



Europäisches Patentamt
European Patent Office
Office européen des brevets



(11) **EP 1 538 229 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 158(3) EPC

(43) Date of publication:
08.06.2005 Bulletin 2005/23

(51) Int Cl.7: **C22C 9/04, C22F 1/08**

(21) Application number: **03794057.4**

(86) International application number:
PCT/JP2003/004470

(22) Date of filing: **08.04.2003**

(87) International publication number:
WO 2004/022805 (18.03.2004 Gazette 2004/12)

(84) Designated Contracting States:
**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HU IE IT LI LU MC NL PT RO SE SI SK TR**
Designated Extension States:
AL LT LV MK

(30) Priority: **09.09.2002 JP 2002263125**

(71) Applicant: **Sambo Copper Alloy Co., Ltd
Osaka 590-0906 (JP)**

(72) Inventors:
• **OISHI, Keiichiro,**
c/o Sambo Copper Alloy Co., Ltd.
Sakai-shi, Osaka 590-0906 (JP)
• **SASAKI, Isao, c/o Sambo Copper Alloy Co., Ltd.**
Sakai-shi, Osaka 590-0906 (JP)
• **OTANI, Junichi,**
c/o Sambo Copper Alloy Co., Ltd.
Sakai-shi, Osaka 590-0906 (JP)

(74) Representative: **Schickedanz, Willi, Dr. Dipl.-Ing.**
Langener Strasse 68
63073 Offenbach (DE)

(54) **HIGH-STRENGTH COPPER ALLOY**

(57) The present invention is a high strength copper alloy that is superior to mechanical properties, workability, corrosion resistance and economy. The present invention discloses high strength copper alloy **characterized in that** said copper alloy consists essentially of 4 to 19 mass percent of Zn, 0.5 to 2.5 mass percent of Si and the remaining mass percent of Cu, wherein said

mass percent of Zn and said mass percent of Si satisfy the relationship $Zn - 2.5 \cdot Si = 0$ to 15 mass percent; mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu m \leq D \leq 3.5 \mu m$; and 0.2% yield strength in recrystallization state of said copper alloy is higher than 250N/mm².

EP 1 538 229 A1

Description**BACKGROUND OF THE INVENTION****1. Field of the Invention**

[0001] The present invention relates to the high strength copper alloy suitable for materials comprising leads, switches, connectors, relays and sliding pieces etc. which are parts of electrical devices, electronic devices, communication equipments, information appliances, measuring instruments, automobiles and so on.

2. Prior Art

[0002] In general, high strength copper alloys are used as materials comprising leads, switches, connectors, relays and sliding pieces etc., which are used as parts of electrical devices, electronic devices, and communication devices, information appliances, measuring instruments, automobiles, and so on. Recently, their devices have been improved toward miniaturization, lightweighting, and higher efficiency, so that there are extremely severe demands for the improvements of characteristics of the materials. For example, the extremely thin plates are employed for the spring contact member of the connector. The higher strength is required for the high strength copper alloy comprising said extremely thin plates in order to thin the plate still more. It is also demanded for the high strength copper alloy to have higher balance between the strength and ductility including the bending characteristics, superiority in productivity and economy without problems of conductivity, stress relaxation characteristic, soldering characteristics, abrasion resistance, and corrosion resistance such as stress corrosion cracking resistance, dezincification corrosion resistance and migration resistance.

[0003] Incidentally, beryllium copper, titanium copper, aluminum bronze, phosphor bronze, nickel silver, brass and brass doped with Sn or Ni are generally well-known for the high strength copper alloys. However, there are following problems for these high strength copper alloys, so that it was impossible to satisfy the above demands.

[0004] The beryllium copper has the highest strength in the copper alloys, but the beryllium is extremely harmful to the humans: in particular the beryllium vapor in fusion state is significantly dangerous for the humans even in a very small amount, so that initial cost of melting arrangement becomes extremely expensive because of difficulty in disposal processes, particularly in a firing treatment of the beryllium copper materials or their products. Therefore, the melting process becomes necessary at the last step of manufacturing to obtain the predetermined characteristics, and then the problems appear in economy including the manufacturing cost.

[0005] In addition, the titanium copper shows the higher strength to next to beryllium copper, but the expensive melting arrangement is required because titanium is active element, and hence it becomes difficult to keep quality and yield in the melting. As well as the beryllium copper, since the melting process becomes necessary at the last step of manufacturing, the problems in economy appear.

[0006] For the aluminum bronze, it is difficult to obtain pure ingots because aluminum is an active element, and furthermore the aluminum bronze has the lower soldering characteristics.

[0007] Moreover, as the phosphor bronze and the nickel silver have the lower hot workability, it is difficult to produce them by hot rolling. Their alloys are usually produced with horizontal continuous casting. Consequently, their alloys are inferior in the productivity, the yield and the energy cost. Additionally, as to a spring phosphor-bronze and a spring nickel-silver which are representative copper alloys with high strength, problems in economy appear because expensive Sn and Ni are abundantly contained in the two alloys.

[0008] The brass or brass doped with Si and Ni is inexpensive, but there are problems with respect to the corrosion resistance such as the stress corrosion cracking and dezincification, and then they are unsuitable for the parts to realize miniaturization and higher efficiency.

[0009] As a result, these conventional high strength copper alloys are not satisfied as the parts used in the various devices with tendency toward miniaturization, lightweighting and higher efficiency, so that the development of a new high strength copper alloy is demanded greatly.

SUMMARY OF THE INVENTION

[0010] Present inventors have paid their attention to the Hall-Petch relationship (E. O. Hall, Proc. Phys. Soc. London. 64 (1951) 747. and N.J. Petch, J. Iron Steel Inst. 174 (1953) 25.) that 0.2% proof stress is proportional to grain size ($D^{-1/2}$), where said 0.2% proof stress is defined by the strength that permanent strain becomes 0.2%, and said 0.2% proof stress is sometimes abbreviated as "proof stress". The present inventors have considered that the high strength copper alloys satisfying the demands of said epoch can be obtained by grain refinement, and then several investigations and experiments have been performed on the grain refinement. From their results, it is found that the micronization

for the crystal grain (grain refinement) of the copper alloys is realized by selecting suitably additive elements in the recrystallization. It is recognized that the strength including mainly the 0.2% proof stress is improved remarkably by making the crystal grain size smaller than a certain size and its strength also increases with decreasing of the grain size. Furthermore, from the results of various experiments with respect to influence of the additive elements for micro-

nization of the grain size, it is clarified that addition of Si to Cu-Zn alloy increases the number of nucleation sites and addition of Co to Cu-Zn-Si alloy suppresses the grain growth. This means that Cu-Zn-Si or Cu-Zn-Si-Co alloy system with fine grains is obtained by exploiting their effects. In other words, the increase of nucleation sites is considered to be due to decreasing of stacking fault energy based on the addition of Si, and the suppression of the grain growth is considered to be due to the formation of fine precipitates based on the addition of Co.

[0011] The present invention is completed based upon these investigated results and relates to new high strength copper alloy superior in mechanical properties, workability and corrosion resistance without problems in economy. In particular the invention is suitable for materials of the parts composing several devices in tendency of miniaturization, lightweighting and higher efficiency. Accordingly, it is the object of the present invention to provide new high strength copper alloy that is extensively applied and extremely rich in utility.

[0012] Namely, it is mainly first object of the present invention to provide the high strength copper alloy (called "first invention copper alloy") suitable for rolled stocks (plates, rods and wires etc.) required high strength, or the work piece of rolled stock (press-forming product and bending product etc.), and this alloy is in the following. In addition, as parts and products suitably manufactured by use of first invention copper alloy, there are the portable or miniature communication equipments which are required thinization (to thin the plate still more) and lightweighting, electronic device parts used for personal computer, medical care instrument parts, accessory parts, machine parts, tubes or plates of heat exchanger, cooling instruments using sea water, parts composing inlet or outlet of sea water in small size ship, wiring tool parts, various instrument parts for automobile, measuring-instrument parts, play tools and daily necessities and so on. There are concretely connectors, relays, switches, sockets, springs, gears, pins, washers, coins for play, keys, tumblers, buttons, hooks, braces, diaphragms, bellows, sliding pieces, bearings, sliding pieces adjusting sound volume, bushes, fuse grips, lead frames and gauge board and so on.

[0013] It is mainly second object of the present invention to provide the high strength copper alloy (called "second invention copper alloy") suitable for rolled stocks (plates, rods and wires etc.) required highly balanced strength and electric conductivity, or the work piece of rolled stock (press-forming product and bending product etc.), where the strength required for first invention copper alloy is not needed. In addition, as parts and products suitably manufactured by use of second invention copper alloy, there are electronic device parts required electric conductivity, measuring-instrument parts, household electric appliance parts, tubes or plates of heat exchanger, cooling instruments using sea water, parts composing inlet or outlet of sea water in small size ship, machine parts, play tools and daily necessities and so on. There are concretely connectors, switches, relays, bushes, fuse grips, lead frames, wiring instruments, keys, tumblers, buttons, hooks, braces, diaphragms, bellows, sliding pieces, bearings, coins for play, and so on.

[0014] Furthermore, it is mainly third object of the present invention to provide the high strength copper alloy (called "third invention copper alloy") suitable for wire drawing materials [general wire material of round cross section and deformed wire material such as rectangle cross section (square etc.), polygon cross section (hexagon etc.) and so on] or the workpiece of wire drawing materials (bending product etc.), where the strength required for first invention copper alloy is needed. In addition, as parts and products suitably manufactured by use of third invention copper alloy, there are electronic device parts, parts for construction, accessory parts, machine parts, play tools, various instrument parts for automobile, measuring-instrument parts, electronic device parts and electrical device parts. There are concretely connectors, keys, header members, nails (nails for play instrument), washers, pins, screws, coiled springs, lead screws, shafts of copying machines etc., wire gauzes (wire gauze for culture or filter for inlet and outlet of seawater used in seawater cooling equipment and small ship etc.), sliding pieces, bearings, bolts and so on.

[0015] The first invention copper alloy consists essentially of 4 to 19 mass percent (preferably 6 to 15 mass percent, more preferably 7 to 13 mass percent) of Zn, 0.5 to 2.5 mass percent (preferably 0.9 to 2.3 mass percent, more preferably 1.3 to 2.2 mass percent) of Si and the remaining mass percent of Cu, wherein said mass percent of Zn and said mass percent of Si satisfy the relationship $Zn - 2.5 \cdot Si = 0$ to 15 mass percent (preferably 1 to 12 mass percent, more preferably 2 to 9 mass percent); mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu m \leq D \leq 3.5 \mu m$ (preferably $0.3 \mu m \leq D \leq 2.5 \mu m$, more preferably $0.3 \mu m \leq D \leq 2 \mu m$); and 0.2% proof stress in recrystallization state of said copper alloy is higher than $250 N/mm^2$ (preferably higher than $300 N/mm^2$).

[0016] In addition, the second invention copper alloy consists essentially of 4 to 17 mass percent (preferably 5 to 13 mass percent, more preferably 6 to 11.5 mass percent) of Zn, 0.1 to 0.8 mass percent (preferably 0.2 to 0.6 mass percent, more preferably 0.2 to 0.5 mass percent) of Si and the remaining mass percent of Cu, wherein said mass percent of Zn and said mass percent of Si satisfy the relationship $Zn - 2.5 \cdot Si = 2$ to 15 mass percent (preferably 4 to 12 mass percent, more preferably 5 to 10 mass percent); mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu m \leq D \leq 3.5 \mu m$ (preferably $0.3 \mu m \leq D \leq 3 \mu m$, more preferably $0.3 \mu m \leq D \leq 2.5 \mu m$); and 0.2% proof stress in recrystallization state of said copper alloy is higher than $250 N/mm^2$ (preferably higher than $300 N/mm^2$).

[0017] Furthermore, the third invention copper alloy consists essentially of 66 to 76 mass percent (preferably 68 to 75.5 mass percent) of Cu, 21 to 33 mass percent (preferably 22 to 31 mass percent) of Zn and 0.5 to 2 mass percent (preferably 0.8 to 1.8 mass percent, more preferably 1 to 1.7 mass percent) of Si, wherein said mass percent of Cu, said mass percent of Zn and said mass percent of Si satisfy the relationships $\text{Cu}-5 \cdot \text{Si}=62$ to 67 (preferably $\text{Cu}-5 \cdot \text{Si}=63$ to 66.5 mass percent) and $\text{Zn}+6 \cdot \text{Si} = 32$ to 38 (preferably $\text{Zn} + 6 \cdot \text{Si}=33$ to 37 mass percent); mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu\text{m} \leq D \leq 3.5 \mu\text{m}$ (preferably $0.3 \mu\text{m} \leq D \leq 3 \mu\text{m}$, more preferably $0.3 \mu\text{m} \leq D \leq 2.5 \mu\text{m}$); and 0.2% proof stress in recrystallization state of said copper alloy is higher than 250N/mm² (preferably higher than 300N/mm²).

[0018] In order to obtain said each invention copper alloy, there are some cases receiving a plurality of recrystallization treatments in which a part or all of the alloy structure is recrystallized by the heat treatment. In such cases, said mean grain size D and said 0.2% proof stress in copper alloy are determined from said two physical quantities of the materials (called "recrystallization materials") obtained from the recrystallization treatment performed at last (called "last recrystallization treatment"). In the case that said recrystallization treatment is performed only once, it goes without saying that the recrystallization treatment is the last recrystallization treatment and the treated materials are the recrystallization materials.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

[0019] Each invention copper alloy is provided with any form shown in the following preferred embodiments.

(Embodiment 1)

[0020] Ingots are worked into plastic working blanks with predetermined forms by the plastic working including the hot working (rolling, extruding and forging etc.) and/or the cold working (rolling and wire drawing etc.). The plastic working blanks receive the recrystallization treatment (last recrystallization treatment) based upon heat treatment (annealing etc.) in the range of the recrystallization temperature, and then become the recrystallization materials. The recrystallization materials are rolled stocks in first and second invention copper alloys, and wire drawing materials in third invention copper alloy.

(Embodiment 2)

[0021] The recrystallization materials of said embodiment 1 are worked into the cold working materials with predetermined forms according to cold working (rolling, wire drawing and forging). The cold working materials are rolled stocks in first and second invention copper alloys, and wire drawing materials in third invention copper alloy.

(Embodiment 3)

[0022] The recrystallization materials of said embodiment 1 are worked into manufacture pieces with predetermined forms according to press working or bending etc.

(Embodiment 4)

[0023] The cold working materials of said embodiment 2 are worked into manufacture pieces with predetermined forms according to press working or bending etc.

[0024] In order to improve the property of first invention copper alloy, it is desired for the copper alloy composition to contain 0.005 to 0.5 mass percent (preferably 0.01 to 0.3 mass percent, more preferably 0.02 to 0.2 mass percent) of Co and/or 0.03 to 1.5 mass percent (preferably 0.05 to 0.7 mass percent, more preferably 0.05 to 0.5 mass percent) of Sn.

[0025] In this case, the contents of Co and Sn are determined from said each range under consideration of the content of Si. In other words, the content of Co is determined to satisfy the relationship $\text{Co}/\text{Si}=0.05$ to 0.5 (preferably $\text{Co}/\text{Si}=0.01$ to 0.3, more preferably $\text{Co}/\text{Si}=0.03$ to 0.2), wherein the value of Co content divided by Si content is defined by Co/Si . Additionally, the content of Sn is determined to satisfy the relationship $\text{Si}/\text{Sn} \geq 1.5$ (preferably $\text{Si}/\text{Sn} \geq 2$, more preferably $\text{Si}/\text{Sn} \geq 3$), wherein the value of Si content divided by Sn content is defined by Si/Sn .

[0026] In first invention copper alloy, it is possible for the copper alloy composition to contain 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent) of Fe and/or 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent) of Ni in substitution for Co or together with Co.

[0027] For said composition, the content of Fe or Ni is determined under consideration of the content of Si. In the case added with Co, the contents of Si and Co are considered. Namely, the content of Fe or Ni is determined to satisfy

the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.005$ to 0.5 (preferably $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.01$ to 0.3 , more preferably $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.03$ to 0.2), wherein the value of total contents containing Co divided by Si content is defined by $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}$. It is desirable for such determination that said total content $(\text{Fe}+\text{Ni}+\text{Co})$ is adjusted to be 0.005 to 0.55 mass percent (more preferably 0.01 to 0.35 mass percent, much more preferably 0.02 to 0.2 mass percent).

[0028] In order to improve the characteristics more in second invention copper alloy, it is preferable to contain Co of 0.005 to 0.5 mass percent (preferably 0.01 to 0.3 mass percent, more preferably 0.02 to 0.2 mass percent) and/or Sn of 0.2 to 3 mass percent (preferably 1 to 2.6 mass percent, more preferably 1.2 to 2.5 mass percent) in alloy composition. In this case, the contents of Co and Sn are determined by considering the relation to Si content. In other words, the content of Co is determined to satisfy the relationship $\text{Co}/\text{Si}=0.02$ to 1.5 (preferably $\text{Co}/\text{Si}=0.04$ to 1 , more preferably $\text{Co}/\text{Si}=0.06$ to 0.5) in the range described above. In addition, the content of Sn is determined to satisfy the relationship $\text{Si}/\text{Sn}\leq 0.5$ (preferably $\text{Si}/\text{Sn}\leq 0.4$, more preferably $\text{Si}/\text{Sn}\leq 0.3$) in the range described above.

[0029] In second invention copper alloy, it is possible to contain Fe of 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent) and/or Ni of 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent) in substitution for Co or together with Co. In this case, the content of Fe or Ni is determined by considering the content of Si (or both contents of Si and Co in case of co-adding Co). In other words, the contents of Fe and Ni are determined to satisfy the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.02$ to 1.5 (preferably $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.04$ to 1 , more preferably $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.06$ to 0.5). It is desirable for such determination that said total content $(\text{Fe}+\text{Ni}+\text{Co})$ is adjusted to be 0.005 to 0.55 mass percent (preferably 0.01 to 0.35 mass percent, more preferably 0.02 to 0.25 mass percent).

[0030] Furthermore, for the first and second invention copper alloys, it is possible to contain at least one element selected from a group of P, Sb, As, Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In and Hf corresponding to characteristics required in their applications.

The contents of these elements are determined appropriately in the range of 0.003 to 0.3 mass percent.

[0031] In order to improve the characteristics of third invention copper alloy, it is preferable to contain Co of 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent, more preferably 0.02 to 0.15 mass percent) and/or Sn of 0.03 to 1 mass percent (preferably 0.05 to 0.7 mass percent, more preferably 0.05 to 0.5 mass percent) in alloy composition.

[0032] In this case, the contents of Co and Sn are determined by considering the content of Si in above range. In other words, the content of Co is determined to satisfy the relationship $\text{Co}/\text{Si}=0.005$ to 0.4 (preferably $\text{Co}/\text{Si}=0.01$ to 0.2 , more preferably $\text{Co}/\text{Si}=0.02$ to 0.15). In addition, the content of Sn is determined to satisfy the relationship $\text{Si}/\text{Sn}\geq 1$ (preferably $\text{Si}/\text{Sn}\geq 1.5$, more preferably $\text{Si}/\text{Sn}\geq 2$).

[0033] For the third invention copper alloy, it is possible to contain Fe of 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent) and/or Ni of 0.005 to 0.3 mass percent (preferably 0.01 to 0.2 mass percent) in substitution for Co or together with Co.

[0034] In this case, the content of Fe or Ni is determined by considering the content of Si (or both contents of Si and Co in case of co-adding Co). In other words, the contents of Fe and Ni are determined to satisfy the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.005$ to 0.4 (preferably $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.01$ to 0.2 , more preferably $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.02$ to 0.15). It is desirable for such determination that said total content $(\text{Fe}+\text{Ni}+\text{Co})$ is adjusted to be 0.005 to 0.35 mass percent (more preferably 0.01 to 0.25 mass percent, much more preferably 0.02 to 0.2 mass percent).

[0035] Furthermore, in alloy composition for third invention copper alloy, it is possible to contain at least one element selected from a group of P, Sb, As, Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In and Hf corresponding to characteristics required in their applications, where each content of P, Sb, or As is 0.005 to 0.3 mass percent and each content of Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In or Hf is 0.003 to 0.3 mass percent, and the total content in cases selecting at least one element from P, Sb and As is 0.005 to 0.25 mass percent.

[0036] By the way, the strength, particularly the 0.2% proof stress, is enhanced by the grain (recrystallized grain) refinement. The present inventors have confirmed experimentally that the 0.2% proof stress is enhanced remarkably for the mean grain size less than $3.5\mu\text{m}$ in comparison with the case larger than $3.5\mu\text{m}$. In addition, by reducing gradually the mean grain size D from $3.5\mu\text{m}$, it is identified that the enhanced ratio of the proof stress increase rapidly at 3 , 2.5 and $2\mu\text{m}$. From such experimental results, it is found that the proof stress (generally higher than $250\text{N}/\text{mm}^2$, preferably higher than $300\text{N}/\text{mm}^2$) required for the parts of the electrical devices, electronic devices, communication equipments and measuring instruments is ensured in the mean grain size D less than $3.5\mu\text{m}$. In the case demanding high strength (the proof stress), it is preferable for mean grain size D to be less than $3.0\mu\text{m}$, and in the case demanding higher strength, it is preferable to be less than $2.5\mu\text{m}$. In order to improve rapidly the strength in the possible range, it is preferable for mean grain size D to be less than $2\mu\text{m}$. On the other hand, although the proof stress is improved with decrease of the mean grain size D , it is predictably difficult to obtain practically grains less than $0.3\mu\text{m}$ because the smallest grain size confirmed by the experiments is $0.3\mu\text{m}$.

[0037] From such points, in order to ensure the proof stress higher than $250\text{N}/\text{mm}^2$ (preferably higher than $300\text{N}/\text{mm}^2$) in the first, second and third invention copper alloys, the recrystallized structure of $0.3\mu\text{m}\leq D\leq 3.5\mu\text{m}$ is required. In other words, it is necessary that the mean grain size D in the recrystallization state (state after the last recrystallization

treatment) distributes in $0.3\mu\text{m} \leq D \leq 3.5\mu\text{m}$ and 0.2% proof stress is higher than 250N/mm^2 . In the case demanding the higher strength for the second and third invention copper alloys, it is preferable to distribute in $0.3\mu\text{m} \leq D \leq 3\mu\text{m}$, and more preferable to distribute in $0.3\mu\text{m} \leq D \leq 2.5\mu\text{m}$. On the other hand, in the first invention copper alloy required sometimes the strength higher than the second and third invention copper alloys, it is preferable to distribute in $0.3\mu\text{m} \leq D \leq 2.5\mu\text{m}$, and more preferable to distribute in $0.3\mu\text{m} \leq D \leq 2\mu\text{m}$.

[0038] Additionally, in the first to third invention copper alloys of which grain refinement is realized by recrystallization due to the suitable heat-treatment (generally annealing), such grain refinement becomes possible in alloy composition described above.

[0039] Namely, in the first to third invention copper alloys, Zn and Si cause the stacking fault energy to decrease, the dislocation density to increase, and the nucleus sites of recrystallized grain generation to increase. The functions which contributes to the grain refinement and the material strengthening due to solid solution into the Cu matrix (both functions are called "grain refinement and strengthening" as following) are given, and the contents of those elements are determined by said ranges as mentioned below. In other words, for first and second invention copper alloys used mainly as the rolled stocks or the manufacture pieces, when the functions of grain refinement and strengthening due to the addition of Zn appear enough, the content of Zn is more than 4 mass percent, and in order to improve largely the strength in first invention copper alloy, it is required that the content is more than 6 mass percent (preferably higher than 7 mass percent). For second invention copper alloy of which strength is allowed to be inferior to the first invention, it is preferable that the content is more than 5 mass percent (more preferably higher than 6 mass percent). On the other hand, when the content of Zn becomes excessively, the sensitivity of the stress-corrosion cracking increases and the bending characteristic deteriorates. Accordingly, when the relation of the content of Si for the applications of the rolled stock and the inhibition function of the stress corrosion cracking is taken into consideration, the content of Zn in the first invention copper alloy is less than 19 mass percent (preferably less than 15 mass percent, more preferably less than 13 mass percent), and the content in the second invention copper alloy is less than 17 mass percent (preferably less than 13 mass percent, more preferably less than 11.5 mass percent).

[0040] On the other hand, although the grain refinement and strengthening functions due to addition of Si appear remarkably in pretty little quantity comparing with Zn, the functions are caused by interaction with Zn. In addition, Si improves the characteristics of the stress-corrosion cracking by co-addition of Zn. However, the surplus addition of Si decreases the electric conductivity of this alloy. When these points are taken into consideration, it is required that the content of Si is higher than 0.5 mass percent for first invention copper alloy which accomplishes the strength improvement and grain refinement. The more or much more preferable content is more than 0.9 or 1.3 mass percent, respectively. However, the electric conductivity, hot workability and cold workability in first invention copper alloy are decreased by the Si content (also called the content of Si) in excess over 2.5 mass percent, and in order to keep those characteristics enough, it is preferable that the Si content is less than 2.3 mass percent, and the more preferable content is less than 2.2 mass percent.

On the other hand, in second invention copper alloy that thinks the balance between the strength and the electric conductivity important, in order to realize the grain-refinement effect required for the predetermined strength, the Si content of 0.1 mass percent at least is necessary, and it is preferable to be higher than 0.2 mass percent. However, in order to ensure the predetermined electric conductivity considering balance with strength, it is required that the Si content is less than 0.8 mass percent, and in order to ensure the electric conductivity enough to be used for the applications, it is preferable to be less than 0.6 mass percent (more preferably less than 0.5 mass percent).

[0041] Furthermore, in first and second invention copper alloys, it is necessary that balance among the effect of grain refinement, stress-corrosion cracking characteristics and the strength is kept by the co-addition of Zn and Si, but it is unsuitable in these alloys to determine independently the individual content in said range. Accordingly, it is necessary that the relation of the Zn and Si contents is specified by the relationship $\text{Zn} - 2.5 \cdot \text{Si}$ and the values of this formulae are determined to be in above predetermined range. In order to obtain the predetermined strength based upon the grain refinement, it is necessary for first invention copper alloy to satisfy the relationship $\text{Zn} - 2.5 \cdot \text{Si} \geq 0$ mass percent, and the preferable relationship is $\text{Zn} - 2.5 \cdot \text{Si} \geq 1$ mass percent (more preferably $\text{Zn} - 2.5 \cdot \text{Si} \geq 2$ mass percent), and it is necessary for second invention copper alloy to satisfy the relationship $\text{Zn} - 2.5 \cdot \text{Si} \geq 2$ mass percent, and the preferable relationship is $\text{Zn} - 2.5 \cdot \text{Si} \geq 4$ mass percent (more preferably $\text{Zn} - 2.5 \cdot \text{Si} \geq 5$ mass percent). On the other hand, in any of first and second invention copper alloys, it is necessary to satisfy the relationship $\text{Zn} - 2.5 \cdot \text{Si} \leq 15$ mass percent because the stress corrosion cracking arises remarkably for $\text{Zn} - 2.5 \cdot \text{Si} > 15$ mass percent. In order to inhibit effectively the stress corrosion cracking, it is preferable to satisfy the relationship $\text{Zn} - 2.5 \cdot \text{Si} \leq 12$ mass percent (more preferably $\text{Zn} - 2.5 \cdot \text{Si} \leq 9$ mass percent for first invention copper alloy, and $\text{Zn} - 2.5 \cdot \text{Si} \leq 10$ mass percent for second invention copper alloy).

[0042] In addition, for the Zn content in third invention copper alloy, the grain refinement and strength are rightly considered as well as first and second invention copper alloys. Furthermore, since the third invention copper alloy is mainly used as wire drawing material and its manufactured piece, the Zn content should be determined in consideration of hot extruding characteristics, so that the Zn content is set to be abundantly in comparison with first and second

invention copper alloys. In order to ensure the hot extruding characteristics enough, it is necessary for Zn content to be higher than 21 mass percent. It is more preferable for Zn content to be higher than 22 mass percent so that hot extruding-wire drawing can be kept more excellent. Although the characteristics of stress-corrosion cracking resistance of third invention copper alloy is inferior in comparison with first and second invention copper alloys, this characteristics can be satisfied enough for use of wire etc. because Zn content is a little in comparison with general Cu-Zn system alloy (for example, JIS-C2700 (65Cu-35Zn)). However, in order to ensure enough the stress-corrosion cracking resistance and cold workability, it is required that Zn content of third invention copper alloy is lower than 33 mass percent. In other words, when Zn content is higher than 33 mass percent, β and γ phases are easy to remain and give a wrong influence upon the cold workability. Furthermore, the stress corrosion cracking resistance and dezincification corrosion become also problems. In order to carry out the hot extrusion-wire drawing well while the stress corrosion cracking resistance and the cold workability are ensured, it is preferable for Zn content to be less than 31 mass percent. In order to ensure the hot extrusion characteristics and the cold workability, it is necessary in third invention copper alloy to consider the Cu content, and the β and γ phases are easy to remain when the Cu content is less than 66 mass percent. On the other hand, when the content is higher than 76 mass percent, it gets difficult to perform the hot extrusion. Therefore, it is necessary for the Cu content to be 66 to 76 mass percent. Furthermore, in order to ensure the cold workability and the hot extrusion characteristics enough, it is preferable to be 68 to 75.5 mass percent.

[0043] In addition, as mentioned above, Si shows the grain refinement, strength improvement and inhibition function of stress-corrosion cracking by adding together with Zn. Accordingly, in the case that the grain refinement and strength improvement are the principal object of third invention copper alloy used as wire drawing material, it is necessary for the content of Si to be higher than 0.5 mass percent as well as first invention copper alloy. Considering that said copper alloy is utilized as wire drawing material, it is preferable to be higher than 0.8 mass percent and the most preferable to be higher than 1 mass percent. However, when the Si content becomes higher than 2 mass percent, the γ or β phase which is a factor obstructing cold workability precipitate. Therefore, it is required to be less than 2 mass percent so that the cold workability is ensured, and if considering that plenty of Zn is added, it is preferable to be less than 1.8 mass percent, and more preferable to be less than 1.7 mass percent.

[0044] Furthermore, in order to ensure the hot extrusion characteristics, cold workability and stress corrosion cracking resistance in third invention copper alloy, it is unsuitable that the individual contents of Cu, Si and Zn are determined independently. Namely, it is necessary that the contents of Cu, Si and Zn are determined so as to satisfy the relationship $\text{Cu} \cdot 5 \cdot \text{Si} = 62$ to 67 mass percent and $\text{Zn} \cdot 6 \cdot \text{Si} = 32$ to 38 mass percent. In other words, even though the contents of Cu, Si and Zn are in said range, the preferable hot workability can not be ensured when the contents of Cu, Si and Zn satisfy the relationships $\text{Cu} \cdot 5 \cdot \text{Si} > 67$ mass percent or $\text{Zn} \cdot 6 \cdot \text{Si} < 32$ mass percent. On the other hands, when $\text{Cu} \cdot 5 \cdot \text{Si} < 62$ mass percent or $\text{Zn} \cdot 6 \cdot \text{Si} > 38$, the cold workability worsens because concentrations of Zn and Si at grain boundary become higher, and β and γ phases became easy to remain. Additionally, it becomes easy for the stress corrosion cracking to appear, and for some applications, problems of dezincification corrosion are also caused easily. In order to ensure enough the cold workability and stress-corrosion cracking resistance without these problems, it is preferable that the contents of Cu, Si and Zn are determined to satisfy the relationships $\text{Cu} \cdot 5 \cdot \text{Si} = 63$ to 66.5 mass percent and $\text{Zn} \cdot 6 \cdot \text{Si} = 33$ to 37 mass percent.

[0045] Incidentally, the grains grow with the rise of temperature or with time, and then in the recrystallization process, the whole of grains does not recrystallize at the same time and the parts easy to recrystallize start to recrystallize at first and a long time becomes necessary until its recrystallization finish in all structures. Therefore, the crystal grains recrystallizing at the initial stage of the recrystallization process continue to grow till the recrystallization process finishes, and then the crystal grains become considerably large at the time point that all structures have recrystallized completely. Consequently, it is preferable to inhibit growth of recrystallized grains in the recrystallization, so that the fine recrystallized grains distribute uniformly in all structures. Co has a function inhibiting growth of the recrystallized grains, and this is the reason of Co addition in first to third invention copper alloys. In other words, Co combines with Si, and the growth of crystal grains is suppressed by forming fine precipitates (Co_2Si of about $0.01 \mu\text{m}$, etc.). In order that the Co shows the function inhibiting the growth of crystal grain, it is necessary for the Co content to be higher than 0.005 mass percent. All of the added Co is not concerned with formation of said precipitate but the solid solution part of Co improves the heat resistance of matrix and stress relaxation characteristic. Accordingly, in order that such functions improving stress relaxation characteristic and heat resistance are shown enough, it is preferable for all copper alloys of first to third inventions to be higher than 0.01 mass percent, and it is more preferable to be higher than 0.02 mass percent. On the other hands, when the Co addition becomes higher than 0.5 mass percent or 0.3 mass percent in the first and second invention copper alloys, and the third invention copper alloy, respectively, it is difficult to improve still more the effect of grain-growth inhibition and the improvement effect of stress relaxation characteristic needed in applications because of those saturation, and then it is useless economically. Furthermore, there is a possibility that such additions lower the bending characteristics because of enlarging of precipitating particle and increasing of precipitating amount. Therefore, it is necessary for content of Co in the first and second invention copper alloys to be lower than 0.5 mass percent and for content of Co in the third invention copper alloy to be lower than 0.3 mass percent. However, in order

to show effectively said functions and to ensure bending characteristics enough, it is preferable that the contents of Co in the first and second invention copper alloys become less than 0.3 mass percent, and it is more preferable that the contents become less than 0.2 mass percent. From the same reasons, it is preferable that the content of Co in the third invention copper alloy becomes less than 0.2 mass percent, and it is more preferable that the content becomes less than 0.15 mass percent.

[0046] In addition, since Co have the close relation with Si in the grain refinement, the content of Co needs to be determined from relation to the content of Si. For the grain refinement with purpose of strength improvement required in applications, it is necessary that the ratio Co/Si in the first and third invention copper alloys is determined to be higher than 0.005 mass percent and the ratio Co/Si in the second invention copper alloy is determined to be higher than 0.02. In other words, when Co/Si dose not reach these values, there is a little formation of said precipitate and the effect of grain-growth inhibition are not shown, and then it is difficult to obtain the strength needed in applications of said invention copper alloys. Furthermore, in order to show the growth inhibition effect of crystal grain enough and improve the strength more, in the first and third invention copper alloys, it is preferable that Co/Si is higher than 0.01 and more preferable that Co/Si is high than 0.02 mass percent. In addition, the preferable and more preferable values in the second invention copper alloy are higher than 0.04 and 0.06, respectively.

[0047] As described above, in the relation to Si content, Co content must be determined to satisfy the ratio Co/Si which becomes higher than the predetermined values, and since said precipitate becomes rough and increases, the bending characteristics are obstructed. For example, when Co/Si in the first invention copper alloy used as the rolled stock becomes higher than 0.5 or Co/Si in the third invention copper alloy used as the wire drawing material or the manufactured piece becomes higher than 0.4, the bending characteristics decreases suddenly. Additionally, even in the second invention copper alloy whose strength has not to satisfy the strength condition required in the first invention copper alloy, when Co/Si exceeds 1.5, it becomes difficult to ensure the minimum condition required for the bending characteristics. Therefore, the upper limit of Co/Si must be determined by comparing said point with the effect of grain growth inhibition, taking the applications, worked history and shapes into consideration in this invention copper alloy. Concretely, the range of Co/Si is determined as follows. In other words, it is necessary that the upper limit of Co/Si in the first invention copper alloy satisfies the relationship $\text{Co/Si} \leq 0.5$, and the preferable and optimum relationships are $\text{Co/Si} \leq 0.3$ and $\text{Co/Si} \leq 0.2$, respectively. In addition, in the second invention copper alloy, it is necessary to satisfy the relationship $\text{Co/Si} \leq 1.5$, and the preferable and optimum relationships are $\text{Co/Si} \leq 1$ and $\text{Co/Si} \leq 0.5$, respectively. Furthermore, in the third invention copper alloy, it is necessary to satisfy the relationship $\text{Co/Si} \leq 0.4$, and the preferable and optimum relationships are $\text{Co/Si} \leq 0.2$ and $\text{Co/Si} \leq 0.15$, respectively.

[0048] Fe and Ni show the same effect inhibiting crystal grain as Co (exactly, its effect due to Fe, Ni is less than or equal to the effect of Co). Therefore, it is possible to contain Fe, Ni as substitutive element of Co. Of course, further improvement of the effect can be expected by co-adding Fe and Ni together with Co. In the case that Fe and/or Ni are added in substitution of Co or with Co, those additions have the remarkable effect in economy because of decreasing of the expensive Co. As to the relationship $(\text{Co}+\text{Fe}+\text{Ni})/\text{Si}$ among the contents of Fe, Ni and Si in the case of the additions of Fe and/or Ni, the content of Fe or Ni is adjusted to be equal to the content of Co, and $(\text{Co}+\text{Fe}+\text{Ni})/\text{Si}$ is set to be equal to the value of Co/Si in single addition of Co, in all of first, second and third invention copper alloys. This admixture is based upon the reason described above on the relationship Co/Si between the contents of Co and Si. In other words, the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}$ in the first invention copper alloy is 0.005 to 0.5 (preferably 0.01 to 0.3, more preferably 0.002 to 0.2), and said relationship in the second invention copper alloy is 0.02 to 1.5 (preferably 0.04 to 1, more preferably 0.06 to 0.5), and said relationship in the third invention copper alloy is 0.005 to 0.4 (preferably 0.01 to 0.2, more preferably 0.02 to 0.15). Incidentally, since Fe and Ni can become substitutive elements with the same function as Co, the total content in the case that two or three elements selected from a group of Fe, Ni and Co are added must be equal to the content of the single addition of Co (the content of Co described above). However, in the case that two or three elements selected from Fe, Ni and Co are added, the upper limit of co-addition content of Fe, Ni and Co (total content) is permitted to be higher than the Co content by about 0.05 mass percent under consideration of the solid solution and precipitation. From said consideration, in the case that two or three elements selected from Fe, Ni and Co are co-added, it is desirable for the upper limit of total content $(\text{Fe}+\text{Ni}+\text{Co})$ to be set higher than the Co content by 0.05 mass percent. In other words, it is desirable that this total content $(\text{Fe}+\text{Ni}+\text{Co})$ in the first and second invention copper alloys are 0.005 to 0.55 mass percent (more preferably 0.01 to 0.35 mass percent, much more preferably 0.02 to 0.25 mass percent), and it is desirable that said total content in the third invention copper alloy is 0.005 to 0.35 mass percent (preferably 0.01 to 0.25 mass percent, much more preferably 0.02 to 0.2 mass percent).

[0049] Sn shows the strength improvement function, grain refinement function and improvement function of stress relaxation characteristic, corrosion resistance and wear resistance, etc. In the first and third invention copper alloys, in order to show the strength improvement function, grain refinement function, improvement function of heat resistance in matrix and improvement function of stress relaxation characteristic, corrosion resistance and wear resistance, it is necessary that the Sn content is higher than 0.03 mass percent, and it is preferable to be higher than 0.05 mass percent. However, when the Sn content becomes higher than 1.5 mass percent or 1 mass percent in the first invention copper

alloy used as the rolled stock or the third invention copper alloy used as wire drawing material, respectively, the bending characteristics decrease suddenly. Therefore, in order to ensure the bending characteristics, it is necessary that the Sn content in the first and third invention copper alloys is less than 1.5 mass percent and less than 1 mass percent, respectively. Additionally, in order to ensure enough the bending characteristics in both the first and third invention copper alloys, it is preferable for the Sn content to be less than 0.7 mass percent, and it is optimum to be less than 0.5 mass percent.

[0050] On the other hand, in the second invention copper alloy which has lower minimum strength than the first and third invention copper alloys, it is preferable to try the strength improvement, grain refinement, improvement of stress relaxation characteristic, stress corrosion crack resistance, corrosion resistance and improvement of wear resistance, while considering the relation with Si content. Accordingly, it is necessary for the Sn content to be higher than 0.2 mass percent, and it is preferable to be higher than 1 mass percent and more preferable to be higher than 1.2 mass percent corresponding to required strength. However, when the Sn content exceeds 3 mass percent, the hot workability is obstructed, and then the bending characteristics become lower, too. Therefore, in order to ensure the workability, it is necessary for Sn content to be less than 3 mass percent, and it is preferable to be less than 2.6 mass percent so as to ensure more satisfactory hot-workability and bending characteristics, and more preferable to be less than 2.5 mass percent.

[0051] Additionally, in the case that Sn is added, it is necessary that its content is determined by considering the relationship (Si/Sn) with the Si content. In the first invention copper alloy whose strength improvement is a principal purpose, when high strength is obtained with increase of Si content, ductility such as bending characteristics decreases remarkably for $\text{Si/Sn} < 1.5$. Therefore, in the first invention copper alloy, it is necessary for the Sn content to satisfy the relationship $\text{Si/Sn} \geq 1.5$. Furthermore, in order to ensure said ductility enough, it is preferable to satisfy the relationship $\text{Si/Sn} \geq 2$, and it is optimum to satisfy the relationship $\text{Si/Sn} \geq 3$. Moreover, in the third invention copper alloy that Sn content is suppressed to a little amount slightly comparing with the first invention copper alloy, from the same reasons described above, it is necessary for Sn content to satisfy the relationship $\text{Si/Sn} \geq 1$. Furthermore, in order to ensure said ductility enough, it is preferable for the Sn content to satisfy the relationship $\text{Si/Sn} \geq 1.5$, and it is optimum to satisfy the relationship $\text{Si/Sn} \geq 2$.

[0052] On the other hand, in the second invention copper alloy of which electric conductivity is required so as to balance with the strength, the addition of Si is restricted. Therefore, in order to ensure the high strength without loss of the ductility, it is necessary for Sn content to satisfy the relationship $\text{Si/Sn} \leq 0.5$ with Si content. For more improvement of the ductility and strength, the preferable and optimum relationships are $\text{Si/Sn} \leq 0.4$ and $\text{Si/Sn} \leq 0.3$, respectively.

[0053] At least one element selected from a group of P, Sb, As, Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In and Hf is added according as the applications of said alloys, and the effects are mainly the grain refinement, improvement of hot workability, improvement of corrosion resistance, action making the accessory elements mixturing inevitably harmless and improvement of stress relaxation characteristic, etc. Such effects are hardly expected in the case that the content of each element is less than 0.003 mass percent, and on the contrary the effects balanced with the additive quantity are not obtained in the case beyond 0.3 mass percent. Accordingly, the addition is useless in economy and rather loses the bending characteristics. However, in the third invention copper alloy with much Zn content, P, Sb and As are especially added for the improvement of dezincification corrosion resistance and stress corrosion cracking resistance. Similarly to the case described above, the effects of P, Pb and As added for such purposes scarcely appear in the addition less than 0.005 mass percent. On the other hand, when the P content exceeds 0.2 mass percent, adversely the cold bending characteristics are lost. Therefore, for the additions of P, Sb and As in the third invention copper alloy, it is necessary for the contents to be 0.005 to 0.2 mass percent, and in the case adding at least two kinds of element from P, Sb and As, it is necessary for the total content to be 0.005 to 0.25 mass percent.

[0054] By the way, annealing is generally adopted for the heat treatment to obtain recrystallization materials (recrystallization treatment), where the annealing keep plastic working blank mentioned in said (1) the temperature of 200 to 600 °C for 20 minutes to 10 hours. In the heat treatment usually carried out by batch processing system, when the time of heat treatment is long, the grains recrystallized at the early stage of heat treatment gradually grow, and then there is possibility that the uniform grain refinement is obstructed, even if the effect of grain growth inhibition appears by the Co addition. However, in the case with such possibility, when the heat treatment (rapid heating treatment at high temperature) of molding material is performed in a short time at higher temperature (body temperature of molding material) than general annealing temperature, the grain refinement due to the recrystallization for both Co addition and no addition is preferably carried out by the growth inhibition of early recrystallized grains. In other words, the recrystallization in many nucleation sites is realized by acting the large thermal energy almost simultaneously in a short time, because the time span generating the crystal growth is not given. To be concrete, for example, the crystalline structure of molding material are completely recrystallized by the heat treatment of said plastic working blank in the range from 450 to 750 °C for 1 to 1000 seconds.

[0055] In addition, the first, second and third invention copper alloys are generally produced as the recrystallization materials of (1), cold working materials of (2) and manufacture pieces of (3)(4), and alloy characteristics such as strength

are improved more by adding the following treatment in the manufacturing process.

[0056] For example, in the case that a working rate in the cold working before obtaining the recrystallized materials is higher than 30 percent (preferably 60 percent), and more concretely when the rolling or wire drawing rate of the cold working in the process obtaining the plastic working blank of (1) is higher than 30 percent (preferably 60 percent), the strength improvement due to the grain refinement is effectively reached by promoting the refinement. In other words, in order that the grain refinement can be caused, the nucleation sites are necessary. As mentioned above, the nucleation sites increase by the cold working with the higher working rate, and the increment rate of nucleation sites becomes large with increasing of working rate. Furthermore, since the recrystallization originates in releasing of strain energy, more fine grains are obtained by increasing of shearing strain through said cold working. As a result, the strength improvement due to the grain refinement is effectively reached. Incidentally, it is preferable that the plastic working blank performed the last recrystallization treatment has the small mean size of grains, and concretely the mean grain size is less than 20 μm (preferably less than 10 μm). As the mean crystal grain size before recrystallization becomes small, the places causing the recrystallized nucleation in the following heat treatment increase, and in particular, when dislocation density at the grain boundaries becomes higher, it is easy to form nucleation sites. However, since the strength increases with decreasing of the mean grain size, the energy cost for manufacturing the high strength copper alloy becomes expensive, and manufacturing time becomes longer. Therefore, it is preferable that the mean grain size of plastic working blank in (1) is determined from balance with said working rate.

In addition, when the recrystallization materials lack the strength, this materials can obtain higher strength by performing the cold working or cold drawing with the working rate of 10 to 60 percent.

[0057] Furthermore, in the case that said plastic working blank is obtained, when the rolling or wire drawing work of one path is performed, it is preferable that the rolling or wire drawing rate is set to be large (higher than 15 percent, preferably 25 percent).

The more refinement of recrystallized grains can be realized by increment of the shearing strain and nucleation sites resulting from the cold working that the rolling and wire drawing rates are higher. In addition, if the rolling is carried out by using of the roll of small diameter or extremely large diameter, or if the wire drawing is carried out by wire dice with large dice angle or extremely small dice angle, the nucleation sites or the local distortion energy increases, so that the further refinement of recrystallized grain can be effectively realized. Furthermore, if the rolling is carried out by the rolling method with different peripheral speed, and in other words if the rolling is carried out varying the velocity by use of the rolling machine providing for top and bottom rolls having different diameters, the large shearing strain is given to the rolling material, so that the grain refinement can be reached.

[0058] Additionally, in each invention copper alloy, according to those applications, the spring elastic limit and stress relaxation characteristic can be remarkably improved by performing the suitable heat treatment (generally annealing in range of 150 to 600 $^{\circ}\text{C}$ for 1 second to 4 hours) without recrystallization. Concretely, heat treatment is carried out for the cold working materials of (2) (including cold working materials in (4)) or the manufacture pieces of (3) (4), for instance, under the condition of 200 $^{\circ}\text{C}$ for 2 hours or 600 $^{\circ}\text{C}$ for 3 seconds.

EXAMPLES

[0059] As embodiment 1, the copper alloy of composition shown in tables 1 to 4 was dissolved in atmospheric air, and prism-shaped ingots of 35 mm in thickness, 80 mm in width and 200 mm in length were obtained. And intermediate plate materials of 6 mm in thickness were formed by hot rolling (four paths) of this ingot at 850 $^{\circ}\text{C}$, and the materials after acid cleaning became final plate materials of 1 mm in thickness by the cold rolling. Each final plate material was performed the heat treatment for one hour at temperature causing the recrystallization of 100 percent (called "recrystallization temperature"), so that there were obtained the first invention copper alloy from No.101 to No.186 by performing complete recrystallization treatment of structure. For the recrystallization treatment, in advance, samples (a square plate with one side of about 20 mm) picked up from each final plate material were annealed for one hour at each temperature rising with spacing of 50 $^{\circ}\text{C}$ starting from 300 $^{\circ}\text{C}$, and the lowest temperature causing the complete recrystallization was found out, so that the lowest temperature was determined as said recrystallization temperature of the samples (refer to Tables 15 to 17).

[0060] Furthermore, the final plate materials of the same quality (same form, same composition) as composing materials of alloy No.102, No.107, No.111, No.154 and No.180 were obtained due to the same process described above, and these final plate materials were recrystallization-treated under condition different from said condition, so that there were obtained the first invention copper alloy No.102A, No.107A, No.111A, No.154A and No.180A with the same composition as No.102, No.107, No.111, No.152 and No.175, respectively. In other words, the first invention copper alloy No.102A, No.107A, No.111A, No.154A and No.180A were obtained by the recrystallization treatment (rapid heating treatment at higher temperature) in which the heating was maintained for a short time at much higher temperature than recrystallization temperature, where the temperature a ($^{\circ}\text{C}$) and heating time b (second) are shown as "a(b)" in the column titled "recrystallization temperature" in Tables 15 to 17. For example, "480(20)" in column of "recrystallization

temperature" of No.102A in Table 15 means the heating at 480 °C for 20 seconds.

[0061] As embodiment 2, the copper alloy of composition shown in Tables 5 to 8 was dissolved in atmospheric air, and prism-shaped ingots of 35 mm in thickness, 80 mm in width and 200 mm in length were obtained. And intermediate plate materials of 6 mm in thickness are formed by hot rolling (four paths) of this ingot at 850 °C, and the materials after acid cleaning became final plate materials of 1 mm in thickness by the cold rolling. Each final plate material was performed by the heat treatment (annealing) for one hour at temperature causing the recrystallization of 100 percent (by recrystallized treatment), so that there were obtained the second invention copper alloy from No.201 to No.281. In addition, the recrystallization temperature was determined in advance by method similar to example 1 (refer Table 18 to 20).

[0062] Furthermore, the final plate materials of the same quality as composing materials of alloy No.202, No.209, No.250 and No.265 were obtained due to the same process described above, and these final plate materials were recrystallized by the above-described rapid heating treatment at higher temperature, so that there were obtained the second invention copper alloy No.202A, No.209A, No.250A and No.265A with the same composition as No.202, No.209, No.250 and No.265, respectively. In other words, condition obtaining alloy No.202A, No.209A, No.250A and No.265A in the rapid heating treatment at high temperature (a (°C) and heating time b (second)) is described as "a(b)" in column titled "recrystallization temperature" of Tables 18 to 20 by the same description as Tables 15 to 17.

[0063] As embodiment 3, the copper alloy of composition shown in Tables 9 to 12 was dissolved in atmospheric air, and column-shaped ingots of 95 mm in diameter and 180 mm in length were obtained. Round bars of 12 mm in diameter were obtained by extruding press (500 t) while heating the ingots at 780 °C. This round bars after cleaning were worked by wire drawing into 8 mm in diameter, and after heat-treating the round bars for one hour at 500 °C and cleaning them, the wires of 4 mm in diameter (molding materials) were obtained by wire drawing. Furthermore, each wire was heat-treated (annealing) for 1 hour at the temperature (recrystallization temperature) that recrystallization of 100 percent was realized (recrystallization treatment), and third invention copper alloys No.301 to 397 were obtained. For the recrystallization treatment, in advance, samples (wires of 20 mm in length (4 mm in diameter)) picked up from each wire were annealed for one hour at each temperature rising with spacing of 50 °C starting from 300 °C, and the lowest temperature causing the complete recrystallization was found out, so that the lowest temperature was determined as said recrystallization temperature of the samples (refer to Tables 21 to 24).

[0064] Furthermore, the wires (molding materials) of the same quality as composing materials of alloy No.302, No.314 and No.338 were obtained due to the same process described above, and these wires were recrystallized by the above-described rapid heating treatment at higher temperature, so that there were obtained the third invention copper alloy No.302A, No.314A and No.338A with the same composition as No.302, No.314 and No.338, respectively. The condition obtaining alloy No.302A, No.314A and No.338A due to the rapid heating treatment at high temperature (temperature a (°C) and heating time b (second)) is described as "a(b)" in column titled "recrystallization temperature" of Tables 21 to 24 by the same descriptive method as Tables 15 to 17.

[0065] As comparative example 1, first comparative example alloys No.401 to No.422 shown in Table 13 were obtained on the basis of the same process as the first embodiment. In addition, as comparative example 2, second comparative example alloys No.423 to No.431 shown in Table 14 were obtained due to the same process as third embodiment. Incidentally, the first comparative example alloys No.401 to 407, respectively, have the same compositions as C2100, C2200, C2300, C2400, C2600, C2680 and C4250 of Japanese Industrial Standards (JIS), and the second comparative example alloys No.423 and 424, respectively, have the same compositions as C2600 and C2700 of JIS. Additionally, in Tables 1 to 12, the expression of relationship "(Co+Fe+Ni)/Si" for alloy that contains only Co without Fe and Ni is replaced by "Co/Si".

[0066] Incidentally, since the following problems in manufacturing process occurred for the comparative example alloys No.421, No.425, No. 427 and No.431, the manufacturing has been abandoned because of impossibility of manufacturing thereafter. In other words, No.421 causes large cracking in the step that ingots are hot-rolled, and No.425 cannot be hot-extruded. No.427 and No.431 rupture in the wire drawing process. Accordingly, their manufacturing was abandoned because it is difficult to carry out the process thereafter.

[0067] In the first invention copper alloys of No.101 to 186 and No.102A, 107A, 111A, 154A, 180A, the second invention copper alloys of No.201 to 281 and No.202A, 209A, 250A, 265A, the third invention copper alloys of No.301 to 397 and No.302A, 314A, No.338A, and the first and second comparative example alloys of No.401 to 431 (except for No.421, No. 425, No. 427 and No. 431 abandoned the manufacturing), the mean grain size D (μm) of recrystallized structures was measured on the basis of intercept method with the use of optical image (JIS-H0501). The results are shown in Tables 15 to 26.

[0068] In the first invention copper alloys of No.101 to No.186 and No.102A, 107A, 111A, 154A, 180A, the second invention copper alloys of No.201 to 281, No.202A, 209A, 250A, 265A and the first comparative example alloys No.401 to 422 (except for No.421), the electric conductivity was measured. The results are shown in Tables 15 to 26 and Table 25. In addition, the electric conductivity (% IACS) is defined by a percentage of the ratio of the volume specific resistance of international standard soft copper ($17.241 \times 10^{-9} \mu\Omega \cdot m$) divided by that of said alloy.

[0069] Additionally, in the first invention copper alloys of No.101 to No.186 and No.102A, 107A, 111A, 154A, 180A, the second invention copper alloys of No.201 to 281, No.202A, 209A, 250A, 265A and the first comparative example alloys of No. 401 to 422 (except for No.421), proof stress (0.2% proof stress), tensile strength and elongation were measured by tensile test using an Amsler-type universal testing machine. Furthermore, after each alloy was cold-rolled until its thickness becomes 0.7mm, 0.2% proof stress, tensile strength and elongation of the rolling materials (called "post workpiece") were measured by the same tensile test as one described above, and then evaluation of bending characteristics and stress corrosion cracking test were carried out. The results are shown in Tables 15 to 20 and Table 26.

In addition, for the first invention copper alloys of No.101 to No.186 and No.102A, 107A, 111A, 154A, 180A and the second invention copper alloys of No.201 to 281, No.202A, 209A, 250A, 265A, it goes without saying that the post workpieces obtained by 30% rolling are also high strength copper alloy of the present invention.

[0070] In addition, the bending characteristics are evaluated from bending rate R/t at cracked moment (R : inside radius at bending positions). This cracking is suffered when the samples that are vertically cut from the worked pieces to the rolling direction are bend in W shape. In Tables 12 to 17 and Table 22, the pieces that the cracking is not caused for $R/t = 0.5$ are indicated by a symbol $\odot$ as superior bending characteristics. The pieces that the cracking is not caused for $R/t = 1.5$ but is found for $0.5 \leq R/t < 1.5$ are indicated by a symbol $\circ$ as preferable bending characteristics (there is no problem in application). The pieces that the cracking is not caused for $R/t = 2.5$ but is found for $1.5 \leq R/t < 2.5$ are indicated by a symbol Δ as general bending characteristics (there is problem in applications but it is possible to use). The pieces that the cracking is caused for $R/t = 2.5$ are indicated by a symbol $\times$ as superior bending characteristics (it is difficult for applications to use).

[0071] In addition, testing of stress corrosion cracking is carried out by use of test container and testing liquid prescribed in JISH3250, and characteristics of stress corrosion cracking resistance are evaluated from the relationship between ammonia atmosphere exposure time and stress relaxation rate (stress of proof stress value 80% of the post workpiece is added on the surface of the post workpiece) by using the fluid which mixed ammonia fluid and water, where two quantities are equal. In Tables 15 to 20 and Table 25, the pieces that the stress relaxation rate is less than 20% in the exposure for 75 hours are indicated by a symbol $\odot$ as superior bending characteristics. The pieces that the stress relaxation rate is higher than 20% in the exposure for 75 hours but less than 20% in the exposure for 30 hours are indicated by a symbol $\circ$ as superior bending characteristics (there is no problem in application). The pieces that the stress relaxation rate is less than 20% in the exposure for 12 hours are indicated by a symbol Δ as general bending characteristics (there is problem in applications but it is possible to use). The pieces that the stress relaxation rate is higher than 20% in the exposure for 12 hours are indicated by a symbol $\times$ as superior bending characteristics (it is difficult for applications to use).

[0072] Additionally, in the third invention copper alloys of No.301 to 397 and No.302A, 314A and 338A, the second invention copper alloys of No.423 to 431 (except No.425, No.427 and No.431 of abandoned manufacture), tensile strength and elongation are determined from tensile testing with use of an Amsler-type universal testing machine. Furthermore, each alloy is straightened to 0.7 mm in thickness, and tensile strength and elongation in the wire drawing material (called "post workpiece") are determined by the same tensile testing as being described above. Additionally, evaluation of bending characteristics and testing of stress corrosion cracking are carried out. The results are shown in Tables 21 to 24 and Table 26. In addition, the post workpieces are obtained by the wire drawing of the third invention copper alloys of No.301 to 397 and No.302A, 314A and 338A and the second invention copper alloys of No.201 to 281, No.202A, 209A, 250A and 265A, and it go without saying that the after working pieces are also the high strength copper alloy of the present invention.

[0073] Additionally, the bending characteristics was evaluated from bending rate R/d when the post workpieces were bent to 90 degree by use of V-block, and the cracking was caused (R (mm): radius of curvature of inner side at the bending portion, d (mm): radius of post workpieces). In Tables 18 to 22, the pieces that the cracking is not caused for $R/d = 0$ are indicated by a symbol $\odot$ as superior bending characteristics. The pieces that the cracking is not caused for $R/d = 0.25$ but found for $0 \leq R/d < 0.25$ are indicated by a symbol $\circ$ as preferable bending characteristics (there is no problem in application). The pieces that the cracking is not caused for $R/d = 0.5$ but found for $0.25 \leq R/d < 0.5$ are indicated by a symbol Δ as general bending characteristics (there is problem in applications but it is possible to use). The pieces that the cracking is caused for $R/d = 0.5$ are indicated by a symbol $\times$ as inferior bending characteristics (it is difficult to use in applications).

[0074] In addition, the stress corrosion cracking test using the post workpiece used for the evaluation of bending characteristics with $R/d=1.5$ and 90 degree bending is carried out by use of test device and test liquid prescribed in JISH3250. After ammonia exposure using the fluid that mixed equal amounts of ammonia aqueous solution and water, and pickling due to sulfuric acid, the stress corrosion cracking resistance was evaluated from the research of cracking existence due to the stereoscopic microscope with 10 times magnification. In Tables 15 to 20 and Table 25, the pieces that the cracking is not caused in the exposure for 40 hours are indicated by a symbol $\odot$ as superior corrosion cracking resistance. The pieces that the cracking is caused in the exposure for 40 hours but is not caused in the exposure for

15 hours are indicated by a symbol ○ as preferable corrosion cracking resistance (there is no problem in application). The pieces that the cracking is caused in the exposure for 15 hours but is not caused in the exposure for 6 hours are indicated by a symbol Δ as general corrosion cracking resistance (there is problem in applications but it is possible to use). The pieces that the cracking is caused in the exposure for 6 hours are indicated by a symbol × as inferior stress corrosion cracking resistance (it is difficult to use in applications).

TABLE 1

Alloy No.	Alloy composition (mass%)											
	Cu	Zn	Si	Co	Fe	P	Sr	Y	Cr	La	Hf	Zn-2.5Si
101	remainder	10.0	0.98									7.550
102	remainder	10.3	1.50									6.550
102A	remainder	10.3	1.50									6.550
103	remainder	9.6	1.58						0.07			5.650
104	remainder	11.1	1.43				0.05					7.525
105	remainder	10.4	1.51					0.02				6.625
106	remainder	8.5	1.66							0.03		4.350
107	remainder	9.7	2.07									4.525
107A	remainder	9.7	2.07									4.525
108	remainder	6.8	2.33									0.975
109	remainder	16.1	0.73									14.275
110	remainder	10.0	1.02	0.11								7.450
111	remainder	10.2	1.52	0.12								6.400
111A	remainder	10.2	1.52	0.12								6.400
112	remainder	11.8	1.44	0.08		0.12						8.200
113	remainder	9.1	1.57	0.11						0.03		5.175
114	remainder	10.1	2.01	0.11								5.075
115	remainder	11.5	2.32	0.14								5.700
116	remainder	11.0	1.52	0.01								7.200
117	remainder	10.2	1.51	0.06								6.425
118	remainder	9.3	1.08	0.23								6.600
119	remainder	4.8	1.58	0.07								0.850
120	remainder	18.1	1.39	0.15								14.625
121	remainder	13.6	1.26	0.09								10.450
122	remainder	10.2	1.49		0.03							6.475
123	remainder	11.2	0.69		0.07							9.475
124	remainder	13.2	1.81		0.12							8.675

TABLE 2

Alloy No.	Alloy composition (mass%)													Si/Sn
	Cu	Zn	Si	Co	Fe	Ni	Sn	As	Mg	Zr	In	Zn-2.5Si	(Co+Fe+Ni)/Si	
125	remainder	8.6	1.31			0.27						5.325	0.206	
126	remainder	10.3	1.95	0.10				0.05				5.425	0.051	
127	remainder	9.8	0.88	0.39								7.600	0.443	
128	remainder	7.1	1.62			0.06						3.050	0.037	
129	remainder	9.5	2.01			0.12						4.475	0.060	
130	remainder	10.0	1.63	0.06	0.01							5.925	0.043	
131	remainder	9.4	1.04	0.10	0.06							6.800	0.154	
132	remainder	10.8	1.58	0.04	0.07							6.850	0.070	
133	remainder	9.3	1.66	0.08		0.02						5.150	0.060	
134	remainder	7.8	1.81	0.16		0.12						3.275	0.155	
135	remainder	12.1	1.73	0.05		0.06						7.775	0.064	
136	remainder	11.8	1.12		0.19	0.08						9.000	0.241	
137	remainder	9.7	1.48		0.04	0.07						6.000	0.074	
138	remainder	8.8	1.63		0.12	0.01						4.725	0.080	
139	remainder	8.6	1.69	0.11	0.09	0.07						4.375	0.160	
140	remainder	5.3	1.32	0.03	0.01	0.04						2.000	0.058	
141	remainder	10.2	0.81	0.01	0.02	0.08						8.175	0.136	
142	remainder	9.4	1.64				0.34					5.300		4.824
143	remainder	8.9	1.56				1.01					5.000		1.545
144	remainder	10.6	1.12				0.05					7.800		22.400
145	remainder	8.2	2.41	0.05			0.29					2.175	0.021	8.310
146	remainder	11.3	2.14	0.10			0.42					5.950	0.047	5.095
147	remainder	7.6	0.57	0.12			0.21					6.175	0.211	2.714
148	remainder	10.8	1.74	0.11			0.35					6.450	0.063	4.971
149	remainder	10.6	1.52	0.09			0.29		0.03			6.800	0.059	5.241
150	remainder	9.6	1.63	0.10			0.30		0.01		0.03	5.525	0.061	5.433
151	remainder	9.8	1.67	0.07			0.25			0.02		5.625	0.042	6.680

Embodiment 1

TABLE 3

Alloy No.	Alloy composition (mass%)																	Embodiment 1
	Cu	Zn	Si	Co	Fe	Ni	Sn	P	Sb	Sr	Mg	Ti	Mn	Zr	Hf	Zn-2.5Si	(Co+Fe+Ni)/Si	
152	remainder	10.7	1.59	0.11			0.32			0.02				0.01		4.675	0.069	4.969
153	remainder	5.9	1.84	0.02			0.23									1.300	0.011	8.000
154	remainder	8.7	1.76	0.06			0.28									4.300	0.034	6.286
154A	remainder	8.7	1.76	0.06			0.28									4.300	0.034	6.286
155	remainder	9.0	1.62				0.47		0.08							4.950		3.447
156	remainder	9.9	1.77	0.09			0.41	0.03	0.05							5.475	0.051	4.317
157	remainder	10.1	1.30	0.44			0.08									6.850	0.338	16.250
158	remainder	9.5	1.61	0.08			0.20									5.475	0.050	8.050
159	remainder	13.3	1.11	0.08			0.21									10.525	0.072	5.286
160	remainder	8.2	1.82		0.12		0.18									3.650	0.066	10.111
161	remainder	4.9	1.79		0.08		0.26									0.425	0.045	6.885
162	remainder	8.9	1.32		0.09		0.82									5.600	0.068	1.610
163	remainder	10.0	2.01			0.12	0.42									4.975	0.060	4.786
164	remainder	11.3	1.38			0.28	0.33									7.850	0.203	4.182
165	remainder	9.0	1.60			0.08	0.25									5.000	0.050	6.400
166	remainder	9.7	1.65	0.06	0.03		0.30									5.575	0.055	5.500
167	remainder	10.5	1.59	0.04	0.07		0.08									6.525	0.069	19.875
168	remainder	11.3	1.45	0.03	0.01		0.12						0.16			7.675	0.028	12.083
169	remainder	8.9	1.62	0.03	0.03		0.18					0.08				4.850	0.037	9.000
170	remainder	9.8	1.58	0.07	0.04		0.11							0.02	0.02	5.850	0.070	14.364
171	remainder	10.0	1.50	0.03	0.05		0.14				0.04					6.250	0.053	10.714
172	remainder	13.2	1.47	0.05	0.05		0.18									9.525	0.068	8.167
173	remainder	7.8	1.24	0.21		0.06	0.12									4.700	0.218	10.333
174	remainder	9.7	1.49	0.09		0.02	0.28									5.975	0.074	5.321
175	remainder	9.5	1.55	0.08		0.01	0.25				0.07					5.625	0.057	6.200
176	remainder	9.3	1.60	0.04		0.04	0.26							0.03		5.300	0.050	6.154
177	remainder	10.2	2.21	0.06		0.05	0.22									4.675	0.050	10.045

TABLE 4

Alloy No.	Alloy composition (mass%)									
	Cu	Zn	Si	Co	Fe	Ni	Sn	Zn-2.5Si	(Co+Fe+Ni)/Si	Si/Sn
178	remainder	6.9	1.19		0.15	0.14	0.54	3.925	0.244	2.204
179	remainder	8.9	1.68		0.09	0.02	0.09	4.700	0.065	18.667
180	remainder	14.2	1.65		0.03	0.09	0.20	10.075	0.073	8.250
180A	remainder	14.2	1.65		0.03	0.09	0.20	10.075	0.073	8.250
181	remainder	9.4	1.62	0.06	0.01	0.02	0.18	5.350	0.056	9.000
182	remainder	10.1	0.89	0.03	0.02	0.01	0.24	7.875	0.067	3.708
183	remainder	11.8	1.45	0.01	0.03	0.02	0.33	8.175	0.041	4.394
184	remainder	8.3	1.20	0.31	0.07		0.05	5.300	0.317	24.000
185	remainder	9.5	1.70	0.15	0.07			5.250	0.129	
186	remainder	9.5	1.70	0.10			0.30	5.250	0.059	5.667

TABLE 5

Alloy No.	Alloy composition (mass%)											(Co+Fe-Ni)/Si
	Cu	Zn	Si	Co	Fe	Ni	P	Sr	Cr	La	Mn	
201	remainder	10.1	0.28									9.400
202	remainder	10.0	0.49									8.775
202A	remainder	10.0	0.49									8.775
203	remainder	9.0	0.51						0.21			7.725
204	remainder	10.5	0.45								0.12	9.375
205	remainder	7.7	0.52									6.400
206	remainder	14.0	0.39									13.025
207	remainder	10.2	0.19	0.03								9.725
208	remainder	9.9	0.31	0.05								9.125
209	remainder	10.0	0.50	0.12								8.750
209A	remainder	10.0	0.50	0.12								8.750
210	remainder	9.5	0.52	0.10			0.03					8.200
211	remainder	8.8	0.50	0.09				0.04				7.550
212	remainder	10.3	0.46	0.07						0.03		9.150
213	remainder	9.7	0.33	0.11								8.875
214	remainder	4.9	0.73	0.21								3.075
215	remainder	15.8	0.70	0.10								14.050
216	remainder	8.5	0.43	0.009								7.425
217	remainder	13.4	0.40	0.05								12.400
218	remainder	10.5	0.52		0.06							9.200
219	remainder	8.7	0.47		0.02							7.525
220	remainder	9.8	0.39		0.07							8.825
221	remainder	9.8	0.73			0.21						7.975
222	remainder	8.3	0.44			0.06						7.200
223	remainder	12.8	0.37			0.07						11.875
224	remainder	8.1	0.55	0.06	0.03							6.725
225	remainder	8.9	0.18	0.26								8.450

TABLE 6

Alloy No.	Alloy composition (mass%)															Si/Sn
	Cu	Zn	Si	Co	Fe	Ni	Sn	Sr	Mg	Y	Ti	Zr	Hf	Zn-2.5Si	(Co+Fe+Ni)/Si	
226	remainder	9.2	0.30	0.36	0.02									8.450	1.200	
227	remainder	8.5	0.49	0.45										7.275	0.918	
228	remainder	7.8	0.38	0.02	0.06									6.850	0.211	
229	remainder	10.1	0.56	0.26	0.05									8.700	0.554	
230	remainder	10.8	0.19	0.04		0.02								10.325	0.316	
231	remainder	9.7	0.66	0.03		0.06								8.050	0.136	
232	remainder	8.8	0.48	0.04		0.04								7.600	0.167	
233	remainder	14.8	0.39		0.02	0.03								13.825	0.128	
234	remainder	4.8	0.50		0.21	0.02								3.550	0.460	
235	remainder	8.5	0.47		0.04	0.05								7.325	0.191	
236	remainder	10.0	0.28	0.04	0.02	0.02								9.300	0.286	
237	remainder	8.1	0.44	0.03	0.02	0.03								7.000	0.182	
238	remainder	10.8	0.57	0.01	0.05	0.02								9.375	0.140	
239	remainder	9.7	0.43				1.41							8.625		0.305
240	remainder	8.2	0.18				2.01							7.750		0.090
241	remainder	8.5	0.20				1.99		0.05					8.000		0.101
242	remainder	7.7	0.15				2.06			0.05		0.01		7.325		0.073
243	remainder	9.1	0.23				2.12				0.07			8.525		0.108
244	remainder	12.3	0.51				1.13							11.025		0.451
245	remainder	9.8	0.18				0.38							9.350		0.474
246	remainder	7.9	0.32	0.11			1.75							7.100	0.344	0.183
247	remainder	7.2	0.33	0.09			1.80						0.04	6.375	0.273	0.183
248	remainder	7.5	0.30	0.12			1.77					0.03		6.750	0.400	0.169
249	remainder	7.9	0.29	0.10			1.68	0.03	0.02					7.175	0.345	0.173
250	remainder	9.1	0.28	0.05			1.92							8.400	0.179	0.146
250A	remainder	9.1	0.28	0.05			1.92							8.400	0.179	0.146
251	remainder	10.4	0.70	0.12			1.50							8.650	0.171	0.467

Embodiment 2

TABLE 7

Alloy No.	Alloy composition (mass%)														Si/Sn
	Cu	Zn	Si	Co	Fe	Ni	Sn	Sb	As	Mg	Y	In	Zn-2.5Si	(Co+Fe-Ni)/Si	
252	remainder	8.5	0.32	0.18			1.58						7.700	0.563	0.203
253	remainder	7.8	0.27	0.15			2.12	0.07					7.125	0.556	0.127
254	remainder	7.4	0.35	0.10			1.75		0.05				6.525	0.286	0.200
255	remainder	8.8	0.21	0.01			1.48						8.275	0.048	0.142
256	remainder	8.4	0.32	0.11			2.28						7.600	0.344	0.140
257	remainder	7.8	0.27	0.09			2.71						7.125	0.333	0.100
258	remainder	10.6	0.14	0.05			0.29						10.250	0.357	0.483
259	remainder	15.1	0.32		0.07		1.56						14.300	0.219	0.205
260	remainder	8.8	0.28		0.08		1.88						8.100	0.286	0.149
261	remainder	9.2	0.23		0.06		1.33						8.625	0.261	0.173
262	remainder	9.0	0.40			0.06	1.75						8.000	0.150	0.229
263	remainder	4.9	0.35			0.08	1.62						4.025	0.229	0.216
264	remainder	8.3	0.74			0.08	1.63						6.450	0.108	0.454
265	remainder	7.7	0.26	0.07	0.02		2.02						7.050	0.346	0.129
265A	remainder	7.7	0.26	0.07	0.02		2.02						7.050	0.346	0.129
266	remainder	7.1	0.27	0.06	0.03		2.22					0.06	6.425	0.333	0.122
267	remainder	8.3	0.27	0.08	0.01		2.00			0.02	0.02		7.625	0.322	0.135
268	remainder	6.9	0.44	0.21	0.01		2.18						5.800	0.500	0.202
269	remainder	8.8	0.36	0.02	0.05		1.58						7.900	0.194	0.228
270	remainder	9.3	0.19	0.04		0.02	0.58						8.825	0.316	0.328
271	remainder	7.8	0.32	0.03		0.05	1.49						7.000	0.250	0.215
272	remainder	11.3	0.44	0.03		0.03	1.68						10.200	0.136	0.262
273	remainder	8.7	0.33		0.02	0.05	1.40						7.875	0.212	0.236
274	remainder	10.6	0.22		0.06	0.02	1.90						10.050	0.364	0.116
275	remainder	7.7	0.28		0.03	0.03	1.66						7.000	0.214	0.169
276	remainder	6.8	0.36	0.05	0.02	0.01	1.58						5.900	0.217	0.228
277	remainder	12.5	0.41	0.12	0.05	0.05	2.28						11.475	0.244	0.180

Embodiment 7

TABLE 8

Alloy No.	Alloy composition (mass%)											
	Cu	Zn	Si	Co	Fe	Ni	Sn	P	Sb	Zn-2.5Si	(Co+Fe+Ni)/Si	Si/Sn
278	remainder	7.7	0.26	0.01	0.04	0.02	1.77			7.050	0.269	0.147
279	remainder	8.3	0.34	0.09		0.03	1.73	0.05	0.03	7.450	0.353	0.197
280	remainder	9.0	0.35	0.13			2.10			8.125	0.371	0.167
281	remainder	9.0	0.40	0.26			2.00			8.000	0.650	0.200

TABLE 9

Alloy No.	Alloy composition (mass%)												
	Cu	Zn	Si	Co	Fe	Ni	Mg	Ti	Mn	In	Cu-5Si	Zn-6Si	(Co+Fe-Ni)/Si
301	71.1	27.7	1.22								64.980	35.02	
302	70.8	27.8	1.38								63.920	36.08	
302A	70.8	27.8	1.38								63.920	36.08	
303	71.1	27.5	1.36					0.07			64.270	35.66	
304	71.5	27.0	1.41						0.12		64.420	35.46	
305	72.6	25.9	1.55								64.800	35.20	
306	68.2	31.1	0.68	0.02							64.800	35.18	0.029
307	71.0	28.0	0.97	0.07							66.110	33.82	0.072
308	70.5	28.1	1.33	0.05							63.870	36.08	0.038
309	72.1	26.3	1.38	0.23							65.190	34.58	0.167
310	73.2	25.1	1.61	0.11							65.130	34.76	0.068
311	71.5	26.7	1.72	0.13							62.850	37.02	0.076
312	75.2	22.9	1.77	0.09							66.390	33.52	0.051
313	71.7	26.8	1.43	0.07							64.550	35.38	0.049
314	72.9	25.5	1.56	0.08							65.060	34.86	0.051
314A	72.9	25.5	1.56	0.08							65.060	34.86	0.051
315	72.4	26.0	1.51	0.07			0.05				64.820	35.06	0.046
316	73.1	25.2	1.58	0.07			0.02			0.02	65.210	34.68	0.044
317	71.6	26.9	1.40		0.08						64.620	35.30	0.057
318	72.6	25.7	1.51		0.22						65.020	34.76	0.146
319	68.4	31.0	0.62		0.01						65.272	34.72	0.013
320	72.4	26.1	1.48			0.05					64.970	34.98	0.034
321	67.8	31.5	0.67			0.01					64.471	35.52	0.013
322	75.3	22.7	1.91			0.08					65.760	34.16	0.042
323	71.2	27.3	1.41	0.03	0.05						64.160	35.76	0.057
324	72.3	26.0	1.64	0.01	0.06						64.093	35.84	0.041
325	68.4	30.8	0.65	0.18	0.01						65.110	34.70	0.292

Embodiment 3

TABLE 10

Alloy No.	Alloy composition (mass%)																Si/Sn
	Cu	Zn	Si	Co	Fe	Ni	Sn	Sr	Y	La	Zr	In	Hf	Cu-5Si	Zn-6Si	(Co+Fe+Ni)/Si	
326	72.5	25.9	1.53	0.05		0.02								64.85	35.08	0.046	
327	70.6	28.1	1.25	0.06		0.01								64.33	35.60	0.056	
328	71.5	27.0	1.44	0.02		0.05								64.29	35.64	0.049	
329	71.7	26.8	1.45		0.06	0.03								64.41	35.50	0.062	
330	70.7	27.6	1.58		0.04	0.04								62.84	37.08	0.051	
331	71.9	26.5	1.55		0.04	0.03		0.03						64.10	35.80	0.045	
332	72.2	26.2	1.48	0.03	0.03	0.02								64.84	35.08	0.054	
333	71.2	27.3	1.38	0.03	0.05	0.01		0.03						64.30	35.58	0.065	
334	71.4	27.0	1.55	0.07	0.01	0.02								63.60	36.30	0.065	
335	73.7	24.5	1.61				0.22							65.62	34.16	7.318	
336	74.0	23.8	1.52				0.73							66.35	32.92	2.082	
337	71.7	26.6	1.42				0.09							64.62	35.12	15.778	
338	73.2	25.0	1.59	0.06			0.13							65.27	34.54	0.038	
338A	73.2	25.0	1.59	0.06			0.13							65.27	34.54	0.038	
339	73.0	25.2	1.60	0.05			0.10				0.03			65.02	34.80	0.031	
340	72.8	25.5	1.57	0.05			0.08				0.01		0.03	64.91	34.92	0.032	
341	72.9	25.3	1.59	0.07			0.13					0.04		64.92	34.84	0.044	
342	75.1	22.8	1.82	0.09			0.23							65.96	33.72	0.049	
343	71.5	26.9	1.41	0.15			0.04							64.45	35.36	0.106	
344	72.3	26.0	1.24	0.07			0.37							66.12	33.44	0.056	
345	71.7	26.3	1.19		0.08		0.74							65.74	33.44	0.067	
346	71.9	26.3	1.45		0.21		0.15							64.64	35.00	0.145	
347	72.5	25.6	1.67		0.05		0.20							64.13	35.62	0.030	
348	71.2	27.1	1.55			0.02	0.11							63.47	36.40	0.013	
349	73.7	24.4	1.71			0.07	0.06			0.03				65.18	34.66	0.041	
350	71.8	26.6	1.42			0.06	0.16							64.66	35.12	0.042	
351	75.1	22.7	1.91	0.13	0.05		0.09							65.57	34.16	0.094	

TABLE 11

Alloy No.	Alloy composition (mass%)													Si/Sn			
	Cu	Zn	Si	Co	Fe	Ni	Sn	P	Sr	Mg	Y	Zr	Hf		Cu-5Si	Zn-6Si	(Co-Fe+Ni)/Si
352	71.7	26.6	1.45	0.04	0.05		0.21							64.400	35.30	0.062	6.905
353	73.3	24.9	1.60	0.02	0.07		0.14							65.270	34.50	0.056	11.429
354	72.8	25.3	1.58	0.03	0.07		0.18						0.02	64.920	34.78	0.063	8.778
355	73.3	24.8	1.63	0.04	0.05		0.12		0.02	0.02				65.170	34.58	0.055	13.583
356	73.1	25.1	1.61	0.04	0.06		0.09				0.03	0.01		65.013	34.76	0.062	17.889
357	75.6	21.9	1.88	0.07		0.01	0.59							66.152	33.18	0.041	3.186
358	72.1	26.2	1.44	0.05		0.04	0.14							64.930	34.84	0.063	10.286
359	72.7	25.5	1.63	0.02		0.05	0.12							64.530	35.28	0.043	13.583
360	71.4	26.8	1.38		0.18	0.04	0.22							64.480	35.08	0.159	6.273
361	72.8	25.2	1.70		0.06	0.03	0.19							64.320	35.40	0.053	8.947
362	73.8	23.8	1.44		0.03	0.06	0.92							66.550	32.44	0.063	1.565
363	71.9	26.4	1.41	0.02	0.02	0.05	0.21							64.840	34.86	0.064	6.714
364	70.0	28.6	0.75	0.12			0.63							66.250	33.10	0.160	1.190
365	71.0	27.1	1.06	0.06	0.02		0.82							65.700	33.46	0.075	1.293
366	73.1	24.9	1.68	0.02	0.07	0.01	0.18							64.740	34.98	0.060	9.333
367	66.8	32.3	0.63	0.12	0.04	0.02	0.05							63.690	36.08	0.286	12.600
368	72.3	26.3	1.40					0.03						65.270	34.70		
369	73.1	25.1	1.65					0.14						64.860	35.00		
370	71.7	26.8	1.43	0.06				0.01						64.552	35.38	0.042	
371	73.1	25.0	1.72	0.09				0.12						64.470	35.32	0.052	
372	72.2	26.2	1.50	0.07				0.05						64.680	35.20	0.047	
373	71.9	26.3	1.61		0.13			0.07						63.840	35.96	0.081	
374	72.3	26.1	1.47			0.07		0.08						64.930	34.92	0.048	
375	71.1	27.5	1.22	0.07	0.02			0.06						65.030	34.82	0.074	
376	72.4	25.9	1.53	0.06		0.01		0.09						64.763	35.08	0.044	
377	73.0	25.2	1.66		0.05	0.03		0.03						64.730	35.16	0.048	
378	73.5	24.7	1.68	0.05	0.03	0.01		0.04						65.090	34.78	0.054	

TABLE 12

Alloy No.	Alloy composition (mass%)													Si/Sn
	Cu	Zn	Si	Co	Fe	Ni	Sn	P	Sb	As	Cu-5Si	Zn-6Si	(Co+Fe+Ni)/Si	
379	71.6	26.5	1.55				0.28	0.06			63.860	35.80		5.536
380	72.5	25.4	1.23	0.07			0.81	0.04			66.300	32.78	0.057	1.519
381	72.6	25.5	1.60	0.08			0.15	0.06			64.610	35.10	0.050	10.67
382	71.6	26.7	1.54		0.05		0.08	0.08			63.850	35.94	0.032	19.25
383	73.3	24.9	1.60	0.02	0.07		0.14				65.270	34.50	0.056	11.43
384	74.7	23.2	1.72	0.01	0.14		0.22	0.06			66.052	33.52	0.086	7.818
385	73.1	25.1	1.44	0.06		0.01	0.17	0.08			65.943	33.74	0.047	8.471
386	72.6	25.6	1.58		0.03	0.06	0.11	0.06			64.660	35.08	0.057	14.36
387	71.8	26.4	1.46	0.09	0.01	0.03	0.19	0.05			64.472	35.16	0.088	7.684
388	72.5	25.9	1.55						0.04		64.750	35.20		
389	73.6	24.6	1.70							0.07	65.100	34.80		
390	71.2	27.4	1.26	0.07						0.10	64.900	34.96	0.056	
391	73.1	25.1	1.68	0.11						0.03	64.700	35.18	0.065	
392	72.1	26.2	1.55	0.07				0.06	0.02		64.350	35.50	0.045	
393	72.2	25.8	1.60				0.35		0.05		64.200	35.40		4.571
394	71.0	27.0	1.26	0.06			0.65		0.08		64.700	34.56	0.048	1.938
395	72.0	26.2	1.25		0.08		0.37	0.05		0.06	65.750	33.70	0.064	3.378
396	72.5	25.1	1.53	0.06	0.02		0.72		0.07	0.01	64.850	34.28	0.052	2.125
397	71.5	26.7	1.48	0.04		0.04	0.21	0.03	0.02	0.02	64.100	35.58	0.054	7.048

Embodiment 3

TABLE 13

Alloy No.	Alloy composition (mass%)										Si/Sn
	Cu	Zn	Si	Co	Fe	Ni	Sn	P	Zn-2.5Si	(Co+Fe+Ni)/Si	
401	94.70	5.3							5.30		
402	89.80	10.2							10.20		
403	85.10	14.9							14.90		
404	79.40	20.6							20.60		
405	69.90	30.1							30.10		
406	65.20	34.8							34.80		
407	88.32	9.5					2.10	0.08	9.50		
408	82.08	17.6	0.32						16.80		
409	96.47	2.1	1.18				0.25		-0.85		4.720
410	78.36	19.9	1.44	0.09			0.21		16.30	0.063	6.857
411	79.78	17.9	0.52	0.05			1.75		16.60	0.096	0.297
412	96.69	2.8	0.48	0.03					1.60	0.063	
413	91.35	8.6	0.04	0.01					8.50	0.250	
414	86.41	10.9	2.61	0.08					4.38	0.031	
415	87.88	10.4	1.13	0.59					7.58	0.522	
416	87.05	11.1	1.23		0.62				8.03	0.504	
417	88.43	10.3	0.72			0.55			8.50	0.764	
418	88.20	9.8	1.31	0.17	0.26	0.26			6.53	0.527	
419	86.90	10.2	1.53	0.09			1.28		6.38	0.059	1.195
420	88.51	9.4	0.76				1.33		7.50		0.571
421	85.97	9.8	0.66	0.07			3.50		8.15	0.106	0.189
422	88.30	8.8	0.45	0.42		0.28	1.75		7.68	1.556	0.257

Comparative example 1

TABLE 14

Alloy No.	Alloy composition (mass%)									
	Cu	Zn	Si	Co	Sn	Cu-5Si	Zn+6Si	(Co+Fe+Ni)/Si	Si/Sn	
423	69.80	30.2				69.80	30.20			
424	64.90	35.1				64.90	35.10			
425	74.97	23.8	1.23			68.82	31.18			
426	66.81	31.9	1.25	0.04		60.56	39.40	0.032		
427	74.74	23.0	2.21	0.05		63.69	36.26	0.023		
428	65.85	32.8	1.25	0.10		59.60	40.30	0.080		
429	67.12	32.5	0.35	0.03		65.37	34.60	0.086		
430	68.80	29.3	0.92	0.05	0.95	64.20	34.82	0.054	0.968	
431	73.31	23.7	1.80	0.04	1.15	64.31	34.50	0.022	1.565	

Comparative example 2

TABLE 15

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
101	2.4	350	308	416	45	504	572	15	⊗	○	16
102	2.2	350	312	481	44	575	676	11	○	○	12
102A	1.8	480(20)	367	493	45	602	691	12	○	○	12
103	2.0	400	347	493	45	593	688	11	○	○	12
104	2.0	400	339	491	44	592	685	11	○	○	12
105	2.1	350	328	489	44	586	682	13	⊗	○	12
106	2.1	350	331	488	45	584	683	12	○	○	12
107	1.9	350	380	528	43	610	739	7	△	⊗	10
107A	1.7	550(10)	403	542	44	627	751	8	○	⊗	10
108	2.0	350	355	508	42	599	725	8	△	⊗	10
109	2.2	350	309	432	43	513	601	9	○	△	17
110	2.1	400	353	448	41	528	625	14	⊗	○	16
111	1.7	400	404	509	40	608	709	12	⊗	⊗	13
111A	1.5	560(13)	444	525	40	626	723	13	⊗	⊗	13
112	1.5	400	431	522	42	626	724	13	⊗	⊗	13
113	1.6	400	417	515	40	615	716	13	⊗	⊗	13
114	1.6	400	438	558	37	657	780	8	△	⊗	11
115	1.1	400	500	610	35	713	834	7	△	⊗	10
116	2.1	350	333	496	44	593	691	10	○	○	13
117	1.7	400	372	501	41	622	733	10	○	⊗	13
118	1.3	400	399	502	39	591	692	10	○	⊗	17
119	2.3	400	312	452	40	548	638	9	○	⊗	13
120	1.5	400	475	583	40	640	785	8	△	△	13
121	1.8	400	406	509	43	602	701	11	○	○	14
122	2.0	350	354	493	45	615	705	11	○	○	13
123	2.2	400	310	415	43	501	598	14	⊗	○	19
124	1.6	400	439	562	38	543	754	8	△	○	11
125	1.5	450	395	507	34	613	701	9	△	⊗	16
126	1.6	400	429	548	37	648	771	8	△	⊗	11
127	1.4	450	381	456	36	558	639	8	△	○	19
128	1.9	400	337	470	39	552	657	10	○	⊗	13

TABLE 16

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (%IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
129	1.5	400	412	544	38	630	742	9	Δ	$\odot$	11
130	1.5	400	392	512	44	614	725	12	$\odot$	$\odot$	13
131	1.7	400	357	478	40	575	665	12	$\odot$	$\odot$	15
132	1.3	400	413	517	40	628	730	11	$\odot$	$\odot$	12
133	1.3	400	404	513	40	624	735	11	$\odot$	$\odot$	12
134	1.4	450	430	558	36	559	764	9	Δ	$\odot$	12
135	1.2	400	430	558	40	561	759	9	$\odot$	$\odot$	12
136	1.8	400	383	510	37	604	702	9	Δ	$\odot$	16
137	1.4	400	391	507	39	618	713	9	$\odot$	$\odot$	13
138	1.3	400	400	515	42	600	708	12	$\odot$	$\odot$	12
139	1.2	450	444	559	36	673	779	7	Δ	$\odot$	13
140	2.0	400	314	434	40	510	614	14	$\odot$	$\odot$	14
141	1.8	400	321	436	43	522	616	15	$\odot$	$\odot$	18
142	1.9	350	357	489	44	547	689	12	$\odot$	$\odot$	12
143	1.7	350	389	512	40	588	702	9	Δ	$\odot$	11
144	2.3	350	325	447	43	515	627	13	$\odot$	$\odot$	16
145	1.3	400	465	585	38	700	810	6	Δ	$\odot$	10
146	1.1	400	490	606	37	712	822	7	Δ	$\odot$	11
147	2.3	400	303	403	42	522	580	14	$\odot$	$\odot$	18
148	1.2	400	443	565	40	701	787	10	$\odot$	$\odot$	12
149	1.3	400	411	536	42	670	757	11	$\odot$	$\odot$	12
150	1.3	400	414	541	43	675	753	11	$\odot$	$\odot$	12
151	1.3	400	410	537	42	671	760	12	$\odot$	$\odot$	12
152	1.2	400	425	552	43	688	770	11	$\odot$	$\odot$	12
153	2.2	400	360	480	40	540	655	12	$\odot$	$\odot$	11
154	1.4	400	402	538	41	645	750	11	$\odot$	$\odot$	11
154A	1.3	710(5)	426	553	43	658	762	12	$\odot$	$\odot$	11
155	1.8	350	363	506	42	593	691	11	$\odot$	$\odot$	12
156	1.3	400	449	573	39	708	795	10	$\odot$	$\odot$	12
157	1.1	450	434	561	36	706	780	7	Δ	$\odot$	17
158	1.4	400	400	530	40	627	735	11	$\odot$	$\odot$	12

Embodiment 1

TABLE 17

Alloy N o.	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bedding characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (%IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
159	1.9	400	392	504	42	592	688	12	O	O	14
160	1.3	400	412	542	40	623	741	10	O	⊗	11
161	2.0	400	355	482	40	560	665	12	O	⊗	11
162	1.4	400	404	502	39	600	701	8	Δ	⊗	12
163	1.2	400	472	595	36	688	800	7	Δ	⊗	10
164	1.5	450	428	510	34	588	698	9	Δ	O	14
165	1.6	400	382	510	40	601	705	11	⊗	⊗	12
166	1.2	400	417	544	40	674	769	10	O	⊗	12
167	1.4	400	409	537	41	648	750	11	⊗	O	13
168	1.3	400	409	524	40	644	738	11	⊗	O	13
169	1.3	400	408	525	40	645	745	11	⊗	⊗	13
170	1.4	400	410	521	42	646	740	12	⊗	⊗	13
171	1.4	400	400	517	42	640	730	13	⊗	⊗	13
172	1.3	400	428	549	40	653	763	10	O	O	13
173	1.9	400	382	474	34	535	654	9	O	⊗	14
174	1.4	400	405	519	40	615	719	12	⊗	⊗	12
175	1.3	400	419	530	41	630	730	13	⊗	⊗	12
176	1.3	400	420	527	41	628	733	13	⊗	⊗	12
177	1.1	400	476	599	36	716	823	7	Δ	⊗	10
178	2.0	450	393	487	34	562	673	9	Δ	⊗	14
179	1.5	400	403	520	41	613	720	12	⊗	⊗	12
180	1.2	400	459	586	38	704	802	8	Δ	O	11
180A	1.1	630(8)	482	597	38	721	813	9	O	O	11
181	1.3	400	405	519	42	609	714	12	⊗	⊗	12
182	2.1	400	336	441	43	515	621	13	⊗	O	18
183	1.5	400	407	518	42	607	708	10	O	O	13
184	1.4	450	423	491	35	553	662	8	Δ	⊗	16
185	1.2	150	456	571	40	694	784	12	O	⊗	12
186	1.2	400	444	567	41	692	778	11	⊗	⊗	13

TABLE 18

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties		Mechanical properties (Post workpiece)		Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity ($\% \text{ IACS}$)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	
201	3.2	350	251	347	41	412	465	15	28
202	2.6	350	257	366	41	433	498	14	23
202A	2.3	530(15)	287	379	42	451	507	15	23
203	2.4	400	288	399	41	452	530	14	24
204	2.4	400	275	390	41	449	525	14	24
205	2.8	350	258	349	41	437	489	13	24
206	3.1	350	265	390	42	486	536	11	25
207	3.1	400	254	346	43	420	484	12	33
208	2.8	400	263	372	41	485	542	10	29
209	2.3	450	301	412	38	500	565	12	27
209A	2.1	520(100)	322	423	40	515	570	13	27
210	2.2	450	315	425	40	515	573	13	27
211	2.3	450	305	418	41	503	568	14	28
212	2.2	450	312	420	40	510	570	13	27
213	2.8	450	274	393	37	480	535	10	29
214	2.4	450	272	412	34	474	537	9	20
215	2.1	400	359	469	42	550	647	8	20
216	2.4	350	261	362	41	455	510	14	24
217	2.5	400	306	411	42	488	558	12	26
218	2.5	400	277	394	40	476	533	12	24
219	2.7	400	257	360	41	448	502	13	25
220	2.6	400	259	375	42	469	522	14	26
221	2.0	450	322	439	35	513	564	9	20
222	3.0	400	256	363	42	467	505	13	25
223	2.8	400	283	398	41	478	534	12	26
224	2.4	400	262	391	40	480	531	12	23
225	2.8	400	270	358	42	430	492	12	32
226	2.4	450	298	405	37	491	570	9	28
227	2.1	450	320	438	35	515	592	9	27

Exhaustive 2

TABLE 19

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)		Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)			
228	2.7	400	259	356	40	445	488	⊗	⊗	27
229	2.1	450	333	448	42	543	579	⊗	⊗	22
230	2.9	400	259	362	43	440	495	⊗	⊗	34
231	2.2	400	301	419	42	512	578	⊗	⊗	21
232	2.4	400	260	388	42	460	526	⊗	⊗	25
233	2.8	400	312	422	43	515	581	⊗	⊗	25
234	2.3	450	260	377	34	456	499	⊗	⊗	21
235	2.4	400	257	386	40	477	525	⊗	⊗	25
236	2.8	400	255	375	42	474	510	⊗	⊗	30
237	2.4	400	268	376	40	474	514	⊗	⊗	25
238	2.3	400	304	408	41	499	553	⊗	⊗	23
239	2.6	350	331	410	41	523	590	⊗	⊗	20
240	3.1	400	313	392	40	530	585	⊗	⊗	24
241	3.0	400	327	400	41	540	591	⊗	⊗	24
242	2.8	400	335	399	41	543	590	⊗	⊗	24
243	2.8	400	351	415	40	551	600	⊗	⊗	24
244	2.7	350	337	433	43	545	612	⊗	⊗	20
245	3.3	350	266	345	42	425	475	⊗	⊗	28
246	1.8	400	354	435	42	600	640	⊗	⊗	22
247	1.7	400	380	443	41	608	655	⊗	⊗	22
248	1.8	400	371	438	42	600	645	⊗	⊗	22
249	1.8	400	365	435	42	599	642	⊗	⊗	22
250	1.8	400	376	443	43	588	645	⊗	⊗	22
250A	1.7	520(20)	390	455	43	600	653	⊗	⊗	22
251	1.4	400	396	473	38	617	673	⊗	⊗	19
252	1.7	400	365	440	40	606	643	⊗	⊗	24
253	1.7	450	390	458	38	595	663	⊗	⊗	23
254	1.8	400	365	430	40	590	636	⊗	⊗	22

Embodiment 2

TABLE 20

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
255	2.3	350	302	385	41	470	525	14	⊕	○	23
256	1.7	400	395	469	41	608	679	12	⊕	○	21
257	1.8	400	411	472	37	630	693	10	△	○	20
258	3.2	400	269	374	43	464	516	11	⊕	○	32
259	2.1	400	411	487	42	628	701	8	△	△	21
260	2.0	400	354	434	42	578	625	12	○	○	22
261	2.2	400	323	404	41	530	578	12	⊕	○	23
262	2.0	400	355	439	40	575	632	11	○	○	20
263	2.4	450	302	381	40	480	524	12	⊕	⊕	21
264	1.5	400	366	469	42	619	678	9	△	⊕	18
265	1.8	400	363	440	40	566	639	12	⊕	○	21
265A	1.7	750(4)	377	450	41	575	645	12	⊕	○	21
266	1.7	400	380	448	40	585	650	12	○	⊕	20
267	1.7	400	379	452	41	590	655	13	⊕	○	21
268	1.4	450	403	492	40	638	700	11	○	⊕	20
269	1.8	400	360	438	41	587	624	12	⊕	○	21
270	3.0	400	271	371	42	492	530	14	⊕	○	28
271	2.0	400	332	413	41	548	590	13	⊕	○	23
272	1.7	400	389	465	42	612	664	12	○	○	20
273	1.9	400	334	416	40	555	590	13	⊕	○	23
274	2.1	400	388	457	40	574	633	12	⊕	○	25
275	2.0	400	334	409	41	536	584	12	⊕	○	23
276	1.8	400	332	410	40	537	586	11	⊕	⊕	22
277	1.5	400	458	531	39	672	721	9	○	○	20
278	2.0	400	341	414	42	550	591	13	⊕	⊕	23
279	1.7	400	388	460	40	605	658	11	○	⊕	22
280	1.7	400	395	475	39	615	680	12	⊕	⊕	21
281	1.3	450	430	492	35	639	702	9	○	⊕	23

Embodiment 2

TABLE 21

Alloy No.	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bonding characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
301	3.1	300	310	502	38	635	729	6	O	Δ	13
302	3.2	300	324	518	35	658	756	6	O	Δ	13
302A	3.0	500(15)	339	527	37	670	765	7	O	Δ	13
303	2.9	350	345	533	35	673	768	6	O	Δ	13
304	2.8	350	352	540	35	685	775	6	O	Δ	13
305	2.9	300	340	535	36	685	776	6	O	Δ	12
306	3.3	350	266	453	39	589	667	7	O	Δ	16
307	2.9	350	305	495	36	621	717	6	O	Δ	15
308	2.7	350	332	526	34	670	762	6	O	Δ	13
309	2.2	350	360	541	32	677	774	5	Δ	O	14
310	2.4	350	372	569	35	713	824	6	O	O	12
311	2.3	350	382	580	32	729	841	5	Δ	O	12
312	1.9	350	392	580	34	751	860	5	Δ	O	11
313	2.6	350	346	541	35	682	784	6	O	O	13
314	2.4	350	360	556	35	716	811	6	O	O	12
314A	2.3	550(10)	372	565	36	725	817	7	O	O	12
315	2.3	350	375	567	36	728	819	6	O	O	12
316	2.3	350	376	569	36	733	822	6	O	O	12
317	2.7	350	338	533	35	670	773	6	O	Δ	12
318	2.4	400	348	546	32	694	792	5	O	O	12
319	3.4	300	253	433	39	559	638	7	O	Δ	17
320	2.7	350	339	535	36	675	776	6	O	O	12
321	3.4	350	255	443	38	568	647	6	O	Δ	16
322	2.1	400	377	574	35	726	832	5	O	O	11
323	2.8	350	342	537	35	685	788	6	O	Δ	12
324	2.6	350	358	555	34	702	805	5	O	O	12
325	2.8	350	293	481	34	615	702	6	Δ	Δ	18
326	2.4	350	353	548	35	803	807	6	O	O	12

TABLE 22

Alloy No.	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity ($\mu\text{S}/\text{MS}$)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
327	2.8	350	329	521	36	655	756	6	O	Δ	13
328	2.8	350	341	536	35	697	792	6	O	Δ	12
329	2.7	350	343	539	35	680	781	6	O	O	12
330	2.7	350	348	545	32	693	800	5	Δ	Δ	12
331	2.5	350	355	551	34	692	804	5	O	O	12
332	2.4	350	348	543	35	698	802	6	O	O	12
333	2.5	350	350	545	35	695	796	6	O	Δ	13
334	2.6	350	361	557	33	710	818	5	O	O	12
335	2.8	350	346	545	35	681	790	5	O	O	11
336	2.8	350	363	556	31	688	806	4	O	O	11
337	2.7	350	352	542	35	688	796	6	O	O	12
338	2.3	350	365	559	36	714	826	6	O	O	12
338A	2.2	640(5)	377	567	37	722	833	7	O	O	12
339	2.2	350	381	570	37	720	832	7	O	O	12
340	2.2	350	375	568	36	723	833	6	O	O	12
341	2.2	350	373	569	36	718	829	6	O	O	12
342	1.8	400	398	594	34	756	865	4	Δ	O	11
343	2.3	350	366	560	34	714	817	6	O	Δ	12
344	2.6	350	348	536	36	670	783	5	O	O	13
345	3.0	350	346	536	32	663	777	4	Δ	Δ	12
346	2.4	350	350	545	34	685	780	5	O	O	13
347	2.5	350	363	558	35	702	809	6	O	O	12
348	2.8	350	337	537	33	678	779	5	O	O	12
349	2.4	350	360	558	35	699	814	6	O	O	11
350	2.7	350	333	527	36	669	764	6	O	O	12
351	1.9	400	416	615	31	780	892	4	Δ	O	11
352	2.5	350	359	551	34	702	810	6	O	O	12
353	2.2	350	367	562	33	720	830	5	O	O	12

TABLE 23

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
354	2.1	350	377	570	33	725	836	5	O	O	12
355	2.1	350	381	572	34	722	836	5	O	O	12
356	2.1	350	375	568	35	733	835	5	O	O	12
357	1.8	350	417	610	31	767	895	4	Δ	O	11
358	2.4	350	354	548	35	699	804	6	O	O	12
359	2.3	350	364	560	34	727	823	6	O	O	12
360	2.4	350	368	551	34	698	801	5	O	Δ	12
361	2.4	350	365	556	34	706	811	6	O	O	11
362	2.4	350	377	564	32	708	818	4	Δ	O	11
363	2.3	350	351	545	34	695	790	6	O	O	12
364	2.9	350	307	480	34	615	698	6	O	Δ	18
365	3.1	350	335	530	31	653	765	4	Δ	Δ	14
366	2.2	350	377	573	33	724	831	5	O	O	11
367	3.1	350	297	478	36	612	693	6	Δ	Δ	16
368	2.9	300	316	510	37	644	740	6	O	O	12
369	2.7	350	339	540	36	670	783	6	O	O	12
370	2.5	350	344	538	36	681	785	6	O	O	12
371	2.3	350	377	575	34	715	833	5	O	O	11
372	2.4	350	353	548	35	693	804	6	O	O	12
373	2.5	350	354	557	33	700	808	5	O	O	12
374	2.6	350	331	531	35	666	770	6	O	O	12
375	2.8	350	330	523	36	654	758	6	O	O	13
376	2.4	350	354	549	35	705	810	6	O	O	12
377	2.4	350	361	558	35	711	824	6	O	O	12
378	2.3	350	369	567	34	723	832	6	O	O	12
379	2.7	350	334	536	33	676	777	6	O	O	12
380	2.7	350	369	553	33	695	802	4	Δ	O	12
381	2.4	350	372	566	34	720	831	5	O	O	12

TABLE 24

Alloy No.	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
382	2.5	350	350	545	34	692	791	6	O	O	12
383	2.5	350	345	539	36	684	782	6	O	O	12
384	2.1	350	389	585	34	737	859	5	Δ	O	11
385	2.3	350	354	547	36	688	803	6	O	O	12
386	2.4	350	359	556	35	698	806	6	O	O	12
387	2.4	350	368	562	34	715	829	6	O	O	12
388	3.0	300	338	530	35	681	770	6	O	O	12
389	2.9	300	342	545	35	675	775	6	O	O	12
390	2.7	350	333	527	34	668	760	6	O	Δ	13
391	2.3	350	372	572	32	720	825	5	Δ	O	12
392	2.4	350	370	563	35	725	814	6	O	O	12
393	2.8	350	354	552	34	685	798	5	O	O	11
394	2.8	350	353	545	33	673	787	5	Δ	O	12
395	2.6	350	352	540	36	678	790	5	O	O	13
396	1.9	350	408	601	31	755	866	4	O	O	11
397	2.5	350	360	555	34	703	815	5	O	O	12

TABLE 25

Alloy No.	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro- conductivity (%ACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
401	6.5	350	136	267	42	345	388	13	⊙	⊙	56
402	4.0	350	198	322	44	387	425	14	⊙	○	44
403	4.5	350	202	345	44	422	464	14	⊙	△	37
404	4.5	350	210	365	45	465	517	12	○	×	32
405	4.5	300	235	419	46	513	582	10	○	×	28
406	4.5	300	226	416	42	508	578	8	△	×	28
407	4.0	350	242	408	40	515	585	7	△	△	28
408	4.0	350	248	388	41	452	490	12	○	×	25
409	4.5	450	241	368	42	443	485	14	⊙	⊙	12
410	1.2	400	501	598	36	668	807	5	×	×	14
411	1.3	400	438	522	37	612	719	5	×	×	17
412	5.5	400	199	328	42	393	436	15	⊙	⊙	16
413	4.5	350	201	307	44	391	415	16	⊙	○	38
414	1.1	400	487	623	36	734	854	4	×	○	7
415	1.3	450	430	510	35	602	712	6	×	○	16
416	1.3	450	440	525	34	613	730	5	×	○	14
417	1.6	450	366	451	34	573	631	8	×	○	22
418	1.2	450	465	538	32	630	752	5	×	○	15
419	1.2	400	448	576	37	647	798	5	×	○	12
420	2.0	350	357	452	38	535	643	8	×	○	16
421	—	—	—	—	—	—	—	—	—	—	—
422	1.6	450	395	470	32	605	678	5	×	○	26

(Comparative example 1)

TABLE 26

Alloy No	Mean grain size (μm)	Recrystallization temperature ($^{\circ}\text{C}$)	Mechanical properties			Mechanical properties (Post workpiece)			Bending characteristics (Post workpiece)	Corrosion cracking resistance	Electro-conductivity (% IACS)
			Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)	Proof stress (N/mm^2)	Tensile strength (N/mm^2)	Elongation (%)			
423	4.5	300	238	419	38	533	609	7	O	x	28
424	4.5	300	237	421	35	535	614	6	O	x	28
425	—	—	—	—	—	—	—	—	—	—	—
426	2.8	350	333	537	28	685	753	2	x	x	13
427	—	—	—	—	—	—	—	—	—	—	—
428	2.7	350	338	546	27	688	748	2	x	x	13
429	4.0	350	246	448	37	572	645	7	O	x	20
430	2.9	350	363	540	29	685	766	2	x	Δ	12
431	—	—	—	—	—	—	—	—	—	—	—

Comparative example 2

INDUSTRIAL APPLICABILITY

[0075] As understood from Tables 15 to 26, in comparison with first and second comparative example alloys having neither alloy composition nor recrystallized structure specified at the beginning, it becomes possible for the first to third invention copper alloys to realize the grain refinement and to improve greatly the machinability and bending characteristics. It is possible for the present invention alloy to be used preferably as plate, rod and wire materials even in difficult applications in which the prior high strength copper alloy cannot be used. In addition, it is possible to obtain the grain refinement and strength improvement by the recrystallization treatment due to the rapid high temperature heating processes. Furthermore, though not shown in Tables 15 to 26, as regards said post workpiece (pieces that the cold rolling and wire drawing are performed additionally for the rolled stock and wire drawing material after the recrystallization) heat-treated for 1 second to 4 hours at 150 to 600 $^{\circ}\text{C}$, it was confirmed that spring deflection limit and stress relaxation characteristics are greatly improved.

Claims

1. A high strength copper alloy **characterized in that** said copper alloy consists essentially of 4 to 19 mass percent of Zn, 0.5 to 2.5 mass percent of Si and the remaining mass percent of Cu, wherein said mass percent of Zn and said mass percent of Si satisfy the relationship $Zn-2.5 \cdot Si=0$ to 15 mass percent; mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu m \leq D \leq 3.5 \mu m$; and 0.2% yield strength in recrystallization state of said copper alloy is higher than 250N/mm².
2. The high strength copper alloy according to Claim 1, wherein said copper alloy contains 0.005 to 0.5 mass percent of Co, wherein said mass percent of Co and said mass percent of Si satisfy the relationship $Co/Si=0.005$ to 0.5.
3. The high strength copper alloy according to Claim 1, wherein said copper alloy contains 0.03 to 1.5 mass percent of Sn, wherein said mass percent of Sn and said mass percent of Si satisfy the relationship $Si/Sn \geq 1.5$.
4. The high strength copper alloy according to Claim 2, wherein said copper alloy contains 0.03 to 1.5 mass percent of Sn, wherein said mass percent of Sn and said mass percent of Si satisfy the relationship $Si/Sn \geq 1.5$.
5. The high strength copper alloy according to Claim 1, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni and said mass percent of Si satisfy the relationship $(Fe + Ni)/Si=0.005$ to 0.5.
6. The high strength copper alloy according to Claim 3, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni and said mass percent of Si satisfy the relationship $(Fe + Ni)/Si=0.005$ to 0.5.
7. The high strength copper alloy according to Claim 2, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni, said mass percent of Co and said mass percent of Si satisfy the relationship $(Fe+Ni+Co)/Si=0.005$ to 0.5.
8. The high strength copper alloy according to Claim 4, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni, said mass percent of Co and said mass percent of Si satisfy the relationship $(Fe+Ni+Co)/Si=0.005$ to 0.5.
9. A high strength copper alloy **characterized in that** said copper alloy consists essentially of 4 to 17 mass percent of Zn, 0.1 to 0.8 mass percent of Si and the remaining mass percent of Cu, wherein said mass percent of Zn and said mass percent of Si satisfy the relationship $Zn-2.5 \cdot Si=2\sim 15$ mass percent; mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu m \leq D \leq 3.5 \mu m$; and 0.2% yield strength in recrystallization state of said copper alloy is higher than 250N/mm².
10. The high strength copper alloy according to Claim 9, wherein said copper alloy contains 0.005 to 0.5 mass percent of Co, wherein said mass percent Co and said mass percent of Si satisfy the relationship $Co/Si=0.02$ to 1.5.
11. The high strength copper alloy according to Claim 9, wherein said copper alloy contains 0.2 to 3 mass percent of Sn, wherein said mass percent of Sn and said mass percent of Si satisfy the relationship $Si/Sn \leq 0.5$.
12. The high strength copper alloy according to Claim 10, wherein said copper alloy contains 0.2 to 3 mass percent of Sn, wherein said mass percent of Sn and said mass percent of Si satisfy the relationship $Si/Sn \leq 0.5$.
13. The high strength copper alloy according to Claim 9, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni and said mass percent of Si satisfy the relationship $(Fe+Ni)/Si=0.02$ to 1.5.
14. The high strength copper alloy according to Claim 11, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent Fe, said mass percent of Ni and said mass percent of Si satisfy the relationship $(Fe+Ni)/Si=0.02$ to 1.5.
15. The high strength copper alloy according to Claim 10, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni, said mass

percent of Co and said mass percent of Si satisfy the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.02$ to 1.5.

16. The high strength copper alloy according to Claim 12, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni, said mass percent of Co and said mass percent of Si satisfy the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.02$ to 1.5.

17. The high strength copper alloy according to any one of Claims 1 through 16, wherein said copper alloy contains at least one element selected from a group of P, Sb, As, Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In and Hf, wherein content of said element is 0.003 to 0.3 mass percent.

18. A high strength copper alloy **characterized in that** said copper alloy consists essentially of 66 to 76 mass percent of Cu, 21 to 33 mass percent of Zn and 0.5 to 2 mass percent of Si and the remaining mass percent of Cu, wherein said mass percent of Cu, said mass percent of Zn and said mass percent of Si satisfy the relationship $\text{Cu}-5 \cdot \text{Si}=62$ to 67 mass percent and $\text{Zn}+6 \cdot \text{Si}=32$ to 38 mass percent; mean grain size D of crystalline structure of said copper alloy distributes in $0.3 \mu\text{m} \leq D \leq 3.5 \mu\text{m}$; and 0.2% yield strength in recrystallization state of said copper alloy is higher than 250N/mm².

19. The high strength copper alloy according to Claim 18, wherein said copper alloy contains 0.005 to 0.3 mass percent of Co, wherein said mass percent of Co and said mass percent of Si satisfy the relationship $\text{Co}/\text{Si}=0.005$ to 0.4.

20. The high strength copper alloy according to Claim 18, wherein said copper alloy contains 0.03 to 1 mass percent of Sn, wherein said mass percent of Si and said mass percent of Sn satisfy the relationship $\text{Si}/\text{Sn} \geq 1$.

21. The high strength copper alloy according to Claim 19, wherein said copper alloy contains 0.03 to 1 mass percent of Sn, wherein said mass percent of Si and said mass percent of Sn satisfy the relationship $\text{Si}/\text{Sn} \geq 1$.

22. The high strength copper alloy according to Claim 18, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni and said mass percent of Si satisfy the relationship $(\text{Fe}+\text{Ni})/\text{Si}=0.005$ to 0.4.

23. The high strength copper alloy according to Claim 20, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni and said mass percent of Si satisfy the relationship $(\text{Fe}+\text{Ni})/\text{Si}=0.005$ to 0.4.

24. The high strength copper alloy according to Claim 19, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni, said mass percent of Co and said mass percent of Si satisfy the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.005$ to 0.4.

25. The high strength copper alloy according to Claim 21, wherein said copper alloy contains 0.005 to 0.3 mass percent of Fe and/or 0.005 to 0.3 mass percent of Ni, wherein said mass percent of Fe, said mass percent of Ni, said mass percent of Co and said mass percent of Si satisfy the relationship $(\text{Fe}+\text{Ni}+\text{Co})/\text{Si}=0.005$ to 0.4.

26. The high strength copper alloy according to any one of Claims 18 through 25, wherein said copper alloy contains at least one element selected from a group of P, Sb, As, Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In and Hf, wherein content of P, Sb, or As is 0.005 to 0.3 mass percent, content of Sr, Mg, Y, Cr, La, Ti, Mn, Zr, In or Hf is 0.003 to 0.3 mass percent, and total content in a case selected from at least P, Sb or As is 0.005 to 0.25 mass percent.

27. The high strength copper alloy according to any one of Claims 1 through 26, wherein said copper alloy is recrystallized material obtained from recrystallization of plastic working blank, which is formed by plastic working including cold working with working rate being more than 30 percent.

28. The high strength copper alloy according to Claim 27, wherein said recrystallized materials are obtained by heat-treatment of said plastic working blank at the range from 450 to 750 °C for 1 to 1000 seconds.

29. The high strength copper alloy according to Claim 27, wherein said cold working materials are obtained by cold rolling works or cold wire drawing of said recrystallized materials.

30. The high strength copper alloy according to Claim 29, wherein said copper alloy is obtained by heat-treatment of

said cold working materials at the range from 150 to 600 °C for 1 second to 4 hours.

5 **31.** The high strength copper alloy according to Claim 29, wherein said copper alloys are manufactured pieces obtained by working said cold working materials to a predetermined form.

32. The high strength copper alloy according to Claim 31, wherein said copper alloy is obtained by heat-treatment of said cold working materials at the range from 150 to 600 °C for 1 second to 4 hours.

10 **33.** The high strength copper alloy according to any one of Claims 1 through 17, wherein said copper alloy is rolled material or manufactured piece with a predetermined form obtained by working said rolled material.

34. The high strength copper alloy according to any one of Claims 18 through 26, wherein said copper alloys are wire drawing material or manufactured pieces with a predetermined form obtained by working said wire drawing material.

15

20

25

30

35

40

45

50

55

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/04470

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl ⁷ C22C9/04, C22F1/08 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl ⁷ C22C9/00-9/10, C22F1/08 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Toroku Jitsuyo Shinan Koho 1994-2003 Kokai Jitsuyo Shinan Koho 1971-2003 Jitsuyo Shinan Toroku Koho 1996-2003 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	US 2002/0057985 A1 (DOWA MINING CO., LTD.), 16 May, 2002 (16.05.02), Claims & JP 2002-88428 A	1-34
A	JP 2002-30364 A (Sumitomo Light Metal Industries, Ltd.), 31 January, 2002 (31.01.02), Claims (Family: none)	1-34
A	US 2002/0006351 A1 (DOWA MINING CO., LTD.), 17 January, 2002 (17.01.02), Claims & JP 2001-294957 A	1-34
☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
* Special categories of cited documents: "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art "&" document member of the same patent family		
Date of the actual completion of the international search 04 July, 2003 (04.07.03)		Date of mailing of the international search report 15 July, 2003 (15.07.03)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

Form PCT/ISA/210 (second sheet) (July 1998)

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP03/04470

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	EP 1045041 A1 (SAMBO COPPER ALLOY CO., LTD.), 18 October, 2000 (18.10.00), Claims & US 2002/0069942 A1 & JP 2000-119775 A	1-34
A	JP 2000-96164 A (The Furukawa Electric Co., Ltd.), 04 April, 2000 (04.04.00), Claims (Family: none)	1-34
A	JP 6-192771 A (Nippon Mining & Metals Co., Ltd.), 12 July, 1994 (12.07.94), Claims (Family: none)	1-34
A	JP 4-246141 A (DOWA MINING CO., LTD.), 02 September, 1992 (02.09.92), Claims (Family: none)	1-34
A	JP 4-224645 A (Japan Energy Corp.), 13 August, 1992 (13.08.92), Claims (Family: none)	1-34
A	JP 3-68731 A (Japan Energy Corp.), 25 March, 1991 (25.03.91), Claims (Family: none)	1-34
A	JP 3-291344 A (The Furukawa Electric Co., Ltd.), 20 December, 1991 (20.12.91), Claims (Family: none)	1-34
A	JP 2-170953 A (Japan Energy Corp.), 02 July, 1990 (02.07.90), Claims (Family: none)	1-34

Form PCT/ISA/210 (continuation of second sheet) (July 1998)