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(54) COPPER ALLOY MATERIAL AND MANUFACTURING METHOD THEREOF

(57) {Problems} To provide a copper alloy material that is excellent in bending property, 0.2% yield stress, electrical conductivity, and stress relaxation resistance, and that is suitable in lead frames, connectors, terminal materials, and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems.

{Means to solve} A copper alloy material, containing 0.1 to 0.8 mass% of Cr, and 0.01 to 0.5 mass% in total of at least one selected from the group consisting of an additional alloying element group 1 and an additional alloying element group 2 described below, with the balance being copper and unavoidable impurities, wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and wherein the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more:
an additional alloying element group 1: at least one selected from the group consisting of Mg, Ti and Zr in an amount of 0.01 to 0.5 mass% in total; and
an additional alloying element group 2: at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P in an amount of 0.005 to 0.5 mass% in total.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy material and a method of producing the same. More particularly, the present invention relates to a copper alloy material that is applied to lead frames, connectors, terminal materials, relays, switches, sockets, and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EV (electric vehicles) and HEV (hybrid electric vehicles), and solar photovoltaic power generation systems, and the present invention relates to a method of producing the copper alloy material.

BACKGROUND ART

[0002] Property items required in copper alloy materials that are used in applications, such as lead frames, connectors, terminal materials, relays, switches, sockets, and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems, include, for example, electrical conductivity, tensile strength, bending property, and stress relaxation resistance. In recent years, systems are exposed to higher voltages, and the use environments are exposed to higher temperatures, so that the level of these demanded properties is ever increasing.

[0003] Along with the change described above, the problems as described below have caused with copper alloy materials.

[0004] First, the environments in which terminals are used are exposed to higher temperature and higher voltage, and the demand for heat resistance is becoming stronger. Particularly, when a contact pressure is applied to a terminal spring unit at a high temperature, the stress deteriorates with the lapse of time, and this causes a problem in the spring reliability. Also, with respect to the applications mentioned above, the environment temperature increases every year. Further, not only the ambient environment but also spontaneous heat are also subjected to temperature increase and electrical current loss, which become problems.

[0005] Secondly, terminals are required to have strong spring property and constant mechanical strength; however, on the other hand, if it is poor in workability in bending (bending property) that is applied to a contact area or a spring area, it is inconvenient in terms of design, and the design of necessary connectors becomes impossible to be achieved. Further, it is generally well known that bending property becomes poor by thickness increasing. However, increase of thickness of the sheet thickness cannot be avoided in large electrical current applications, and there is a problem that cracks occur even under bending at a level equivalent to that of conventional connector products.

[0006] Copper (Cu), in the state of pure metal, cannot be used as spring materials, since the spring strength of Cu does not reach a level that satisfies the required properties. Thus, for example, Mg or Sn is added to Cu to cause solid solution strengthening, or Cr or Zr is added to Cu to cause precipitation strengthening, and the resulting copper alloys can be utilized as a spring material. Further, a material with high electrical conductivity and excellent heat resistance is needed for applications under large electrical current.

[0007] Under such circumstances, Cu-Cr-based alloys are known to exhibit mechanical strength of a medium level and high electrical conductivity. Patent Literature 1 discloses that when Mg is added to a Cu-Cr-based alloy, stamping (press-punching) workability is improved. Patent Literature 2 discloses that when Zr is added to a Cu-Cr-based alloy, bending property is improved. Patent Literature 3 discloses that when Ti is added to a Cu-Cr-based alloy, stress relaxation resistance is improved. As shown in Patent Literatures 1 to 3, examples are known for the additional alloying elements and compositions in known highly electrically-conductive copper alloys.

[0008] Further, Patent Literature 4 discloses that in a Cu-Cr-Zr-based alloy, when the ratio of coincidence boundary $\Sigma 3$ in the grain boundaries is 10% or more, bending property is excellent. Further, Patent Literature 5 discloses that in a Cu-Cr-Zr-based alloy, an improvement in bending property is achieved, by controlling orientation distribution density of Brass orientation to 20 or less, and by controlling the sum of orientation distribution density of Brass orientation, S orientation and Copper orientation to 10 to 50.

[0009] Further, as disclosed in Patent Literatures 6 to 8, Cu-Mg-based alloys are known. Patent Literature 6 discloses that when the surface grain size of a Cu-Mg-P-based alloy is controlled, mold abrasion upon stamping is reduced. Patent Literature 7 discloses that by controlling the particle size of a Mg-P-based compound that is precipitated and dispersed in a Cu-Mg-P-based alloy, migration resistance is improved. Patent Literature 8 discloses that by suppressing precipitation of coarse intermetallic compounds with particle size of 0.1 μm or more in a Cu-Mg-P-based alloy, the resultant copper alloy is high in electrical conductivity, and is improved in bending property.

CITATION LIST

PATENT LITERATURES

[0010]

Patent Literature 1: JP-A-11-323463 ("JP-A" means unexamined published Japanese patent application)
Patent Literature 2: Japanese Patent No. 3803981
Patent Literature 3: JP-A-2002-180159
Patent Literature 4: Japanese Patent No. 4087307
Patent Literature 5: JP-A-2009-132965
Patent Literature 6: Japanese Patent No. 3353324
Patent Literature 7: Japanese Patent No. 4756197
Patent Literature 8: JP-A-2011-241412

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0011] However, in the inventions described in Patent Literatures 1, 2 and 3, definitions of the alloying elements and definitions of the grain size of Cu-Cr-based alloys are provided, but they do not give any improvement in properties of the matrix itself by texture control (control of the texture or control of the grain boundary state) through production process conditions.

[0012] Further, in the inventions described in Patent Literatures 6, 7 and 8, definitions of the alloying elements and definitions of the grain size and the precipitate particle size of Cu-Mg-based alloys are provided, but they do not give any improvement in properties of the matrix itself by texture control (control of the texture or control of the grain boundary state) through production process conditions.

[0013] Also, in Patent Literature 4, when a Cu-Cr-Zr-based alloy is subjected to final cold-rolling at a particular high degree of working, dynamic recrystallization is induced, and the ratio of coincidence grain boundary $\Sigma 3$ is made to 10% or more, to improve bending property, but it does not give any improvement in stress relaxation resistance. In Patent Literature 5, when a Cu-Cr-Zr-based copper alloy is subjected to cold-rolling at a particular degree of working and to a heat treatment at a low temperature, the density of orientation distribution of Brass orientation is controlled to be 20 or less, and the sum of the density of orientation distribution of Brass orientation, S orientation and Copper orientation is controlled to be 10 to 50, to improve bending property, but it does not give any improvement in stress relaxation resistance.

[0014] As described in above, with the conventional alloy compositions and production methods, it is difficult to attain properties of electrical conductivity, tensile strength, bending property, and stress relaxation resistance, each of which are required in future, respectively at a high level and excellent in a well-balanced manner.

[0015] In view of the problems described above, the present invention is contemplated for providing a copper alloy material that is excellent in mechanical strength and electrical conductivity, and among them, in particular, that has favorable stress relaxation resistance and bending property in an excellently balanced manner of these two properties, and the present invention is contemplated for providing a method of producing the copper alloy material. This copper alloy material is suitable for lead frames, connectors, and terminal materials of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems; connectors and terminal materials of, for example, parts to be mounted on vehicles; relays, switches, sockets, and the like.

SOLUTION TO PROBLEM

[0016] The inventors of the present invention have studied keenly, and have conducted research on copper alloys suitable for electrical or electronic part applications. As a result, the inventors found that, in the texture of Cu-Cr-based or Cu-Mg-based copper alloy materials having a specific alloy composition, when the Cube orientation {100} <001> is accumulated at a ratio of 3% or more in the surface direction (ND) of a rolled sheet, and the ratio of coincidence grain boundary (CSL grain boundary) $\Sigma 3$ in grain boundaries is 20% or more, mechanical strength, electrical conductivity, as well as bending property and stress relaxation resistance can be simultaneously enhanced. The present invention was made based on these findings.

[0017] That is, the present invention it to provide the following means:

(1) A copper alloy material, containing 0.1 to 0.8 mass% of Cr, and 0.01 to 0.5 mass% in total of at least one selected from the group consisting of an additional alloying element group 1 and an additional alloying element group 2

described below, with the balance being copper and unavoidable impurities, wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and wherein the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more:

> an additional alloying element group 1: at least one selected from the group consisting of Mg, Ti and Zr in an amount of 0.01 to 0.5 mass% in total; and
> an additional alloying element group 2: at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P in an amount of 0.005 to 0.5 mass% in total.

(2) The copper alloy material described in item (1), containing at least one selected from the additional alloying element group 1 and at least one selected from the additional alloying element group 2 in an amount of 0.01 to 0.5 mass% in total.

(3) The copper alloy material described in item (1) or (2), wherein the copper alloy material has a tensile strength of 400 MPa or greater and an electrical conductivity of 75%IACS or higher.

(4) A method of producing the copper alloy material described in any one of items (1) to (3), comprising: casting a copper alloy raw material which gives the composition described in item (1), to give an ingot [Step 1-1]; homogenization heat treatment of the ingot at 600 to 1,025°C for 10 minutes to 10 hours [Step 1-2]; hot-rolling at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98% [Step 1-3]; cold-rolling at a working ratio of 50 to 99% [Step 1-4]; intermediate heat treatment at 300 to 1,000°C for 5 seconds to 180 minutes [Step 1-5]; cold-rolling at a working ratio of 50 to 95% [Step 1-6]; aging at 400 to 650°C for 30 to 180 minutes [Step 1-9]; and strain-relief annealing at 550 to 700°C for 5 seconds to 10 minutes [Step 1-11], in this order.

(5) A copper alloy material, containing 0.01 to 0.5 mass% of Mg, with the balance being copper and unavoidable impurities, wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and wherein the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more.

(6) A copper alloy material, containing 0.01 to 0.5 mass% of Mg, and 0.01 to 0.3 mass% in total of at least one selected from the group consisting of Zn, Sn, Ag, Si and P, with the balance being copper and unavoidable impurities, wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and wherein the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more.

(7) The copper alloy material described in item (5) or (6), wherein the copper alloy material has a tensile strength of 250 MPa or greater and an electrical conductivity of 75%IACS or higher.

(8) A method of producing the copper alloy material described in any one of items (5) to (7), comprising: casting a copper alloy raw material which gives the composition described in item (5) or (6), to give an ingot [Step 2-1]; homogenization heat treatment of the ingot at 600 to 1,025°C for 10 minutes to 10 hours [Step 2-2]; hot-rolling at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98% [Step 2-3]; cold-rolling at a working ratio of 50 to 99% [Step 2-4]; intermediate heat treatment at 300 to 800°C for 5 seconds to 180 minutes [Step 2-5]; cold-rolling at a working ratio of 50 to 95% [Step 2-6]; heat treatment at 300 to 800°C for 5 seconds to 180 minutes [Step 2-7]; cold-rolling at a working ratio of 10 to 80% [Step 2-8]; and strain-relief annealing at 300 to 600°C for 5 to 60 seconds [Step 2-9], in this order.

[0018] Hereinafter, a first embodiment of the present invention means to include the Cu-Cr-based alloy materials described in the above items (1) to (3) and the method of producing the same described in the above item (4).

[0019] A second embodiment of the present invention means to include the Cu-Mg-based alloy materials described in the above items (5) to (7) and the method of producing the same described in the above item (8).

[0020] Herein, the present invention means to include both of the above first and second embodiments, unless otherwise specified.

ADVANTAGEOUS EFFECTS OF INVENTION

[0021] The copper alloy material of a Cu-Cr-based primarily of the present invention is excellent in stress relaxation resistance and bending property, and has excellent mechanical strength and electrical conductivity, and the copper alloy material is suitable in lead frames, connectors, terminal materials, relays, switches, sockets and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems.

[0022] Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawing.

BRIEF DESCRIPTION OF DRAWINGS

[0023]

{Fig. 1}
Figs. 1(a) and 1(b) are explanatory diagrams for the method of testing stress relaxation resistance in the example section, in which Fig. 1(a) shows the state before heat treatment, and Fig. 1(b) shows the state after the heat treatment.

MODE FOR CARRYING OUT THE INVENTION

[0024] Preferable embodiments of the copper alloy material of the present invention will be described in detail. Herein, the term "copper alloy material" (before working, having a predetermined alloy composition) means a product obtained after a copper alloy raw material is worked into a predetermined shape (for example, sheet, or strip). Herein, explanation of the embodiments will be given on a sheet material and a strip material.

[0025] The copper alloy material of the present invention is one that properties thereof are defined, with the accumulation ratio of the texture in a predetermined direction of a rolled sheet, and a particular coincidence grain boundary in grain boundaries; however, this means that it is enough for a copper alloy material to have those properties, and the shape of the copper alloy material is not intended to be limited to a sheet material, and a strip material is also acceptable.

[0026] Next, the respective alloy composition and alloying elements thereof are explained.

[0027] In the first embodiment of the present invention, Cu-Cr-based alloys are used, as a copper alloy material having electrical conductivity, mechanical strength, bending property and stress relaxation resistance that are required in connectors of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems. In the first embodiment of the present invention, in order to attain both of the area ratio of the Cube orientation that improves bending property in connection with the texture, and the length ratio of the coincidence grain boundary $\Sigma 3$, which improves stress relaxation resistance, to the total grain boundary length, respectively to a desired occupancy ratio, the copper alloy material contains Cr in an amount of 0.1 to 0.8 mass%, and at least one selected from the group consisting of the additional alloying element group 1 and the additional alloying element group 2 in an amount of 0.01 to 0.5 mass% in total, respectively as an addition amount to Cu:

the additional alloying element group 1: at least one selected from the group consisting of Mg, Ti and Zr in an amount of 0.01 to 0.5 mass% in total; and
the additional alloying element group 2: at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P in an amount of 0.005 to 0.5 mass% in total.

[0028] Preferably, the copper alloy material contains at least one selected from the additional alloying element group 1 and at least one selected from the additional alloying element group 2 in an amount of 0.01 to 0.5 mass% in total. More preferably, the copper alloy material contains Cr in an amount of 0.15 to 0.5 mass%, and contains at least one selected from the additional alloying element group 1 and at least one selected from the additional alloying element group 2, in an amount of 0.1 to 0.5 mass% in total. This is because when the amounts to be added are defined to be in these ranges, since the matrix is in a state close to the pure copper texture, a balance can be achieved between acceleration of development of the Cube orientation and attainment of a state with lowered stacking fault energy caused by partial solid solution. In a precipitation-type Cu-Cr-based alloy, in addition to the conditions described above, a precipitate before being subjected to a heat treatment that finally determines the texture suppresses partial coarsening of grains, and stable development of the Cube orientation is accelerated.

[0029] In the second embodiment of the present invention, Cu-Mg-based alloys are used, as a copper alloy material having electrical conductivity, mechanical strength, bending property and stress relaxation resistance, which are required in connectors of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems. In the second embodiment of the present invention, in order to attain both of the area ratio of the Cube orientation that improves bending property in connection with the texture, and the length ratio of the coincidence grain boundary $\Sigma 3$, which improves stress relaxation resistance, to the total grain boundary length, respectively to a desired occupancy ratio, the copper alloy material contains Mg in an amount of 0.01 to 0.5 mass%, as an addition amount to Cu. In the second embodiment of the present invention, the copper alloy material may contain, in addition to Mg, at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P, as an additional alloying element, in an amount of 0.01 to 0.3 mass% in total, and preferably, the copper alloy material may contain the additional alloying element in a total amount of 0.05 to 0.3 mass%. This is because when the amounts to be added are defined to be in these ranges, since the matrix is in a state close to the pure copper texture, a balance can be achieved between acceleration of development of the Cube orientation and attainment of a state with lowered stacking fault energy caused by solid solution.

[0030] Hereinbelow, explanation is given with respect to alloying elements to the precipitation-type Cu-Cr-based copper-based alloy, in the first embodiment of the present invention.

(Cr)

[0031] The first embodiment of the present invention is directed to Cu-Cr-based alloys in order to secure mechanical strength and electrical conductivity. The addition amount of Cr is 0.1 to 0.8 mass%, preferably 0.15 to 0.5 mass%. When the addition amount of Cr is set within this range, a precipitate of the simple substance of Cr and/or a compound of Cr with another element is precipitated into the copper matrix, and thereby the matrix is brought to a state closer to pure copper with exhibiting precipitation strength, to accelerate nucleation and growth of the Cube orientation {001} <100> in the sheet thickness direction (ND). On the other hand, if the addition amount of Cr is too large, such a precipitate is precipitated in excess, so that solid solution does not sufficiently proceed in the subsequent heat treatment, and the mechanical strength after aging tends to be lowered. Further, the stacking fault energy (hereinafter, also called SFE) increases, an increase in the coincidence grain boundary $\Sigma 3$ upon the heat treatment is suppressed, and there is a tendency that sufficient stress relaxation resistance may not be obtained. On the contrary, if the addition amount of Cr is too small, such effects of addition may not be obtained.

[0032] Herein, the term "compound" refers to a substance composed of two or more kinds of elements, and, for example, a substance composed of Cr or the like and one or more kinds of other elements (including Cu). The term precipitate as used herein means to include precipitates or crystallization products in which these compounds exist within grains of the Cu matrix or on grain boundaries. Herein, examples of Cr-based precipitates include not only the simple substance of Cr but also Cr-based compounds, such as Cr_3Si and CrSi, when Si is added. These compounds vary depending on the alloying elements.

(Alloying elements Mg, Ti, Zr, Zn, Fe, Sn, Ag, Si and P)

[0033] In the first embodiment of the present invention, the copper alloy material contains, in addition to the Cr as a main alloying element, an additional alloying element of at least one selected from the group consisting of the additional alloying element group 1 and the additional alloying element group 2 described below, in an amount of 0.01 to 0.5 mass% in total. The additional alloying elements are classified into two groups, from the viewpoint of their actions.

the additional alloying element group 1: at least one selected from the group consisting of Mg, Ti and Zr in an amount of 0.01 to 0.5 mass% in total; and

the additional alloying element group 2: at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P in an amount of 0.005 to 0.5 mass% in total.

[0034] It is preferable that the copper alloy material contain at least one selected from the additional alloying element group 1 and at least one selected from the additional alloying element group 2 in an amount of 0.01 to 0.5 mass% in total.

[0035] Preferable ranges of the respective amounts of addition of these additional alloying elements are as follows. The addition amount of Mg is preferably 0.01 to 0.5 mass%, more preferably 0.05 to 0.3 mass%. The addition amount of Ti is preferably 0.01 to 0.2 mass%, more preferably 0.02 to 0.1 mass%. The addition amount of Zr is preferably 0.01 to 0.2 mass%, more preferably 0.01 to 0.1 mass%. The addition amount of Zn is preferably 0.05 to 0.3 mass%, more preferably 0.1 to 0.2 mass%. The addition amount of Fe is preferably 0.05 to 0.2 mass%, more preferably 0.1 to 0.15 mass%. The addition amount of Sn is preferably 0.05 to 0.3 mass%, more preferably 0.1 to 0.2 mass%. The addition amount of Ag is preferably 0.05 to 0.2 mass%, more preferably 0.05 to 0.1 mass%. The addition amount of Si is preferably 0.01 to 0.1 mass%, more preferably 0.02 to 0.05 mass%. The addition amount of P is preferably 0.005 to 0.1 mass%, more preferably 0.005 to 0.05 mass%. If the addition amounts of those elements are smaller than the above, the effects of addition may not be obtained.

[0036] These additional alloying elements respectively accomplish the following roles.

[0037] Mg forms a solid solution and improves the stress relaxation resistance. If the addition amount of Mg is too large, Mg-based compounds are formed and adversely affect melting, casting and hot-rolling, thereby conspicuously making manufacturability poor. Further, in addition to causing a lowering in electrical conductivity, nucleation and growth of the Cube orientation {001} <100> in the ND are suppressed by an increase in the amount of solid solution, resulting in that bending property becomes insufficient.

[0038] Ti and Zr improve the stress relaxation resistance and mechanical strength through solid solution, precipitation and crystallization. If the amounts of addition of Ti and Zr are too large, Ti-based or Zr-based compounds are formed, to adversely affect melting, casting and hot-rolling, thereby conspicuously making manufacturability poor. Further, when the amounts of addition of Ti and Zr are too large so that Ti and Zr exist even in a solid solution state, Ti and Zr cause a lowering in electrical conductivity, and also, nucleation and growth of the Cube orientation {001} <100> in the ND is suppressed by an increase in the amount of solid solution, resulting in that bending property becomes insufficient.

[0039] When Zn exists in the predetermined addition amount in the range described above, peeling resistance of plating and solder is enhanced, and Zn contributes to mechanical-strength enhancement, even though to a small extent. If the addition amount of Zn is too large, Zn causes a lowering in electrical conductivity due to solid solution, and also, nucleation and growth of the Cube orientation {001} <100> in the ND are suppressed by an increase in the amount of solid solution, resulting in that bending property becomes insufficient.

[0040] When Fe exists in the predetermined addition amount in the range described above, Fe precipitates out finely into the matrix in the form of compound or simple substance. Simple substance precipitates out, to contribute to precipitation-hardening. Also, even Fe-based compounds also precipitate. In all cases, there is an effect of making grains fine by suppressing the growth of grains, and bending property is enhanced favorably, by improving the dispersed state of the grains of the Cube orientation {001} <100>.

[0041] Sn accelerates solid-solution strengthening, and also work hardening upon rolling. Further, when Sn is added together with Mg, the stress relaxation resistance can be further improved than in the case of adding either one of the elements singly. If the addition amount of Sn is too large, Sn causes a lowering in electrical conductivity due to solid solution, and also, nucleation and growth of the Cube orientation {001} <100> in the ND are suppressed by an increase in the amount of solid solution, resulting in that bending property becomes insufficient.

[0042] Ag exhibits an effect of improving the stress relaxation resistance even added singly, and when Ag is added together with Mg, Zr and/or Ti, the stress relaxation resistance can be further improved than in the case of adding either one of the elements singly. If the addition amount of Ag is too large, the effects are saturated, and particularly, the cost is largely affected, which is not preferable.

[0043] Si exhibits an effect of improving the stress relaxation resistance even added singly, and when Si is added together with Mg, Zr and/or Ti, the stress relaxation resistance can be further improved than in the case of adding either one of the elements singly. Further, Si has an effect of improving pressability. If the addition amount of Si is too large, Si causes a lowering in electrical conductivity due to solid solution, and also, nucleation and growth of the Cube orientation {001} <100> in the ND are suppressed by an increase in the amount of solid solution, resulting in that bending property becomes insufficient.

[0044] P can make the metal flow at the time of melt-casting favorable, or can improve the stress relaxation resistance by added singly or in the form of a compound. If the addition amount of P is too large, P causes a lowering in electrical conductivity due to solid solution, and also, nucleation and growth of the Cube orientation {001} <100> in the ND are suppressed by an increase in the amount of solid solution, resulting in that bending property becomes insufficient.

[0045] Hereinbelow, explanation is given with respect to alloying elements to the solid-solution-type Cu-Mg-based copper-based alloy, in the second embodiment of the present invention.

[0046] The second embodiment of the present invention contains Mg in an amount of 0.01 to 0.5 mass% as an essential alloying element. In addition to the Mg, the copper alloy material may further contain, as an optional alloying element, at least one selected from the group consisting of Zn, Sn, Ag, Si and P in an amount of 0.01 to 0.3 mass% in total.

[0047] Preferable ranges of the respective amounts of addition of these main alloying element and additional alloying elements are as follows. The addition amount of Mg is preferably 0.01 to 0.3 mass%, more preferably 0.05 to 0.25 mass%. The addition amount of Zn is preferably 0.05 to 0.3 mass%, more preferably 0.1 to 0.2 mass%. The addition amount of Sn is preferably 0.05 to 0.2 mass%, more preferably 0.1 to 0.15 mass%. The addition amount of Ag is preferably 0.01 to 0.15 mass%, more preferably 0.05 to 0.1 mass%. The addition amount of Si is preferably 0.01 to 0.05 mass%, more preferably 0.02 to 0.03 mass%. The addition amount of P is preferably 0.001 to 0.1 mass%, more preferably 0.005 to 0.05 mass%.

(Alloying elements Mg, Zn, Sn, Ag, Si and P)

[0048] Those alloying elements exhibit the actions and effects described above.

[0049] In the present invention, the unavoidable impurities that are included in the balance are usual ones, and examples thereof include O, F, S and C. The content of each of the unavoidable impurities is preferably 0.001 mass% or less, respectively.

(Texture)

[0050] The analysis of the crystal orientation of the rolled face in the present invention is conducted using the EBSD method. The EBSD method, which stands for electron backscatter diffraction, is a technique of crystal orientation analysis using reflected electron Kikuchi-line diffraction (Kikuchi pattern) that occurs when a sample is irradiated with an electron beam under a scanning electron microscope (SEM). In the present invention, a sample area, which is measured 500 μm on each of the four sides and which contains 200 or more grains, is subjected to an analysis of the orientation, by scanning in a stepwise manner at an interval of 0.5 μm.

[0051] With respect to the EBSD analysis, in order to obtain a clear Kikuchi-line diffraction image, it is preferable to mirror polish the substrate surface, with polishing particles of colloidal silica, after mechanical polishing, and then to conduct the analysis. Further, the measurement is conducted from the sheet surface.

[0052] In the present invention, the area ratio of the Cube orientation {001} <100> means the ratio of the area of grains having an orientation in which the deviation from an ideal orientation of the Cube orientation {001} <100> is within 15° (a deviation angle of ±15° or less), to the total measured area. The data obtained from the orientation analysis based on EBSD includes the orientation data to a depth of several tens nanometers, through which the electron beam penetrates into the sample. However, since the depth is sufficiently small as compared with the width to be measured, the data is described in terms of ratio of an area, i.e. area ratio, in the present specification. Further, since the orientation distribution changes in the sheet thickness direction, it is preferable to carry out the orientation analysis by EBSD at several arbitrary points along the sheet thickness direction, to calculate the average. Unless otherwise specified, the area ratio of a crystal plane having a certain crystal orientation is referred to the area ratio measured in this manner.

[0053] In the present invention, the area ratio of the Cube orientation {001} <100> on a rolled face is 3% or more, preferably 6% or more. The upper limit is not particularly limited, but is generally 90% or less. When the area ratio of the Cube orientation is controlled as such, bending property can be improved.

[0054] In the present invention, it is meant to define the area ratio of the Cube orientation {001} <100> when observed the surface of a rolled face (a face rolled by being brought into contact with a rolling roll).

(Coincidence grain boundary Σ3)

[0055] The coincidence grain boundaries are special grain boundaries with high geometric consistency, and the smaller value of Σ that is defined as a reciprocal of the coincident site lattice density means that this consistency is higher. Among the coincidence grain boundaries, coincidence grain boundary Σ3 is known to have less disorder of regularity in the grain boundaries and lower grain boundary energy. In particular, since there are fewer defects that accelerate stress relaxation in the texture, heat resistance is excellent.

[0056] In the present invention, the ratio of the coincidence grain boundary Σ3 in the grain boundaries is 20% or more, preferably 30% or more, and more preferably 40% or more. The upper limit is not particularly limited, but is generally 90% or less. When the ratio of the coincidence grain boundary Σ3 is controlled as such, the stress relaxation resistance can be improved. Herein, the ratio of the coincidence grain boundary Σ3 is a value obtained by determining the sum of lengths of the coincidence grain boundary Σ3 to the total sum of the lengths of grain boundaries on an observed plane analyzed by an ESBD method or the like, by the following formula: (sum of lengths of coincidence grain boundary E3)/(sum of lengths of the entire grain boundaries) x 100 (%). In the below, description is given on the details of the coincidence grain boundary Σ3 and the method for measuring the length thereof.

[0057] The analysis of the coincidence grain boundary Σ3 is carried out via a CSL (coincidence site lattice boundary) analysis, using a software "Orientation Imaging Microscopy V5" (trade name) manufactured by EDAX TSL. The coincidence grain boundary Σ3 is a grain boundary in which, for example, adjoining grains are in a relationship of having an angle of rotation of 60° about the axis of rotation of <111>. Thus, a grain boundary corresponding to the coincidence grain boundary Σ3 is analyzed from the orientation relationship of neighboring grain boundaries, using the software. Then, measurement is made on the total grain boundary length and the length of the coincidence grain boundary Σ3 of a rolled face in the area measured, and the value of: (length of coincidence grain boundary Σ3)/(total grain boundary length) x 100 (%), is defined as the ratio of the coincidence grain boundary Σ3. In the analysis using the software, a case in which adjoining pixels have a tilt (deviation) of 15° or greater is considered as a grain boundary.

[0058] Specifically, in a measurement region which measures about 500 μm on each of the four sides and includes 200 or more grains, measurement is carried out via an EBSD method under the conditions of a scan step of 0.5 μm, and the length of the coincidence grain boundary Σ3 and the total grain boundary length are measured using the software. In an object of measurement, a case in which the orientation difference (deviation) of adjoining pixels is 15° or more is considered as a grain boundary, and the coincidence grain boundary Σ3 is determined from the orientation relationships of adjoining pixels. In the measurement range measured in this manner, the ratio of the sum of lengths of the coincidence grain boundary Σ3 to the sum of lengths of the entire grain boundaries is calculated from the length of the entire grain boundaries and the length of the coincidence grain boundary Σ3 on a rolled face, by the following formula: (sum of lengths of coincidence grain boundary E3)/(sum of lengths of entire grain boundaries) × 100, and this value is designated as the "ratio of the coincidence grain boundary E3 in the grain boundaries". In the present specification, this may be simply referred to as "ratio (%) of coincidence grain boundary Σ3".

(Production method)

[0059] Next, explanation is given on the method of producing the copper alloy material of the present invention (the method of controlling the crystal orientation and the grain boundary state).

[0060] In the first embodiment of the present invention, a Cu-Cr-based copper alloy can be produced by, in the following order: subjecting an ingot obtained by casting [Step 1-1] to homogenization heat treatment [Step 1-2]; making the resultant ingot into a thin sheet by hot-working [Step 1-3] (specifically, hot-rolling) and subsequent cold-working [Step 1-4] (specifically, cold-rolling); and further conducting intermediate heat treatment (intermediate annealing) [Step 1-5]; cold-working [Step 1-6] (specifically, cold-rolling); aging (aging-precipitation heat treatment) [Step 1-9]; and strain-relief annealing [Step 1-11]. After the cold-working [Step 1-6] and before the aging [Step 1-9], if necessary, heat treatment [Step 1-7] and cold-working [Step 1-8] (specifically, cold-rolling) may be further carried out in this order. Further, after the aging [Step 1-9] and before strain-relief annealing [Step 1-11], if necessary, finish cold-working [Step 1-10] (specifically, cold-rolling) may be further carried out.

[0061] The conditions for the steps of aging [Step 1-9], cold-working [Step 1-10] and strain-relief annealing [Step 1-11] are appropriately set, according to desired properties, such as mechanical strength and electrical conductivity.

[0062] In the copper alloy material of the first embodiment of the present invention, with respect to the texture, a driving force for development of the Cube orientation is given via the hot-working [Step 1-3], and the coincidence grain boundary $\Sigma3$ develops upon the aging [Step 1-9] and, if conducted, the heat treatment [Step 1-7], among the above series of steps. Then, the texture is roughly determined via the intermediate heat treatment [Step 1-5], and the texture is finally determined with rotation of the orientation that occurs in the cold-working (for example, cold-rolling) [Step 1-6], [Step 1-8] or [Step 1-10] that is conducted at the last.

[0063] The heat treatment [Step 1-7] and cold-working [Step 1-8] can be omitted. Although these steps are not carried out, if the aging [Step 1-9] is carried out under predetermined conditions, a desired texture can be obtained. When the heat treatment [Step 1-7] is carried out, the aging [Step 1-9] can be carried out in a shorter time period.

[0064] The cold-working [Step 1-6] has, in addition to an effect of adjusting the sheet thickness, an effect of giving a strain to the material and accelerating development of the coincidence grain boundary $\Sigma3$ in the subsequent heat treatment.

[0065] In the first embodiment of the present invention, when the heat treatment [Step 1-7] is finished, a texture is obtained in which the area ratio of the Cube orientation and the ratio of the coincidence grain boundary $\Sigma3$ to the entire grain boundaries are almost finally determined. Thus, if this texture is in an intended range of control, any combination of cold-working and heat treatment, in the steps that follow the heat treatment [Step 1-7], may be freely carried out, in connection with, for example, making the material into a thin sheet by the cold-working [Step 1-8], precipitation-hardening and electrical-conductivity enhancement by the aging [Step 1-9] (enhancement of mechanical strength and restoration of electrical conductivity), mechanical-strength enhancement by the cold-working [Step 1-10] after the aging [Step 1-9], restoration of spring property and/or elongation by the strain-relief annealing [Step 1-11], and the like.

[0066] Specifically, examples in the first embodiment of the present invention include the following representative examples of the heat treatment/working conditions and preferable conditions of the steps.

[0067] It is preferable to carry out the homogenization heat treatment [Step 1-2] at 600 to 1,025°C for 10 minutes to 10 hours. The homogenization heat treatment time period may be set to 2 to 10 hours. The hot-working [Step 1-3] is preferably carried out at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98%. The cold-working [Step 1-4] is preferably carried out at a working ratio of 50 to 99%. This working ratio may also be set to 50 to 95%. The intermediate heat treatment (intermediate annealing) [Step 1-5] is preferably carried out at 300 to 1,000°C for 5 seconds to 180 minutes. The cold-working [Step 1-6] is preferably carried out at a working ratio of 50 to 95%.

[0068] The heat treatment [Step 1-7] is preferably carried out at 650 to 1,000°C for 5 to 60 seconds. The cold-working [Step 1-8] is preferably carried out at a working ratio of 10 to 60%.

[0069] The aging (aging-precipitation heat treatment) [Step 1-9] is preferably carried out at 400 to 650°C for 30 to 180 minutes. The finish cold-working [Step 1-10] is preferably carried out at a working ratio of 0 to 70%. Herein, a working ratio of 0% means that the relevant working is not conducted, and in this case, the cold-working [Step 1-10] is omitted. The strain-relief annealing [Step 1-11] is preferably carried out at 550 to 700°C for 5 seconds to 10 minutes. The strain-relief annealing time period may be set to 5 to 60 seconds.

[0070] After the respective heat treatment or rolling, pickling or surface-polishing may be conducted depending on the state of oxidation or roughness of the material surface, and/or a correction with a tension leveler may be conducted depending on the material shape. After the hot-rolling [Step 1-3], generally, water-cooling (quenching) is conducted.

[0071] Preferable examples of the combination of those steps in the first embodiment of the present invention include Production Method 1 to Production Method 4 in the example section described below.

[0072] Herein, the working ratio refers to a value calculated as in the following formula:

$$\text{Working ratio (\%)} = (t_1 - t_2)/t_1 \times 100$$

wherein, "t_1" represents the sheet thickness before the rolling, and "t_2" represents the sheet thickness after the rolling.

[0073] In the second embodiment of the present invention, a Cu-Mg-based copper alloy can be produced by, in the following order: subjecting an ingot obtained by casting [Step 2-1] to homogenization heat treatment [Step 2-2]; making the resultant ingot into a thin sheet by hot-working [Step 2-3] (specifically, hot-rolling) and subsequent cold-working [Step 2-4] (specifically, cold-rolling); and further conducting intermediate heat treatment (intermediate annealing) [Step 2-5]; cold-working [Step 2-6] (specifically, cold-rolling); heat treatment [Step 2-7]; finish cold-working [Step 2-8] (specifically, cold-rolling); and strain-relief annealing [Step 2-9].

[0074] The conditions for the strain-relief annealing [Step 2-9] are appropriately set, according to desired properties, such as mechanical strength, electrical conductivity, elongation, and spring property (stress relaxation resistance).

[0075] In the copper alloy material of the second embodiment of the present invention, with respect to the texture, a driving force for development of the Cube orientation is given via the hot-working [Step 2-3], and the coincidence grain boundary $\Sigma3$ develops upon the heat treatment [Step 2-7], among the above series of steps. Then, the texture is roughly determined via the intermediate heat treatment [Step 2-5], and the texture is finally determined with rotation of the orientation that occurs in the cold-working [Step 2-8] that is conducted at the last (i.e. the finish cold-rolling).

[0076] The cold-working [Step 2-6] has, in addition to an effect of adjusting the sheet thickness, an effect of giving a strain to the material and accelerating development of the coincidence grain boundary $\Sigma3$ in the subsequent heat treatment [Step 2-8].

[0077] In the second embodiment of the present invention, when the heat treatment [Step 2-7] is finished, a texture is obtained in which the area ratio of the Cube orientation and the ratio of the coincidence grain boundary $\Sigma3$ to the entire grain boundaries are almost finally determined. Thus, if this texture is in an intended range of control, any combination of cold-working and heat treatment, in the steps that follow the heat treatment [Step 2-7], may be freely carried out, in connection with, for example, making the material into a thin sheet by the cold-working [Step 2-8] together with mechanical-strength enhancement, restoration of spring property and/or elongation by the strain-relief annealing [Step 2-9], and the like. On the other hand, there is a risk that a heat treatment at a temperature higher than 600°C or a working such as cold-rolling at a rolling reduction ratio greater than 80% may change the area ratios of crystal orientations and/or the grain boundary state. Therefore, in the second embodiment of the present invention, in the steps that follow the heat treatment [Step 2-7], no heat treatment at such a high temperature and no working at such a high working ratio is conducted.

[0078] Specifically, examples in the second embodiment of the present invention include the following representative examples of the heat treatment/working conditions and preferable conditions of the steps.

[0079] It is preferable to carry out the homogenization heat treatment [Step 2-2] at 600 to 1,025°C for 10 minutes to 10 hours. The homogenization heat treatment time period may be set to 1 to 5 hours. The hot-working [Step 2-3] is preferably carried out at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98%. The cold-working [Step 2-4] is preferably carried out at a working ratio of 50 to 99%. This working ratio may also be set to 50 to 95%. The intermediate heat treatment (intermediate annealing) [Step 2-5] is preferably carried out at 300 to 800°C for 5 seconds to 180 minutes. The cold-working [Step 2-6] is preferably carried out at a working ratio of 50 to 95%. The heat treatment [Step 2-7] is preferably carried out at 300 to 800°C for 5 seconds to 180 minutes. This heat treatment temperature may be set at 300 to 600°C, 400 to 800°C, or 600 to 800°C. This heat treatment time period may be set to 30 to 180 minutes, or 5 to 60 seconds. The cold-working [Step 2-8] is preferably carried out at a working ratio of 10 to 80%.

[0080] The strain-relief annealing [Step 2-9] is preferably carried out at 300 to 600°C for 5 to 60 seconds.

[0081] After the respective heat treatment or rolling, pickling or surface-polishing may be conducted depending on the state of oxidation or roughness of the material surface, and/or a correction with a tension leveler may be conducted depending on the material shape. After the hot-rolling [Step 2-3], generally, water-cooling (quenching) is conducted.

[0082] Preferable examples of the combination of those steps in the second embodiment of the present invention include Production Method 10 to Production Method 14 in the example section described below.

[0083] The copper alloy material of the first embodiment of the present invention can satisfy the properties that are required in lead frames, connectors, terminal materials, and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems. Among the relevant properties, the copper alloy material satisfies an electrical conductivity of 75%IACS or higher, preferably 80%IACS or higher. The copper alloy material satisfies a tensile strength of 400 MPa or higher. Bending property is evaluated by the value (R/t) obtained by dividing the minimum bending radius (R: unit mm) in 90° W bending in which bending is possible without cracking, by the sheet thickness (t: unit mm). The bending property varies depending on the extent of tensile strength which the copper alloy material in interest has. The copper alloy material satisfies $R/t \leq 0.5$ when the tensile strength is 400 MPa or more and less than 550 MPa, and satisfies $R/t = 0.5$ to 1 when the tensile strength is 550 MPa or more and less than 700 MPa. Further, the stress relaxation resistance is evaluated by the stress relaxation ratio (SR) determined according to Japan Copper and Brass Association JCBA T309:2004 (method for testing stress relaxation by bending of thin sheet strips of copper and copper alloys), and the copper alloy material can satisfy a stress relaxation ratio of 35% or less. A specific measurement method for the stress relaxation ratio (SR) will be described in detail in the example section below. With respect to these bending property and stress relaxation resistance, the copper alloy material has favorable properties that are superior to: the results of the two properties of copper alloy materials, having the same composition as the present invention, produced via conventional methods; and a balance of the two properties.

[0084] The copper alloy material of the second embodiment of the present invention can satisfy the properties that are required in lead frames, connectors, terminal materials, and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems. Among the relevant properties, the copper alloy material satisfies an electrical conductivity of 75%IACS or higher, preferably 80%IACS or higher. The copper alloy material satisfies a tensile strength of 250 MPa or higher. Bending property is evaluated by the value (R/t) obtained by dividing the minimum bending radius (R: unit mm) in which bending is possible without cracking, by the sheet thickness (t: unit mm). The bending property varies depending on the extent of tensile strength which the copper alloy material in interest has. Under the conditions of a tested sheet thickness 0.4 to 2 mmt and a bending width 10 mmw, the copper alloy material satisfies R/t = 0 in 180° bending in the case where the tensile strength of 250 MPa or more and less than 400 MPa, and the copper alloy material satisfies R/t = 0 in 90° bending in the case where the tensile strength of 400 MPa or more and less than 500 MPa. Further, with respect to the stress relaxation resistance, the copper alloy material can satisfy the stress relaxation ratio (SR) of 35% or less. With respect to these bending property and stress relaxation resistance, the copper alloy material has favorable properties that are superior to: the results of the two properties of copper alloy materials, having the same composition as the present invention, produced via conventional methods; and a balance of the two properties.

EXAMPLES

[0085] The present invention will be described in more detail based on examples given below, but the invention is not meant to be limited by these.

Example 1-1 and Comparative Example 1-1 (Cu-Cr-based alloy)

[0086] With any of alloy compositions as shown in Table 1-1 and Table 1-2, a copper alloy, containing Cr as a main alloying element, and containing, as an additional alloying element, at least one selected from the group consisting of: (the additional alloying element group 1) of at least one selected from the group consisting of Mg, Ti and Zr; and (the additional alloying element group 2) of at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P, with the balance being Cu and unavoidable impurities, was melted in a high-frequency melting furnace, followed by casting [Step 1-1], to obtain an ingot. Then, the ingot was subjected to homogenization heat treatment [Step 1-2] at 600 to 1,025°C for 10 minutes to 10 hours, followed by hot-rolling [Step 1-3] at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98%, and water-cooling; then, cold-rolling [Step 1-4] at a working ratio of 50 to 99%, and intermediate heat treatment [Step 1-5] at 300 to 1,000°C for 5 seconds to 180 minutes; and then, cold-rolling [Step 1-6] at a working ratio of 50 to 95%. The steps heretofore are the upstream process. The resultant sheet in this state was used as a supplied material, and sample specimens of copper alloy materials of Test Nos. 1-1 to 1-22 (Examples according to this invention) and Test Nos. 1-23 to 1-50 (Comparative Examples) were produced, by any one of production methods of Production Method 1 to Production Method 7 described below, as the downstream process. When the conditions of the upstream process were changed, the changed conditions will also be indicated in the Production Method 1 to Production Method 7.

[0087] Separately, as Production Method 8 and Production Method 9, the entire process of examples carried out by production process corresponding to Examples in the Patent Literature 4 and Patent Literature 5 will be described below, respectively.

(Production Method 1)

[0088] After the completion of the upstream process (from casting [Step 1-1] to cold-rolling [Step 1-6]; hereinafter, the same will be applied to), to the respective supplied material, aging [Step 1-9] was carried out at 400 to 650°C for 30 to 180 minutes, followed by cold-rolling [Step 1-10] at a working ratio of 25%, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace. Instead of the conditions described above, the homogenization heat treatment [Step 1-2] was carried out at 600 to 1,025°C for 2 to 10 hours, and the cold-rolling [Step 1-4] was carried out at a working ratio of 50 to 99%. The heat treatment [Step 1-7] and cold-rolling [Step 1-8] were not carried out.

(Production Method 2)

[0089] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 1-7] was carried out at 650 to 1,000°C for 5 to 60 seconds, followed by cold-rolling [Step 1-8] at a working ratio of 25%, aging [Step 1-9] at 400 to 650°C for 30 to 180 minutes, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace. The cold-rolling [Step 1-10] was not carried out.

(Production Method 3)

[0090] After the completion of the upstream process, to the respective supplied material, aging [Step 1-9] was carried out at 400 to 650°C for 30 to 180 minutes, followed by cold-rolling [Step 1-10] at a working ratio of 50%, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace. The heat treatment [Step 1-7] and cold-rolling [Step 1-8] were not carried out.

(Production Method 4)

[0091] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 1-7] was carried out at 650 to 1,000°C for 5 to 60 seconds, followed by cold-rolling [Step 1-8] at a working ratio of 30%, aging [Step 1-9] at 400 to 650°C for 30 to 180 minutes, and cold-rolling [Step 1-10] at a working ratio of 25%, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace.

(Production Method 5)

[0092] After the completion of the upstream process, to the respective supplied material, aging [Step 1-9] was carried out at 450 to 600°C for 30 to 180 minutes, followed by cold-rolling [Step 1-10] at a working ratio of 25%, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace. Instead of the conditions described above, the hot-rolling [Step 1-3] was carried out at a working temperature of 300 to 450°C at a working ratio of 30 to 98%. The heat treatment [Step 1-7] and cold-rolling [Step 1-8] were not carried out.

(Production Method 6)

[0093] After the completion of the upstream process, to the respective supplied material, aging [Step 1-9] was carried out at 400 to 650°C for 30 to 180 minutes, followed by cold-rolling [Step 1-10] at a working ratio of 25%, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace. Instead of the conditions described above, the cold-rolling [Step 1-6] was carried out at a working ratio of 30%. The heat treatment [Step 1-7] and cold-rolling [Step 1-8] were not carried out.

(Production Method 7)

[0094] After the completion of the upstream process, to the respective supplied material, aging [Step 1-9] was carried out at 300 to 350°C for 30 to 180 minutes, followed by cold-rolling [Step 1-10] at a working ratio of 25%, and then strain-relief annealing [Step 1-11] of keeping the resultant sheet at 550 to 700°C for 5 to 60 seconds in a running furnace. The heat treatment [Step 1-7] and cold-rolling [Step 1-8] were not carried out.

(Production Method 8) (Production process corresponding to Example of Patent Literature 4)

[0095] After casting to obtain an ingot, the ingot was subjected to homogenization treatment (since the conditions in Patent Literature 4 are at 900°C or higher for 300 minutes or more, the conditions were set to at 950°C for 500 minutes). Then, the resultant ingot was subjected to hot-working and solution heat treatment, final cold-rolling to make the thickness to 0.15 mm, and aging. The conditions for cold-rolling were set in accordance with the contents of the Patent Literature 4, and the degree of working in each pass was set to 20%, while the overall degree of working was set to 98%. Although Patent Literature 4 has no description on hot-working conditions, the hot-rolling was conducted successfully, followed by water-cooling. Further, the solution heat treatment was carried out at 800°C for one hour. The aging was carried out at 400°C for about 30 minutes.

(Production Method 9) (Production process corresponding to Example of Patent Literature 5)

[0096] After casting to obtain an ingot, the ingot was heated to 950°C and was successfully subjected to hot-rolling to a thickness 8 mm, followed by water-cooling. Then, the resultant sheet was subjected to cold-rolling to a thickness 1 mm, followed by annealing at 800°C for 300 minutes (Patent Literature 5 describes simply that annealing is carried out, but has no description on a specific annealing time period, and the annealing time period was set to 300 minutes). Then, the resultant sheet was subjected to cold-working at a degree of working of 40%, followed by heat treatment at 500°C for one minute, which were repeated three times, to a thickness 0.22 mm.

[0097] In the Production Methods 1 to 7, after the respective heat treatment or rolling, pickling or surface-polishing was conducted depending on the state of oxidation or roughness of the material surface, and/or a correction with a tension leveler was conducted depending on the material shape.

[0098] Among the sample specimens described above, the sample specimens produced via the Production Method 1 were examined on properties as described below. The thickness of each of the sample specimens was set to 0.15 mm, unless otherwise specified. The results of the Examples according to this invention are shown in Table 2-1, and the results of the Comparative Examples are shown in Table 2-2, respectively. The results of the sample specimens produced via the Production Method 5, each of which were Comparative Examples, are shown in Table 3-1 and Table 3-2. Table 4-1 shows the results of the sample specimens of the Examples according to this invention produced via the Production Methods 2 to 4, respectively, and Table 4-2 shows the results of the sample specimens of the Comparative Examples produced via the Production Methods 6 to 9, respectively.

a. Area ratio of the Cube orientation {0 0 1} <1 0 0>:

[0099] The measurement was conducted with the EBSD method in a measurement region of about 500 μm on each of the four sides, under the conditions of a scan step of 0.5 μm. As described above, the area of atomic planes of grains having a deviation angle from the Cube orientation within ±15° was determined, and the area ratio of the grains in the Cube orientation was obtained, by dividing the thus-determined area by the total measurement area. In the following tables, this is simply indicated as "Cube area ratio (%)".

b. Ratio of coincidence grain boundary Σ3 in grain boundaries:

[0100] The measurement was conducted with the EBSD method in a measurement region of about 500 μm on each of the four sides, under the conditions of a scan step of 0.5 μm. When the orientation difference between the two neighboring crystals (grains) was 15° or greater, it was defined a grain boundary in the measurement object, and the ratio of the sum of lengths of coincidence grain boundary Σ3, to the sum of lengths of the entire grain boundaries, was calculated. In the following tables, the values of: (sum of lengths of coincidence grain boundary E3)/(sum of lengths of the entire grain boundaries) × 100, is indicated as "Ratio of coincidence grain boundary Σ3 (%)".

d-1. Bending property:

[0101] The bending property was tested and evaluated according to JIS Z 2248.

[0102] A test piece was taken, by cutting out from the respective sample specimen perpendicularly to the rolling direction, into a size with width 10 mm and length 25 mm. The respective test piece was subjected to W-bending such that the axis of bending would be perpendicular to the rolling direction, which is designated as GW (Good Way), and separately subjected to W-bending such that the axis of bending would be parallel to the rolling direction, which is designated as BW (Bad Way). The occurrence (i.e. whether occurred or not) of cracks at the thus-bent portion was examined, by observing the bent portion under an optical microscope with a magnification of 200x. t represents the sheet thickness (mm), and R represents the minimum bending radius (mm) in 90° W bending. In each of the GW and BW, a sample specimen, which satisfied $R/t \leq 0.5$, when the tensile strength was 400 MPa or more and less than 550 MPa, while which satisfied $R/t \leq 1$, when the tensile strength was 550 MPa or more and less than 700 MPa, and which was capable of being bent at the R value or greater, the sample specimen was judged "fair (o)", and when cracks occurred, such a sample specimen was judged "poor (x)". Furthermore, a sample specimen was judged "good (⊙)", in the case where it satisfied the conditions described above, it had other properties (tensile strength, electrical conductivity, and stress relaxation resistance) not conspicuously inferior to the conventional materials having the same alloy composition, and it was capable of being bent at a smaller bending radius R.

e. Tensile Strength [TS]:

[0103] Three test pieces were cut out from the respective sample specimen in the direction parallel to the rolling direction, according to JIS Z2201-13B, followed by measuring, according to JIS Z2241, to obtain the average value as shown in the tables.

f. Electrical conductivity [EC]:

[0104] The electrical conductivity was calculated by using the four-terminal method to measure the specific resistance of the respective sample specimen in a thermostat bath that was maintained at 20°C (±0.5°C). The spacing between terminals was set to 100 mm. A sample specimen having an electrical conductivity (EC) of 75%IACS or higher was judged "fair (o)", and one with less than 75%IACS was judged "poor (×)".

g. Stress relaxation ratio [SR]:

[0105] The stress relaxation ratio (SR) was measured, according to Japan Copper and Brass Association JCBA T309:2004 (method for testing stress relaxation by bending of thin sheet strips of copper and copper alloys), under the conditions of maintaining at 150°C for 1,000 hours, as described below. By using a cantilever block-type jig, an initial stress that was 80% of the yield stress (proof stress), as a load, was applied to the respective test piece, to obtain a displacement amount after subjecting to the test at 150°C for 1,000 hours, thereby to determine the stress relaxation ratio (SR) from the displacement amount. Thus, the stress relaxation resistance was evaluated.

[0106] Figs. 1(a) and 1(b) each are a drawing explaining the method of testing the stress relaxation resistance, in which Fig. 1(a) shows the state before heat treatment, and Fig. 1(b) shows the state after the heat treatment. As shown in Fig. 1(a), the position of a test piece 1 when the initial stress of 80% of the yield stress was applied to the test piece 1 cantilevered on a test bench 4, is defined as the distance δ_0 from the reference position. This test piece was kept in a thermostat at 150°C for 1,000 hours (which corresponds to the heat treatment at the state of the test piece 1). The position of the test piece 2 after removing the load, is defined as the distance H_t from the reference position, as shown in Fig. 1(b). The reference numeral 3 denotes the test piece to which no stress was applied, and the position of the test piece 3 is defined as the distance H_1 from the reference position. Based on the relationships among those positions, the stress relaxation ratio (%) was calculated as: $\{(H_t-H_1)/(\delta_0-H_1)\}\times100$. In the formula, δ_0 represents the distance from the reference position to the test piece 1; H_1 represents the distance from the reference position to the test piece 3; and H_t represents the distance from the reference position to the test piece 2.

[0107] With respect to the results, a sample specimen having a stress relaxation ratio (SR) of less than 35% was judged "fair (o)", and a sample specimen having a stress relaxation ratio (SR) of 35% or higher was judged "poor (×)". Furthermore, a sample specimen of Example according to this invention was judged "good (⊙)", in the case where it satisfied the conditions of a stress relaxation ratio (SR) of less than 35% as described above, it had other properties (tensile strength, electrical conductivity, and bending property) not conspicuously inferior to the conventional materials having the same alloy composition, and it had a smaller stress relaxation ratio (SR)

Table 1-1

Alloy No.	Cr	Mg	Ti	Zr	Zn	Fe	Sn	Ar	Si	P	Cu
1	0.25	0.01									Balance
2	0.25	0.05									
3	0.25	0.10									
4	0.25	0.15								0.005	
5	0.25	0.05					0.10				
6	0.25	0.10					0.10				
7	0.25	0.15					0.10				
8	0.25	0.10					0.05				
9	0.25	0.10					0.10	0.08			
10	0.25	0.10			0.05		0.10				
11	0.40	0.10					0.10				
12	0.50	0.10					0.10				
13	0.25	0.10		0.07			0.10				
14	0.35	0.10		0.10			0.10				
15	0.25	0.10					0.10		0.03		
16	0.25		0.05				0.10		0.03		
17	0.25		0.05	0.05			0.10		0.03		
18	0.30				0.20		0.25				
19	0.30				0.20		0.25		0.02		
20	0.50		0.06			0.08		0.10	0.03		
21	0.30			0.10					0.03		
22	0.30			0.10							

Table 1-2

Alloy No.	Cr	Mg	Ti	Zr	Zn	Fe	Sn	Ag	Si	P	Cu
23	*0.05*										Balance
24	0.25										
25	0.40										
26	0.60										
27	0.75										
28	*1.00*										
29	*1.50*										
30	0.25	*0.001*									
31	0.25	*0.60*									
32	0.25		*0.002*								
33	0.25		*0.55*								
34	0.25			*0.001*							
35	0.25			*0.65*							
36	0.25				*0.002*						
37	0.25					*0.002*					
38	0.25					*0.70*					
39	0.25						*0.002*				
40	0.25						*0.60*				
41	0.25							*0.003*			
42	0.25								*0.001*		
43	0.25								*0.80*		
44	0.25									*0.001*	
45	0.25									*0.60*	
46	0.25	*0.001*					*0.002*				
47	0.25	*0.30*	*0.40*								
48	0.25			*0.50*	*0.10*						
49	0.25	*0.35*					*0.25*				
50	0.25				*0.35*				*0.35*		
Note: Underlined values are outside the defined range of the first embodiment of the present invention.											

[0108] Table 1-1 show copper alloys (Alloy Nos. 1 to 22) according to the present invention having alloy compositions in the range defined in the present invention, and Table 1-2 show copper alloys (Alloy Nos. 23 to 50) of Comparative Examples having alloy compositions outside the range defined in the present invention. The unit is mass%. An empty cell means no addition of the alloying element. The balance was Cu and unavoidable impurities.

[0109] Hereinafter, in the evaluations of the alloys, two methods as described below are provided. Alloy properties are defined to include bending property, tensile strength, electrical conductivity, and stress relaxation resistance, and when an alloy satisfied favorable properties in which each of the properties had values that were the specified values according to the present invention or preferable values or more/or less, the alloy is judged to be favorable in the alloy properties. When even any one of the properties was not satisfied, the alloy is judged to be poor in the alloy properties. Furthermore, when a copper alloy material having the alloy composition of the present invention and obtained with the production method of the present invention, any one or both of bending property and stress relaxation resistance were improved more than those of copper alloy materials having the same alloy composition and obtained with the conventional production method, the copper alloy material of the present invention is judged to be excellent that has not obtained conventionally.

[0110] With respect to the texture which are defined to include the area ratio of the Cube orientation and the ratio of coincidence grain boundary Σ3 of the product, when a copper alloy material satisfied the definitions in the present invention, the texture is judged to fulfill the defined range, and when a copper alloy material did not satisfy even any one of these definitions, the texture is judged to be outside the defined range. Furthermore, with respect to the respective production process shown in the Production Method 1 to Production Method 9, when the production process conditions were in the range defined in the present invention, the production process conditions are judged to be in the range defined in the present invention. Contrary to the above, when even any one of the production process conditions did not satisfy the conditions defined in the present invention, and when a step that was outside the range defined in the present invention was combined with, the production process conditions are judged to be outside the range defined in the present invention, respectively.

Table 2-1

Test No.	Production method	Alloy No.	TS (MPa)	Electrical conductivity	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
1-1	Production Method 1	1	465	○	90	27
1-2		2	485	○	87	35
1-3		3	485	○	86	36
1-4		4	490	○	83	38
1-5		5	510	○	83	38
1-6		6	520	○	81	40
1-7		7	530	○	77	42
1-8		8	525	○	83	38
1-9		9	535	○	80	43
1-10		10	530	○	79	42
1-11		11	540	○	79	28
1-12		12	560	○	77	43
1-13		13	520	○	80	28
1-14		14	550	○	78	42
1-15		15	555	○	78	41
1-16		16	545	○	77	38
1-17		17	555	○	76	42
1-18		18	540	○	77	33
1-19		19	535	○	75	36
1-20		20	565	○	79	42
1-21		21	550	○	78	47
1-22		22	560	○	81	55

Table 2-1 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
1-1	⦿	25	35	⦿	0	Example according to this invention
1-2	⦿	22	33	⦿	0	
1-3	⦿	21	16	⦿	0	
1-4	⦿	19	27	⦿	0	
1-5	⦿	18	22	⦿	0	
1-6	⦿	16	32	⦿	0	
1-7	⦿	15	13	⦿	0	
1-8	⦿	16	25	⦿	0	
1-9	⦿	16	21	⦿	0	
1-10	⦿	16	21	⦿	0	
1-11	⦿	16	27	⦿	0.5	
1-12	⦿	16	32	⦿	0.5	
1-13	⦿	17	16	⦿	0.33	
1-14	⦿	8	9	⦿	0.5	
1-15	⦿	17	25	⦿	0	
1-16	⦿	11	22	⦿	0	
1-17	⦿	8	22	⦿	0	
1-18	⦿	31	27	⦿	0.33	
1-19	⦿	29	30	⦿	0.33	
1-20	⦿	11	32	⦿	0.5	
1-21	⦿	7	23	⦿	0.5	
1-22	⦿	8	31	⦿	0.4	

Table 2-2

Test No.	Production method	Alloy No.	TS (MPa)	Electric conductivity	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
1-23	Production Method 1	23	*265*	○	96	*10*
1-24		24	480	○	94	*12*
1-25		25	635	○	88	*13*
1-26		26	665	○	86	*15*
1-27		27	675	○	83	*17*
1-28		28	678	○	78	25
1-29		29	*Production was stopped, due to cracks occurred in hot-working.*			
1-30		30	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-31		31	*Production was stopped, due to cracks occurred in hot-working.*			
1-32		32	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-33		33	*Production was stopped, due to cracks occurred in hot-working.*			
1-34		34	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-35		35	*Production was stopped, due to cracks occurred in hot-working.*			
1-36		36	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-37		37	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-38		38	490	×	*33*	48
1-39		39	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-40		40	500	×	*35*	42
1-41		41	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-42		42	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-43		43	490	×	*25*	46
1-44		44	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-45		45	490	×	*22*	45
1-46		46	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*			
1-47		47	*Production was stopped, due to cracks occurred in hot-working.*			
1-48		48	*Production was stopped, due to cracks occurred in hot-working.*			
1-49		49	510	×	*45*	43
1-50		50	495	×	*55*	46

Note: Underlined numbers or descriptions mean that the relevant items were outside the ranges defined in the first embodiment of the present invention, or desired properties were not obtained. The same is applied to Tables 3-1, 3-2 and 4-2.

Table 2-2 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
1-23	*×*	*70*	30	○	0	Comparative example
1-24	*×*	*55*	17	○	0	
1-25	*×*	*50*	16	○	0.5	
1-26	*×*	*45*	10	○	0.8	
1-27	*×*	*43*	5	○	0.8	
1-28	○	33	*2*	*×*	*2*	
1-29	*Production was stopped, due to cracks occurred in hot-working.*					
1-30	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-31	*Production was stopped, due to cracks occurred in hot-working.*					
1-32	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-33	*Production was stopped, due to cracks occurred in hot-working.*					
1-34	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-35	*Production was stopped, due to cracks occurred in hot-working.*					
1-36	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-37	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-38	○	31	14	○	0	
1-39	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-40	○	30	20	○	0	
1-41	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-42	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-43	○	30	20	○	0	
1-44	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-45	○	30	20	○	0	
1-46	*The texture and properties were the same as those of Alloy No. 24 (Test No. 1-24).*					
1-47	*Production was stopped, due to cracks occurred in hot-working.*					
1-48	*Production was stopped, due to cracks occurred in hot-working.*					
1-49	○	19	34	○	0	
1-50	○	29	27	○	0	

[0111] Table 2-1 shows Examples according to this invention in which the alloy composition was in the range defined in the present invention, and the copper alloy material was produced via the production method in the range defined in the present invention. With respect to these Examples according to this invention, the copper alloy materials satisfied the texture defined in the present invention, and had favorable alloy properties.

[0112] Further, Table 2-2 shows Comparative Examples in which the alloy composition was outside the range defined in the present invention, but the copper alloy material was produced via the production method in the range defined in the present invention. With respect to these Comparative Examples, any one or more of the alloy properties was poor, or cracking in the hot-working occurred in the middle course of the production, resulting in that it was impossible for the copper alloy material to be subjected to the subsequent process. It is understood that although the texture and the production conditions were in the ranges defined in the present invention, the copper alloy material, whose alloy composition was outside the range defined in the present invention, had alloy properties inferior to the desired alloy properties, or suffered problems in the production, resulting in giving defective products.

Table 3-1

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
2-1	Production Method 5	1	475	○	88	23
2-2		2	495	○	85	33
2-3		3	480	○	84	28
2-4		4	515	○	81	36
2-5		5	515	○	81	36
2-6		6	520	○	79	38
2-7		7	545	○	75	40
2-8		8	540	○	81	36
2-9		9	550	○	78	41
2-10		10	550	○	77	28
2-11		11	550	○	77	35
2-12		12	575	○	75	33
2-13		13	535	○	78	34
2-14		14	570	○	76	36
2-15		15	570	○	76	39
2-16		16	560	○	75	36
2-17		17	570	×	*74*	37
2-18		18	560	○	75	33
2-19		19	550	×	*73*	35
2-20		20	580	○	77	40
2-21		21	570	○	76	45
2-22		22	575	○	79	44

Table 3-1 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
2-1	○	29	*2*	×	*0.6*	Comparative example
2-2	○	26	*2*	×	*0.6*	
2-3	○	23	*2*	×	*0.6*	
2-4	○	21	*1*	×	*0.75*	
2-5	○	20	*2*	×	*0.75*	
2-6	○	20	*2*	×	*0.75*	
2-7	○	19	*1*	×	*0.75*	
2-8	○	20	*1*	×	*0.75*	
2-9	○	20	*2*	×	*1.25*	
2-10	○	20	*1*	×	*1.25*	
2-11	○	20	*2*	×	*1.25*	
2-12	○	20	*1*	×	*1.5*	
2-13	○	20	*1*	×	*1.25*	
2-14	○	11	*2*	×	*1.25*	
2-15	○	20	*2*	×	*1.5*	
2-16	○	13	*2*	×	*1.33*	
2-17	○	10	*2*	×	*1.5*	
2-18	○	33	*2*	×	*1.25*	
2-19	○	31	*2*	×	*1.25*	
2-20	○	13	*2*	×	*1.5*	
2-21	○	9	*1*	×	*1.25*	
2-22	○	10	*1*	×	*1.25*	

Table 3-2

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
2-23	Production Method 5	23	*275*	○	92	*11*
2-24		24	500	○	78	*13*
2-25		25	530	○	75	*15*
2-26		26	575	×	*73*	*16*
2-27		27	580	×	*70*	*18*
2-28		28	605	×	*68*	*17*
2-29		29	*Production was stopped, due to cracks occurred in hot-working.*			
2-30		30	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-31		31	*Production was stopped, due to cracks occurred in hot-working.*			
2-32		32	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-33		33	*Production was stopped, due to cracks occurred in hot-working.*			
2-34		34	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-35		35	*Production was stopped, due to cracks occurred in hot-working.*			
2-36		36	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-37		37	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-38		38	510	×	*48*	*15*
2-39		39	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-40		40	515	×	*57*	25
2-41		41	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-42		42	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-43		43	505	×	*40*	30
2-44		44	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-45		45	510	×	32	*15*
2-46		46	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*			
2-47		47	*Production was stopped, due to cracks occurred in hot-working.*			
2-48		48	*Production was stopped, due to cracks occurred in hot-working.*			
2-49		49	520	×	*55*	*14*
2-50		50	505	×	*63*	*16*

Table 3-2 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
2-23	×	72	2	○	0	Comparative example
2-24	×	52	2	×	0.7	
2-25	×	48	2	×	1	
2-26	×	43	1	×	1.5	
2-27	×	41	2	×	1.5	
2-28	×	38	1	×	2	
2-29	*Production was stopped, due to cracks occurred in hot-working.*					
2-30	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-31	*Production was stopped, due to cracks occurred in hot-working.*					
2-32	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-33	*Production was stopped, due to cracks occurred in hot-working.*					
2-34	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-35	*Production was stopped, due to cracks occurred in hot-working.*					
2-36	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-37	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-38	○	32	1	×	1	
2-39	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-40	○	31	2	×	1	
2-41	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-42	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-43	○	28	1	×	0.75	
2-44	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-45	○	32	1	×	1	
2-46	*The texture and properties were the same as those of Alloy No. 24 (Test No. 2-24).*					
2-47	*Production was stopped, due to cracks occurred in hot-working.*					
2-48	*Production was stopped, due to cracks occurred in hot-working.*					
2-49	○	19	1	×	1.25	
2-50	○	27	2	×	1	

[0113] Table 3-1 shows Comparative Examples in which the alloy composition was in the range defined in the present invention, but the copper alloy material was produced via the production method outside the range defined in the present invention. Further, Table 3-2 shows Comparative Examples in which the alloy composition was outside the range defined in the present invention, and the copper alloy material was produced via the production method outside the range defined in the present invention.

[0114] With respect to these Comparative Examples 2-1 to 2-22 and 2-23 to 2-50 produced via the Production Method 5, since the thermal history made by hot-rolling [Step 1-3] was insufficient, no desired area ratio of the Cube orientation was obtained.

[0115] It is understood that even if the alloy composition was in the range defined in the present invention but the copper alloy material was produced via the production method outside the range defined in the present invention, no defined texture was obtained, resulting in poor alloy properties. It is understood that if the alloy composition was outside the range defined in the present invention, the alloy properties were poor regardless of the texture state. If the alloy composition was outside the range defined in the present invention, the resultant copper alloy material was poor in the alloy properties, regardless that the copper alloy material was produced via any production method that was in the range or outside the range defined in the present invention.

Table 4-1

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
3-1	Production Method 2	3	526	○	84	25
3-2		6	542	○	78	32
3-3		9	546	○	79	43
3-4		11	675	○	78	42
3-5		15	530	○	76	36
3-6		18	611	○	75	48
3-7		20	625	○	77	43
3-8		22	630	○	80	34
3-9	Production Method 3	3	580	○	86	24
3-10		6	575	○	80	28
3-11		9	580	○	79	43
3-12		11	615	○	78	48
3-13		15	610	○	77	27
3-14		18	590	○	78	27
3-15		20	625	○	78	43
3-16		22	635	○	81	48
3-17	Production Method 4	3	485	○	84	28
3-18		6	480	○	79	35
3-19		9	525	○	78	43
3-20		11	575	○	77	42
3-21		15	575	○	75	41
3-22		18	545	○	76	26
3-23		20	560	○	76	44
3-24		22	570	○	80	47

Table 4-1 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
3-1	⦿	25	16	⦿	0	Example according to this invention
3-2	⦿	23	21	⦿	0	
3-3	⦿	19	21	⦿	0	
3-4	⦿	19	27	⦿	0.8	
3-5	⦿	18	25	⦿	0	
3-6	⦿	16	27	⦿	0.33	
3-7	⦿	9	32	⦿	0.5	
3-8	⦿	8	31	⦿	0.4	
3-9	⦿	25	16	⦿	0	
3-10	⦿	23	21	⦿	0	
3-11	⦿	19	21	⦿	0	
3-12	⦿	18	27	⦿	0.5	
3-13	⦿	16	25	⦿	0.75	
3-14	⦿	28	27	⦿	0.33	
3-15	⦿	8	32	⦿	0.5	
3-16	⦿	7	31	⦿	0.6	
3-17	⦿	25	16	⦿	0	
3-18	⦿	23	21	⦿	0	
3-19	⦿	19	21	⦿	0	
3-20	⦿	18	27	⦿	0.5	
3-21	⦿	16	25	⦿	0.5	
3-22	⦿	27	27	⦿	0.33	
3-23	⦿	8	32	⦿	0.5	
3-24	⦿	7	31	⦿	0.4	

Table 4-2

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
3-25	Production Method 6	3	474	○	90	*18*
3-26		6	486	○	83	*16*
3-27		9	495	○	83	*17*
3-28		11	621	○	83	*15*
3-29		15	476	○	81	*10*
3-30		18	556	○	81	*15*
3-31		20	611	○	82	*14*
3-32		22	591	○	84	*13*
3-33	Production Method 7	3	469	×	*51*	*14*
3-34		6	482	×	*44*	*16*
3-35		9	486	×	*45*	*16*
3-36		11	617	×	*44*	*18*
3-37		15	473	×	*43*	*18*
3-38		18	552	×	*42*	*15*
3-39		20	609	×	*44*	*11*
3-40		22	588	×	*46*	*13*

Table 4-2 (continued-1)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
3-25	×	*40*	18	○	0	Comparative example
3-26	×	*38*	24	○	0	
3-27	×	*36*	24	○	0	
3-28	×	*36*	29	○	0.5	
3-29	×	*36*	27	○	0	
3-30	×	*47*	29	○	0.25	
3-31	×	*38*	34	○	0.7	
3-32	×	*36*	33	○	0.4	
3-33	×	*41*	*2*	○	0	
3-34	×	*38*	*2*	○	0	
3-35	×	*37*	*2*	○	0	
3-36	×	*36*	*2*	×	*1.3*	
3-37	×	*36*	*2*	○	0	
3-38	×	*47*	*1*	○	0.8	
3-39	×	*38*	*2*	×	*1.3*	
3-40	×	*37*	*1*	×	*1.3*	

Table 4-2 (continued-2)

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
3-41	Production Method 8	3	509	○	84	29
3-42		6	524	○	80	33
3-43		9	527	○	79	41
3-44		11	657	○	78	42
3-45		15	515	○	76	41
3-46		18	594	○	75	26
3-47		20	648	○	79	35
3-48		22	628	○	80	42
3-49	Production Method 9	3	592	×	*64*	*15*
3-50		6	603	×	*69*	*16*
3-51		9	613	×	*65*	*18*
3-52		11	743	×	*65*	*14*
3-53		15	597	×	*67*	*15*
3-54		18	677	×	*68*	*17*
3-55		20	733	×	*64*	*8*
3-56		22	712	×	*61*	*10*

Table 4-2 (continued-3)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	R/t	Remarks
3-41	○	27	1	×	0.6	Comparative example
3-42	○	25	2	×	0.8	
3-43	○	20	1	×	0.8	
3-44	○	23	2	×	1.3	
3-45	○	21	2	×	0.8	
3-46	○	29	1	×	1.3	
3-47	○	16	1	×	1.5	
3-48	○	13	2	×	1.3	
3-49	×	42	1	×	1.2	
3-50	×	40	2	×	1.5	
3-51	×	35	1	×	1.3	
3-52	×	38	1	×	1.3	
3-53	×	36	2	×	1.3	
3-54	×	50	1	×	1.3	
3-55	○	18	1	×	1.5	
3-56	○	16	2	×	1.3	

[0116] Table 4-1 and Table 4-2 show the results of the alloy properties of the copper alloy materials produced via the Production Methods 2 to 5 and 6 to 9, respectively, for Alloy Nos. 3, 6, 9, 11, 15, 18, 20 and 22, respectively, as the representative alloy compositions. When the copper alloy material was produced via the production method in any of the Production Methods 2 to 4 each in the range defined in the present invention, the resultant copper alloy materials each satisfied the alloy properties. When the copper alloy material was produced via the production method in any of the Production Methods 6 and 7 outside the range defined in the present invention, any of the alloy properties was conspicuously inferior to the desired properties, or even if the resultant copper alloy material satisfied the desired properties, the properties were conspicuously inferior to the properties as compared to those of Examples according to this invention.

[0117] Among these, with respect to Comparative Examples 3-25 to 3-32 produced via the Production Method 6, since the working ratio in the cold-rolling [Step 1-6] before the aging [Step 1-9] was too low, no desired state of coincidence grain boundary $\Sigma3$ was obtained, resulting in poor stress relaxation resistance.

[0118] Further, with respect to Comparative Examples 3-33 to 3-40 produced via the Production Method 7, since the heating temperature in the aging [Step 1-9] was so low that the thermal history was insufficient, no desired state of coincidence grain boundary $\Sigma3$ was obtained, resulting in poor stress relaxation resistance. Also, the area ratio of the

Cube orientation was also so small that the resultant copper alloy materials each were poor in electrical conductivity and also poor in bending property.

[0119] Further, the sample specimens of Comparative Examples produced via the Production Method 8 corresponding to Patent Literature 4 or the Production Method 9 corresponding to Patent Literature 5, each resulted in poor in bending property, unlike the sample specimens according to the present invention. Also, the sample specimens of those Comparative Examples each were poor in electrical conductivity, and even some of them were poor in stress relaxation resistance.

Example 2-1 and Comparative Example 2-1 (Cu-Mg-based alloy)

[0120] With any of alloy compositions as shown in Table 5-1 and Table 5-2, a copper alloy, containing Mg as an essential alloying element, and containing, as an optional alloying element, at least one selected from the group consisting of Zn, Fe, Sn, Ag and Si, with the balance being Cu and unavoidable impurities, was melted in a high-frequency melting furnace, followed by casting [Step 2-1], to obtain an ingot. Then, the ingot was subjected to homogenization heat treatment [Step 2-2] at 600 to 1,025°C for 1 to 5 hours, followed by hot-rolling [Step 2-3] at a working temperature of 500 to 900°C at a working ratio of 30 to 98%, and water-cooling; then, cold-rolling [Step 2-4] at a working ratio of 50 to 99%, and intermediate heat treatment [Step 2-5] at 300 to 800°C for 5 seconds to 180 minutes; and then, cold-rolling [Step 2-6] at a working ratio of 50 to 95%. The steps heretofore are the upstream process. The resultant sheet in this state was used as a supplied material, and sample specimens of copper alloy materials of Test Nos. 4-1 to 4-10 (Examples according to this invention) and Test Nos. 4-11 to 4-18 (Comparative Examples) were produced, by any one of production methods of Production Methods 10 to 17 described below or Production Method 8 or 9 described above, as the downstream process. When the conditions of the upstream process were changed, the changed conditions will also be indicated in the Production Methods 10 to 17.

(Production Method 10)

[0121] After the completion of the upstream process (from casting [Step 2-1] to cold-rolling [Step 2-6]; hereinafter, the same will be applied to), to the respective supplied material, heat treatment [Step 2-7] was carried out at 300 to 600°C for 30 to 180 minutes, followed by cold-rolling [Step 2-8] at a working ratio of 20%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds. Instead of the conditions described above, the cold-rolling [Step 2-4] was carried out at a working ratio of 50 to 95%.

(Production Method 11)

[0122] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 300 to 600°C for 30 to 180 minutes, followed by cold-rolling [Step 2-8] at a working ratio of 40%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds.

(Production Method 12)

[0123] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 600 to 800°C for 5 to 60 seconds, followed by cold-rolling [Step 2-8] at a working ratio of 20%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds.

(Production Method 13)

[0124] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 600 to 800°C for 5 to 60 seconds, followed by cold-rolling [Step 2-8] at a working ratio of 45%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds.

(Production Method 14)

[0125] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 400 to 800°C for 5 to 60 seconds, followed by cold-rolling [Step 2-8] at a working ratio of 75%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds.

(Production Method 15)

[0126] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 300 to 600°C for 30 to 180 minutes, followed by cold-rolling [Step 2-8] at a working ratio of 20%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds. Instead of the conditions described above, the hot-rolling [Step 2-3] was carried out at a working temperature of 300 to 500°C at a working ratio of 30 to 98%.

(Production Method 16)

[0127] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 300 to 600°C for 30 to 180 minutes, followed by cold-rolling [Step 2-8] at a working ratio of 40%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds. Instead of the conditions described above, the hot-rolling [Step 2-3] was carried out at a working temperature of 300 to 500°C at a working ratio of 30 to 98%.

(Production Method 17)

[0128] After the completion of the upstream process, to the respective supplied material, heat treatment [Step 2-7] was carried out at 600 to 800°C for 5 to 60 seconds, followed by cold-rolling [Step 2-8] at a working ratio of 90%, and then strain-relief annealing [Step 2-9] of keeping the resultant sheet at 300 to 600°C for 5 to 60 seconds.

[0129] The (Production Method 8) and (Production Method 9) were carried out in the same manner as in the Example 1-1 and Comparative Example 1-1.

[0130] In the Production Methods 10 to 17, after the respective heat treatment or rolling, pickling or surface-polishing was conducted depending on the state of oxidation or roughness of the material surface, and/or a correction with a tension leveler was conducted depending on the material shape.

[0131] Among the sample specimens described above, the sample specimens produced via the Production Method 10 were examined on properties as described below. The thickness of each of the sample specimens was set to 0.15 mm, unless otherwise specified. The results of the Examples according to this invention are shown in Table 6-1, and the results of the Comparative Examples are shown in Table 6-2, respectively. The results of the sample specimens produced via the Production Method 15, each of which were Comparative Examples, are shown in Table 7-1 and Table 7-2. Table 8-1 shows the results of the sample specimens of the Examples according to this invention produced via the Production Methods 11 to 14, respectively, and Table 8-2 shows the results of the sample specimens of the Comparative Examples produced via the Production Methods 16 to 17 or 8 to 9, respectively.

d-2. Bending property:

[0132] The bending property was tested and evaluated according to JIS Z 2248. To the sample specimens with TS = 250 to 400 MPa, 180° contact bending (the press-bending method, R=0) was conducted, and to the sample specimens with TS = 400 to 500 MPa, 90° bending (W bending, R = 0) was conducted. A test piece was taken, by cutting out from the respective sample specimen perpendicularly to the rolling direction, into a size with width 10 mm and length 25 mm. The respective test piece was subjected to the bending such that the axis of bending would be perpendicular to the rolling direction, which is designated as GW (Good Way), and separately subjected to the bending such that the axis of bending would be parallel to the rolling direction, which is designated as BW (Bad Way). The occurrence (i.e. whether occurred or not) of cracks at the thus-bent portion was examined, by observing the bent portion under an optical microscope with a magnification of 200x. In each of the GW and BW, a sample specimen, which had a favorable bending property without cracking under the respective conditions, was judged "fair (o)", and when cracks occurred, such a sample specimen was judged "poor (x)". Furthermore, a sample specimen was judged "good (⊙)", in the case where it satisfied the conditions described above, it had an improved bending property as compared to the conventional materials having the same alloy composition and a similar level of mechanical strength.

[0133] With respect to the above a. Cube area ratio, b. Ratio of coincidence grain boundary Σ3, e. Tensile Strength [TS], f. Electrical Conductivity [EC], and g. Stress relaxation ratio [SR], the tests and evaluations were carried out in the same manner as in the Example 1-1 and Comparative Example 1-1.

Table 5-1

Alloy No.	Mg	Zn	Sn	Ag	Si	P	Cu
2-1	0.10						Balance
2-2	0.20					0.02	
2-3	0.05		0.05				
2-4	0.10		0.10			0.03	
2-5	0.20		0.10				
2-6	0.15				0.03		
2-7	0.10	0.10			0.02		
2-8	0.10	0.20					
2-9	0.40	0.20				0.03	
2-10	0.10			0.05			

Table 5-2

Alloy No.	Mg	Zn	Sn	Ag	Si	P	Cu
2-11	*0.003*						Balance
2-12	*0.70*						
2-13	*0.001*		*0.002*			*0.002*	
2-14	0.20		*0.80*			*0.002*	
2-15	0.35		*0.25*		*0.10*		
2-16		*0.20*	*0.20*	*0.10*			
2-17	0.25	*0.003*				*0.03*	
2-18	0.05			*0.90*			
Note: Underlined values are outside the defined range of the second embodiment of the present invention.							

[0134] Table 5-1 show copper alloys (Alloy Nos. 2-1 to 2-10) according to the present invention having alloy compositions in the range defined in the present invention, and Table 5-2 show copper alloys (Alloy Nos. 2-11 to 2-18) of Comparative Examples having alloy compositions outside the range defined in the present invention. The unit is mass%. An empty cell means no addition of the alloying element. The balance was Cu and unavoidable impurities.

[0135] Hereinafter, in the evaluations of the alloys, two methods as described below are provided. Alloy properties are defined to include bending property, tensile strength, electrical conductivity, and stress relaxation resistance, and when an alloy satisfied favorable properties in which each of the properties had values that were the specified values according to the present invention or preferable values or more/or less, the alloy is judged to be favorable in the alloy properties. When even any one of the properties was not satisfied, the alloy is judged to be poor in the alloy properties. Furthermore, when a copper alloy material having the alloy composition of the present invention and obtained with the production method of the present invention, any one or both of bending property and stress relaxation resistance were improved more than those of copper alloy materials having the same alloy composition and obtained with the conventional production method, the copper alloy material of the present invention is judged to be excellent that has not obtained conventionally.

[0136] With respect to the texture which are defined to include the area ratio of the Cube orientation and the ratio of coincidence grain boundary $\Sigma 3$ of the product, when a copper alloy material satisfied the definitions in the present invention, the texture is judged to fulfill the defined range, and when a copper alloy material did not satisfy even any one of these definitions, the texture is judged to be outside the defined range. Furthermore, with respect to the respective production process shown in the Production Method 10 to Production Method 17, Production Method 8, and Production Method 9, when the production process conditions were in the range defined in the present invention, the production process conditions are judged to be in the range defined in the present invention. Contrary to the above, when even any one of the production process conditions did not satisfy the conditions defined in the present invention, and when a step that was outside the range defined in the present invention was combined with, the production process conditions are judged to be outside the range defined in the present invention, respectively.

Table 6-1

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
4-1	Production Method 10	2-1	310	○	92	28
4-2		2-2	330	○	83	26
4-3		2-3	350	○	88	29
4-4		2-4	360	○	81	32
4-5		2-5	380	○	79	35
4-6		2-6	375	○	80	27
4-7		2-7	380	○	88	30
4-8		2-8	360	○	86	33
4-9		2-9	365	○	75	29
4-10		2-10	325	○	91	33

Table 6-1 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	Remarks
4-1	◎	23	45	○	Example according to this invention
4-2	◎	22	40	○	
4-3	◎	20	38	◎	
4-4	◎	20	35	◎	
4-5	◎	16	37	◎	
4-6	◎	21	32	◎	
4-7	◎	21	30	◎	
4-8	◎	19	30	◎	
4-9	◎	16	31	◎	
4-10	◎	22	37	○	

Table 6-2

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
4-11	Production Method 10	2-11	*200*	○	98	*5*
4-12		2-12	435	×	*65*	33
4-13		2-13	*215*	○	97	*8*
4-14		2-14	425	×	*35*	45
4-15		2-15	400	×	*45*	38
4-16		2-16	380	○	77	33
4-17		2-17	*220*	○	97	*15*
4-18		2-18	565	○	77	25

Note: Underlined numbers or descriptions mean that the relevant items were outside the ranges defined in the second embodiment of the present invention, or desired properties were not obtained. The same is applied to Tables 7-1, 7-2 and 8-2.

Table 6-2 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	Remarks
4-11	×	*66*	*1*	○	Comparative example
4-12	○	18	*2*	×	
4-13	×	*60*	*2*	○	
4-14	○	21	*1*	×	
4-15	○	19	*2*	×	
4-16	×	*45*	*1*	×	
4-17	×	*36*	*1*	○	
4-18	○	33	*1*	×	

[0137] Table 6-1 shows Examples according to this invention in which the alloy composition was in the range defined in the present invention, and the copper alloy material was produced via the production method in the range defined in the present invention. With respect to these Examples according to this invention, the copper alloy materials satisfied the texture defined in the present invention, and had favorable alloy properties.

[0138] Further, Table 6-2 shows Comparative Examples in which the alloy composition was outside the range defined in the present invention, but the copper alloy material was produced via the production method in the range defined in the present invention. With respect to these Comparative Examples, any one or more of the alloy properties was poor, or cracking in the hot-working occurred in the middle course of the production, resulting in that it was impossible for the copper alloy material to be subjected to the subsequent process. It is understood that although the texture and the production conditions were in the ranges defined in the present invention, the copper alloy material, whose alloy composition was outside the range defined in the present invention, had alloy properties inferior to the desired alloy properties, or suffered problems in the production, resulting in giving defective products.

Table 7-1

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
5-1	Production Method 15	2-1	315	○	92	34
5-2		2-2	330	○	83	27
5-3		2-3	345	○	88	29
5-4		2-4	355	○	81	33
5-5		2-5	385	○	79	29
5-6		2-6	375	○	80	28
5-7		2-7	380	○	88	31
5-8		2-8	380	○	86	32
5-9		2-9	380	○	75	29
5-10		2-10	330	○	91	33

Table 7-1 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	Remarks
5-1	○	23	*1*	×	Comparative example
5-2	○	22	*2*	×	
5-3	○	20	*1*	×	
5-4	○	21	*2*	×	
5-5	○	17	*1*	×	
5-6	○	22	*1*	×	
5-7	○	22	*1*	×	
5-8	○	20	*2*	×	
5-9	○	19	*2*	×	
5-10	○	23	*1*	×	

Table 7-2

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
5-11	Production Method 15	2-11	200	○	98	6
5-12		2-12	435	×	65	33
5-13		2-13	215	○	97	12
5-14		2-14	425	×	35	45
5-15		2-15	400	×	45	29
5-16		2-16	380	○	77	33
5-17		2-17	235	○	97	15
5-18		2-18	565	○	77	25

Table 7-2 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	Remarks
5-11	×	67	1	○	Comparative example
5-12	○	18	2	×	
5-13	×	57	2	○	
5-14	○	21	1	×	
5-15	○	19	1	×	
5-16	×	44	1	×	
5-17	×	37	2	○	
5-18	○	33	2	×	

[0139] Table 7-1 shows Comparative Examples in which the alloy composition was in the range defined in the present invention, but the copper alloy material was produced via the production method outside the range defined in the present invention. Further, Table 7-2 shows Comparative Examples in which the alloy composition was outside the range defined in the present invention, and the copper alloy material was produced via the production method outside the range defined in the present invention.

[0140] With respect to these Comparative Examples 5-1 to 5-10 and 5-11 to 5-18 produced via the Production Method 15, since the thermal history made by hot-rolling [Step 2-3] was insufficient, no desired area ratio of the Cube orientation was obtained.

[0141] It is understood that even if the alloy composition was in the range defined in the present invention but the copper alloy material was produced via the production method outside the range defined in the present invention, no defined texture was obtained, resulting in poor alloy properties. It is understood that if the alloy composition was outside the range defined in the present invention, the alloy properties were poor regardless of the texture state. If the alloy composition was outside the range defined in the present invention, the resultant copper alloy material was poor in the alloy properties, regardless that the copper alloy material was produced via any production method that was in the range or outside the range defined in the present invention.

Table 8-1

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
6-1	Production Method 11	2-4	385	○	83	25
6-2		2-5	400	○	86	28
6-3		2-7	410	○	79	25
6-4		2-8	410	○	88	27
6-5		2-9	400	○	86	25
6-6	Production Method 12	2-4	360	○	83	32
6-7		2-5	380	○	89	33
6-8		2-7	380	○	80	30
6-9		2-8	360	○	90	25
6-10		2-9	365	○	88	29
6-11	Production Method 13	2-4	390	○	82	32
6-12		2-5	420	○	89	35
6-13		2-7	420	○	80	30
6-14		2-8	425	○	90	26
6-15		2-9	410	○	88	29
6-16	Production Method 14	2-4	425	○	80	32
6-17		2-5	455	○	82	30
6-18		2-7	460	○	75	30
6-19		2-8	470	○	85	33
6-20		2-9	435	○	81	29

Table 8-1 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	Remarks
6-1	⦿	24	35	⦿	Example according to this invention
6-2	⦿	18	37	⦿	
6-3	⦿	22	30	⦿	
6-4	⦿	29	30	⦿	
6-5	⦿	25	31	⦿	
6-6	⦿	27	22	⦿	
6-7	⦿	16	24	⦿	
6-8	⦿	21	25	⦿	
6-9	⦿	32	20	⦿	
6-10	⦿	26	19	⦿	
6-11	⦿	26	12	⦿	
6-12	⦿	16	15	⦿	
6-13	⦿	21	17	⦿	
6-14	⦿	32	15	⦿	
6-15	⦿	26	9	⦿	
6-16	⦿	32	7	⦿	
6-17	⦿	28	8	⦿	
6-18	⦿	26	12	⦿	
6-19	⦿	33	10	⦿	
6-20	⦿	27	5	⦿	

Table 8-2

Test No.	Production Method	Alloy No.	TS (MPa)	Electric conductive	EC (%IACS)	Ratio of coincidence grain boundary Σ3 (%)
6-21	Production Method 16	2-4	380	○	83	32
6-22		2-5	405	○	87	30
6-23		2-7	400	○	80	28
6-24		2-8	415	○	86	30
6-25		2-9	390	○	86	27
6-26	Production Method 17	2-4	500	○	82	*4*
6-27		2-5	520	○	86	*5*
6-28		2-7	535	○	81	*8*
6-29		2-8	530	○	89	*6*
6-30		2-9	525	○	88	*6*
6-31	Production Method 8	2-4	475	○	82	*2*
6-32		2-5	500	○	89	*3*
6-33		2-7	515	○	81	*5*
6-34		2-8	490	○	90	*15*
6-35		2-9	490	○	88	*12*
6-36	Production Method 9	2-4	360	○	82	28
6-37		2-5	380	○	86	25
6-38		2-7	380	○	79	25
6-39		2-8	375	○	89	27
6-40		2-9	370	○	86	25

Table 8-2 (continued)

Test No.	Stress relaxation resistance	SR (%)	Cube area ratio (%)	Bending property	Remarks
6-21	○	26	2	×	Comparative example
6-22	○	16	1	×	
6-23	○	23	1	×	
6-24	○	31	2	×	
6-25	○	24	2	×	
6-26	×	48	1	×	
6-27	×	46	0	×	
6-28	×	45	0	×	
6-29	×	45	1	×	
6-30	×	45	0	×	
6-31	×	45	2	×	
6-32	×	40	1	×	
6-33	×	40	1	×	
6-34	×	38	2	×	
6-35	×	36	2	×	
6-36	○	26	2	×	
6-37	○	16	0	×	
6-38	○	21	1	×	
6-39	○	32	1	×	
6-40	○	26	0	×	

[0142] Table 8-1 and Table 8-2 show the results of the alloy properties of the copper alloy materials produced via the Production Methods 11 to 14, 16 to 17, 8, and 9, respectively, for Alloy Nos. 2-4, 2-5, 2-7, 2-8, and 2-9, respectively, as the representative alloy compositions. When the copper alloy material was produced via the production method in any of the Production Methods 11 to 14 each in the range defined in the present invention, the resultant copper alloy materials each satisfied the alloy properties. When the copper alloy material was produced via the production method in any of the Production Methods 16 to 17, 8 and 9 outside the range defined in the present invention, any of the alloy properties was conspicuously inferior to the desired properties, or even if the resultant copper alloy material satisfied the desired properties, the properties were conspicuously inferior to the properties as compared to those of Examples according to this invention. Further, similar to the above, Comparative Examples produced via the Production Method 8 corresponding to the Patent Literature 4 and the Production Method 9 corresponding to the Patent Literature 5, each resulted in poor properties.

[0143] Among these, with respect to Comparative Examples 6-21 to 6-25 produced via the Production Method 16, since the thermal history caused by the hot-rolling [Step 2-3] was insufficient, no desired area ratio of the Cube orientation was obtained, resulting in poor bending property.

[0144] Further, in Comparative Examples 6-26 to 6-30 produced via the Production Method 17, since the copper alloy materials were worked with high deformation at an excessively high working ratio in the final cold-rolling [Step 2-8], grains underwent rotation, and the orientation relationships involving the area ratios of coincidence grain boundary Σ3 and/or the Cube orientation were destroyed, resulting in poor stress relaxation resistance and poor bending property.

[0145] In Comparative Examples 6-31 to 6-35 produced via the Production Method 8, when compared with the Examples according to the present invention in terms of the production conditions, no cold-rolling (corresponding to the [Step 2-4]) after the hot-rolling (corresponding to the [Step 2-3]) was carried out, and the working ratio in the final cold-rolling (corresponding to the [Step 2-6]) was too high. In the textures obtained in these Comparative Examples, the area ratio of the Cube orientation was too low, which was as low as less than 3%, and the ratio of coincidence grain boundary Σ3 was too low, which was as low as less than 20%, resulting in poor stress relaxation resistance and poor bending property.

[0146] In Comparative Examples 6-36 to 6-40 produced via the Production Method 9, when compared with the Examples according to the present invention in terms of the production conditions, there is a difference that the heating time period in the intermediate heat treatment (corresponding to the [Step 2-5]) was too long, and that a heat treatment (corresponding to the [Step 2-7]) was repeated three times. In the textures obtained in these Comparative Examples, the area ratio of the Cube orientation was too low, which was as low as less than 3%, resulting in poor bending property.

[0147] As is understood from the above Examples according to this invention, the copper alloy material of the present invention is suitable in lead frames, connectors, terminal materials, and the like of, for example, parts to be mounted on vehicles and surrounding infrastructures primarily for EVs and HEVs, and solar photovoltaic power generation systems.

[0148] Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

[0149] This application claims priority on Patent Application No. 2011-186253 filed in Japan on August 29, 2011, which is entirely herein incorporated by reference.

Claims

1. A copper alloy material, containing 0.1 to 0.8 mass% of Cr, and 0.01 to 0.5 mass% in total of at least one selected from the group consisting of an additional alloying element group 1 and an additional alloying element group 2 described below, with the balance being copper and unavoidable impurities,
wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more:

an additional alloying element group 1: at least one selected from the group consisting of Mg, Ti and Zr in an amount of 0.01 to 0.5 mass% in total; and
an additional alloying element group 2: at least one selected from the group consisting of Zn, Fe, Sn, Ag, Si and P in an amount of 0.005 to 0.5 mass% in total.

2. The copper alloy material according to claim 1, containing at least one selected from the additional alloying element group 1 and at least one selected from the additional alloying element group 2 in an amount of 0.01 to 0.5 mass% in total.

3. The copper alloy material according to claim 1 or 2, wherein the copper alloy material has a tensile strength of 400 MPa or greater and an electrical conductivity of 75%IACS or higher.

4. A method of producing the copper alloy material according to any one of claims 1 to 3, comprising: casting a copper alloy raw material which gives the composition according to claim 1, to give an ingot [Step 1-1]; homogenization heat treatment of the ingot at 600 to 1,025°C for 10 minutes to 10 hours [Step 1-2]; hot-rolling at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98% [Step 1-3]; cold-rolling at a working ratio of 50 to 99% [Step 1-4]; intermediate heat treatment at 300 to 1,000°C for 5 seconds to 180 minutes [Step 1-5]; cold-rolling at a working ratio of 50 to 95% [Step 1-6]; aging at 400 to 650°C for 30 to 180 minutes [Step 1-9]; and strain-relief annealing at 550 to 700°C for 5 seconds to 10 minutes [Step 1-11], in this order.

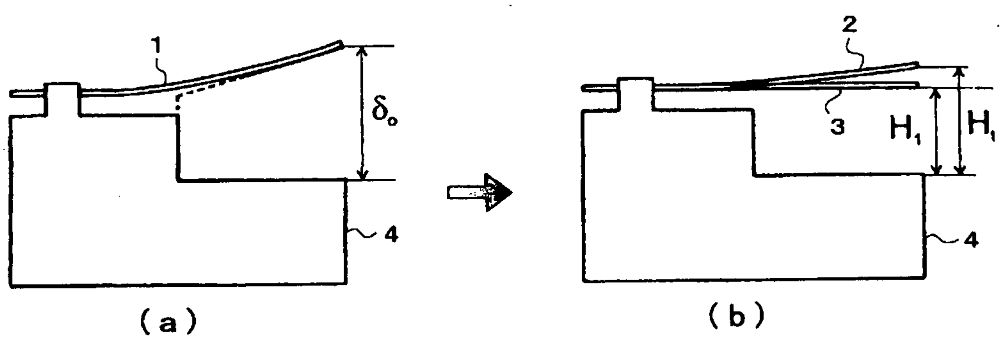
5. A copper alloy material, containing 0.01 to 0.5 mass% of Mg, with the balance being copper and unavoidable impurities,
wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more.

6. A copper alloy material, containing 0.01 to 0.5 mass% of Mg, and 0.01 to 0.3 mass% in total of at least one selected from the group consisting of Zn, Sn, Ag, Si and P, with the balance being copper and unavoidable impurities, wherein in a crystal orientation analysis of a rolled face in an electron backscatter diffraction analysis, the area ratio of grains having an orientation in which a deviation from the Cube orientation {001} <100> is within 15° is 3% or more, and
wherein the ratio of coincidence grain boundary Σ3 in grain boundaries is 20% or more.

7. The copper alloy material according to claim 5 or 6, wherein the copper alloy material has a tensile strength of 250 MPa or greater and an electrical conductivity of 75%IACS or higher.

8. A method of producing the copper alloy material according to any one of claims 5 to 7, comprising: casting a copper alloy raw material which gives the composition according to claim 5 or 6, to give an ingot [Step 2-1]; homogenization heat treatment of the ingot at 600 to 1,025°C for 10 minutes to 10 hours [Step 2-2]; hot-rolling at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98% [Step 2-3]; cold-rolling at a working ratio of 50 to 99% [Step 2-4]; intermediate heat treatment at 300 to 800°C for 5 seconds to 180 minutes [Step 2-5]; cold-rolling at a working ratio of 50 to 95% [Step 2-6]; heat treatment at 300 to 800°C for 5 seconds to 180 minutes [Step 2-7]; cold-rolling at a working ratio of 10 to 80% [Step 2-8]; and strain-relief annealing at 300 to 600°C for 5 to 60 seconds [Step 2-9], in this order.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/071857

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/00(2006.01)i, *C22C1/10*(2006.01)i, *C22C9/02*(2006.01)i, *C22C9/04*(2006.01)i, *C22C9/06*(2006.01)i, *C22C9/10*(2006.01)i, *C22F1/08*(2006.01)i, *H01B1/02*(2006.01)i, *H01B5/02*(2006.01)i, *H01B13/00*(2006.01)i,

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)

C22C9/00, C22C1/10, C22C9/02, C22C9/04, C22C9/06, C22C9/10, C22F1/08, H01B1/02, H01B5/02, H01B13/00, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2009-263784 A (Nippon Mining & Metals Co., Ltd.), 12 November 2009 (12.11.2009), entire text & WO 2009/123140 A1 & KR 10-2010-0095476 A & CN 101981212 A	1-8
A	JP 2007-291518 A (Dowa Metaltech Co., Ltd.), 08 November 2007 (08.11.2007), entire text (Family: none)	1-8
A	JP 3-162553 A (Nippon Mining Co., Ltd.), 12 July 1991 (12.07.1991), entire text (Family: none)	1-8

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

* Special categories of cited documents:

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"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 21 November, 2012 (21.11.12)	Date of mailing of the international search report 04 December, 2012 (04.12.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (July 2009)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/071857

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C22F1/00(2006.01)n

(According to International Patent Classification (IPC) or to both national classification and IPC)

Form PCT/ISA/210 (extra sheet) (July 2009)

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