5	700°C×2hr	84	100.4	not bad	not bad

[0046] As described above, according to the present invention, it is possible to inexpensively provide a copper alloy which has an excellent corrosion cracking resistance and an excellent dezincing resistance while maintaining excellent characteristics of conventional brasses and which can be easily hot-worked.

Claims

1. A copper alloy comprising 58 to 66 wt% of copper, 0.3 to 0.5 wt% of tin, 0.01 to 0.5 wt% of silicon, 0.02 to 0.15 wt% of phosphorus, at least one of 0.3 to 3.0 wt% of bismuth and 0.3 to 3.5 wt% of lead, and optionally at least one of 0.02 to 3.0 wt% of nickel and 0.02 to 0.6 wt% of iron, with the balance being zinc and unavoidable impurities, wherein a proportion of an alpha phase is 80 vol% or more.

2. A copper alloy as set forth in claim 1, wherein an apparent content B' of zinc in said copper alloy is in the range of from 34 to 39 wt%, said apparent content B' of zinc being expressed by the following expression:

$$B' = [(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$$

wherein A denotes the content (wt%) of copper and B denotes the content (wt%) of zinc, t_1, t_2, t_3 and t_4 denoting zinc equivalents of tin, silicon, nickel and iron, respectively (t_1=2.0, t_2 = 10.0, t_3 = -1.3, t_4 = 0.9), and q_1, q_2, q_3 and q_4 denoting the contents (wt%) of tin, silicon, nickel and iron, respectively.

3. A method for producing a copper alloy, said method comprising the steps of:

preparing raw materials of a copper alloy comprising 58 to 66 wt% of copper, 0.3 to 0.5 wt% of tin, 0.01 to 0.5 wt% of silicon, 0.02 to 0.15 wt% of phosphorus, at least one of 0.3 to 3.0 wt% of bismuth and 0.3 to 3.5 wt% of lead, and optionally at least one of 0.02 to 3.0 wt% of nickel and 0.02 to 0.6 wt% of iron, with the balance being zinc and unavoidable impurities;
casting the raw materials to form an ingot;
hot working said ingot;
cold or hot working the hot worked ingot;
annealing the cold or hot worked ingot at a temperature of 300 to 600 °C for two minutes to five hours; and
cooling the annealed ingot at a cooling rate of 0.2 to 10 °C/sec.

4. A method for producing a copper alloy as set forth in claim 3, wherein an apparent content B' of zinc in said copper alloy is in the range of from 34 to 39 wt%, said apparent content B' of zinc being expressed by the following expression:

$$B' = [(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$$

wherein A denotes the content (wt%) of copper and B denotes the content (wt%) of zinc, t_1, t_2, t_3 and t_4 denoting zinc equivalents of tin, silicon, nickel and iron, respectively (t_1= 2.0, t_2 = 10.0, t_3 = -1.3, t_4 = 0.9), and q_1, q_2, q_3 and q_4 denoting the contents (wt%) of tin, silicon, nickel and iron, respectively.

Patentansprüche

1. Kupferlegierung enthaltend 58 bis 66 Gew.-% Kupfer, 0,3 bis 0,5 Gew.-% Zinn, 0,01 bis 0,5 Gew.-% Silizium, 0,02 bis 0,15 Gew.-% Phosphor, wenigstens eines von 0,3 bis 3,0 Gew.-% Bismut und 0,3 bis 3,5 Gew.-% Blei, sowie optional wenigstens eines von 0,02 bis 3 Gew.-% Nickel und 0,02 bis 0,6 Gew.-% Eisen, wobei der Rest Zink und unvermeidbare Verunreinigungen sind, und, wobei der Anteil einer Alpha-Phase 80 Vol.-% oder mehr beträgt.

2. Kupferlegierung nach Anspruch 1, wobei der scheinbare Gehalt B' von Zink in der Kupferlegierung in einem Bereich zwischen 34 und 39 Gew.-% liegt, wobei der scheinbare Gehalt B' von Zink durch die nachfolgende Gleichung ausgedrückt wird:

$$B' = [(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$$

worin A den Gehalt (Gew.-%) an Kupfer bezeichnet und B den Gehalt (Gew.-%) an Zink bezeichnet, t_1, t_2, t_3 und t_4 Zinkäquivalente von Zinn, Silizium, Nickel bzw. Eisen bedeuten (t_1 = 2,0, t_2 = 10,0, t_3 = -1,3, t_4 = 0,9) sowie q_1, q_2, q_3 und q_4 die Mengen (Gew.-%) an Zinn, Silizium, Nickel bzw. Eisen bedeuten.

3. Verfahren zum Herstellen einer Kupferlegierung, wobei das Verfahren die nachfolgenden Schritte umfasst:

   Herstellen von Rohmaterialien einer Kupferlegierung enthaltend 58 bis 66 Gew.-% Kupfer, 0,3 bis 0,5 Gew.-% Zinn, 0,01 bis 0,5 Gew.-% Silizium, 0,02 bis 0,15 Gew.-% Phosphor, wenigstens eines von 0,3 bis 3,0 Gew.-% Bismut und 0,3 bis 3,5 Gew.-% Blei, sowie optional wenigstens eines von 0,02 bis 3,0 Gew.-% Nickel und 0,02 bis 0,6 Gew.-% Eisen, wobei der Rest Zink und unvermeidliche Verunreinigungen sind,
   Gießen der Rohmaterialien, um einen Gussblock zu formen, Warmbearbeiten des Gussblocks,
   Kalt- oder Warmbearbeiten des warmbearbeiteten Gussblocks, Glühen des kalt- oder warmbearbeiteten Gussblocks bei einer Temperatur zwischen 300 und 600°C für zwei Minuten bis fünf Stunden und
   Abkühlen des geglühten Gussblocks mit einer Abkühlrate von 0,2 bis 10 °C/Sek.

4. Verfahren zum Herstellen einer Kupferlegierung nach Anspruch 3, wobei der scheinbare Gehalt B' von Zink in der Kupferlegierung in einem Bereich zwischen 34 und 39 Gew.-% liegt, wobei der scheinbare Gehalt B' von Zink durch die nachfolgende Gleichung ausgedrückt wird:

$$B' = [(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4) / (A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)] \times 100$$

worin A den Gehalt (Gew.-%) an Kupfer bezeichnet und B den Gehalt (Gew.-%) an Zink bezeichnet, t_1, t_2, t_3 und t_4 Zinkäquivalente von Zinn, Silizium, Nickel bzw. Eisen bedeuten (t_1 = 2,0, t_2 = 10,0, t_3 = -1,3, t_4 = 0,9) sowie q_1, q_2, q_3 und q_4 die Mengen (Gew.-%) an Zinn, Silizium, Nickel bzw. Eisen bedeuten.

Revendications

1. Alliage de cuivre, comprenant 58 à 66 % en poids de cuivre, 0,3 à 0,5 % en poids d'étain, 0,01 à 0,5 % en poids de silicium, 0,02 à 0,15 % en poids de phosphore, au moins un parmi 0,3 à 3,0 % en poids de bismuth et 0,3 à 3,5 % en poids de plomb, et en option au moins un parmi 0,02 à 3,0 % en poids de nickel et 0,02 à 0,6 % en poids de fer, le reste étant du zinc et des impuretés inévitables, dans lequel une proportion d'une phase alpha est de 80 %

en volume ou plus.

2. Alliage de cuivre selon la revendication 1, dans lequel une teneur apparente B' de zinc dans ledit alliage de cuivre est dans la plage de 34 à 39 % en poids, ladite teneur apparente B' de zinc étant exprimée par l'expression suivante :

$$B'=[(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)/(A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)]x100$$

dans laquelle A désigne la teneur (pourcentage en poids) de cuivre et B désigne la teneur (pourcentage en poids) de zinc, t_1, t_2, t_3 et t_4 désignent les équivalents-zinc de l'étain, du silicium, du nickel et du fer, respectivement (t_1 = 2,0, t_2 = 10,0, t_3 = - 1,3, t_4 = 0,9), et q_1, q_2, q_3 et q_4 désignent les teneurs (pourcentage en poids) d'étain, de silicium, de nickel et de fer, respectivement.

3. Procédé pour produire un alliage de cuivre, ledit procédé comprenant les étapes consistant à :

préparer des matériaux bruts d'un alliage de cuivre comprenant 58 à 66 % en poids de cuivre, 0,3 à 0,5 % en poids d'étain, 0,01 à 0,5 % en poids de silicium, 0,02 à 0,15 % en poids de phosphore, au moins un parmi 0,3 à 3,0 % en poids de bismuth et 0,3 à 3,5 % en poids de plomb, et en option au moins un parmi 0,02 à 3,0 % en poids de nickel et 0,02 à 0,6 % en poids de fer, le reste étant du zinc et des impuretés inévitables;
couler les matériaux bruts pour former un lingot ;
travailler à chaud ledit lingot ;
travailler à froid ou à chaud le lingot travaillé à chaud ;
recuire le lingot travaillé à froid ou à chaud à une température de 300 à 600 °C pendant deux minutes à cinq heures ; et
refroidir le lingot recuit à une vitesse de refroidissement de 0,2 à 10 °C/seconde.

4. Procédé pour produire un alliage de cuivre selon la revendication 3, dans lequel une teneur apparente B' de zinc dans ledit alliage de cuivre est dans la plage de 34 à 39 % en poids, ladite teneur apparente B' de zinc étant exprimée par l'expression suivante :

$$B'=[(B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)/(A + B + t_1q_1 + t_2q_2 + t_3q_3 + t_4q_4)]x100$$

dans laquelle A désigne la teneur (pourcentage en poids) de cuivre et B désigne la teneur (pourcentage en poids) de zinc, t_1, t_2, t_3 et t_4 désignent les équivalents-zinc de l'étain, du silicium, du nickel et du fer, respectivement (t_1 = 2,0, t_2 = 10,0, t_3 = - 1,3, t_4 = 0,9), et q_1, q_2, q_3 et q_4 désignent les teneurs (pourcentage en poids) d'étain, de silicium, de nickel et de fer, respectivement.