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(54) COPPER ALLOY SHEET MATERIAL AND PROCESS FOR PRODUCING SAME

(57) {Problems} To provide a copper alloy sheet material, which is excellent in the bending property, which has an excellent mechanical strength, which is less in anisotropy in those characteristics in the parallel direction to rolling and the perpendicular direction to rolling, and which is suitable for lead frames, connectors, terminal materials, and the like in electrical or electronic equipments, for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like.

{Means to solve} A copper alloy sheet material, having a composition containing Ni in an amount of 1.0 mass% to 5.0 mass%, and Si in an amount of 0.1 mass% to 2.0 mass%, with the balance being copper and unavoidable impurities, wherein, in a crystal orientation analysis by an electron backscatter diffraction method, an area ratio of grains having an orientation in which a deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 5% to 50%, and 40 to 100 grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° are dispersed within 60 μm square; and a method of producing the same.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy sheet material and a method of producing the same, which can be applied, for example, to lead frames, connectors, terminal materials, relays, switches, sockets, and the like, for electrical or electronic equipments.

BACKGROUND ART

[0002] Characteristics required for copper alloy materials that are used in applications for electrical or electronic equipments, include, for example, electrical conductivity, proof stress (yield stress), tensile strength, bending property, and stress relaxation resistance. In recent years, the demanded levels for the characteristics become higher, concomitantly with the size reduction, weight reduction, enhancement of the performance, high density packaging, or the temperature rise in the use environment, of electrical or electronic equipments.
[0003] Conventionally, in addition to iron-based materials, copper-based materials, such as phosphor bronze, red brass, and brass, have also been widely used in general as the materials for electrical or electronic equipments. These copper alloys are enhanced in the mechanical strength through a combination of solid solution strengthening of tin (Sn) or zinc (Zn) and work hardening through cold-working, such as rolling or drawing. In this method, the electrical conductivity is insufficient, and the bending property and/or the stress relaxation resistance are also insufficient, due to that high mechanical strength is attained by making a working ratio high in the cold-working.
[0004] As a strength-enhancing method for replacing the above method, precipitation strengthening is available by which a fine second phase is precipitated in the material. This strengthening method has advantages of enhancing the mechanical strength, as well as, simultaneously, enhancing the electrical conductivity, and thus this method has been applied to many alloy systems. However, along with the recent downsizing of parts to be used in electronic equipments and automobiles, as a copper alloy sheet material to be used therein, a copper alloy-based material higher in the mechanical strength has become to be subjected to bending at a smaller radius, and there is a strong demand for a copper alloy sheet material excellent in the bending property. Further, even in a sheet material having a high strength, a high spring property and a favorable bending property, it is not preferable that there is a difference in characteristics between a parallel direction to rolling and a perpendicular direction to rolling, and it is important that favorable characteristics are exhibited in any direction. In particular, when used as an ultra-small terminal, the sheet material is subjected to micromachining in a pin type at a narrow width, and it is important that favorable characteristics are exhibited in any direction, in this case also. In a conventional Cu-Ni-Si-based alloy, in order to obtain high mechanical strength, high work hardening is obtained by increasing a rolling working ratio, but this method deteriorates the bending property as described above, and thus it is difficult to achieve a good balance between high mechanical strength and favorable bending property.
[0005] In order to improve the bending property, there are some proposals based on controlling of crystal orientation. For example, the following disclosures have been made on Cu-Ni-Si-based copper alloys. Patent Literature 1 discloses, in a Cu-Ni-Si-based copper alloy, a copper alloy sheet material excellent in the bending property, which sheet material has a given grain size and a crystal orientation in which X-ray diffraction intensities I from the {3 1 1}, {2 2 0}, and {2 0 0} planes satisfy a certain condition. Further, Patent Literature 2 discloses, in a Cu-Ni-Si-based copper alloy, a copper alloy sheet material excellent in the bending property, which sheet material has a crystal orientation in which the X-ray diffraction intensities from the {2 0 0} and {2 2 0} planes satisfy a certain condition. Further, Patent Literature 3 discloses, in a Cu-Ni-Si-based copper alloy, a copper alloy sheet material excellent in the bending property, which sheet material is controlled on a ratio of the Cube orientation {0 0 1} <1 0 0> to 50% or less. Patent Literature 4 discloses, in a Cu-Ni-Si-based copper alloy, a copper alloy sheet material favorable in the bending property, which sheet material has a recrystallized crystal structure from a distorted state due to strong cold working, whereby the crystal structure is converted into one whose anisotropy is small, and also elongation is improved. Patent Literature 5 discloses, in a Cu-Ni-Si-based copper alloy, a copper alloy sheet material excellent in the bending property and small in strength anisotropy, which sheet material is controlled in a grain size, and a ratio of the Cube orientation {0 0 1} <1 0 0> to 20% to 60%. Patent Literature 6 discloses, in a Cu-Ni-Si-based copper alloy, a copper alloy sheet material improved in fatigue property, without deteriorating mechanical strength, electrical conductivity, and bending property, by controlling a grain size, and a ratio of the Cube orientation {0 0 1} <1 0 0> to 5 to 50%.
[0006] In the inventions described in Patent Literatures 1 and 2, only limited specific planes among the expansive distribution of crystal orientations are focused, in the analysis of crystal orientations with X-ray diffraction from the specific planes. Further, in the invention described in Patent Literature 3, the control of the crystal orientation is realized by a reduction of a working ratio in rolling after solution heat treatment. Further, the area and the dispersibility of the Cube orientation grains are not described in Patent Literature 3, and the bending property and the anisotropy in mechanical

strength are not disclosed in Patent Literature 3. In the invention described in Patent Literature 4, a crystal structure in a distorted state due to strong cold-rolling is recrystallized, to realize a crystal structure small in anisotropy, and to improve elongation, thereby to realize a favorable bending property. However, improvement in characteristics by controlling crystal orientation is not carried out at all in Patent Literature 4. In the invention described in Patent Literature 5, a process, e.g. a rolling reduction ratio in cold-rolling before a solution treatment, and a temperature rising speed in the solution treatment, is controlled, to accumulate the Cube orientation and to reduce anisotropy in mechanical strength and bending property. However, in Patent Literature 5, a temperature rising speed in the solution treatment is slow, and thus the temperature rising time period is long. As a result, the Cube orientation grains are coarsened, a homogeneous dispersibility of the Cube orientation grains is poor, and anisotropy in mechanical strength is also large. Further, in the invention described in Patent Literature 6, cold-rolling before the solution treatment is conducted at a rolling reduction ratio as high as 85% to 99.8%, and a heating temperature and a holding time period in the subsequent solution treatment are controlled, to cause accumulation in the Cube orientation, and to improve the fatigue property. However, in Patent Literature 6, the Cube orientation grains that are obtained as a result of the solution treatment are coarsened, the homogeneous dispersibility of the Cube orientation grains is poor, and anisotropy in mechanical strength is also large.

[0007] Further, a low Young's modulus (modulus of longitudinal elasticity) is required, as one of the characteristics required for copper alloy materials for use in electrical or electronic equipments. Recently, along with the progress in the downsizing of electronic parts, such as connectors, the tolerances in the size accuracy of terminals and in the press working have been becoming severe to achieve. By lowering the Young's modulus of a copper alloy material, the effects of variation in size, which affect to a contact pressure, can be decreased, and thus the designing of parts becomes readily. With regard to measurement of Young's modulus, there are two methods including: a method in which Young's modulus is calculated from a gradient in an elastic region in a stress-strain curve obtained by a tensile test; and a method in which Young's modulus is calculated from a gradient in an elastic region in a stress-strain curve when a beam (cantilever beam) is bent.

CITATION LIST

PATENT LITERATURES

[0008]

Patent Literature 1: JP-A-2006-009137
Patent Literature 2: JP-A-2008-013836
Patent Literature 3: JP-A-2006-283059
Patent Literature 4: JP-A-2005-350695
Patent Literature 5: JP-A-2011-162848
Patent Literature 6: JP-A-2011-012321

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0009] In view of the problems in the conventional arts as described above, the present invention is contemplated for providing a copper alloy sheet material, which is excellent in the bending property, which has an excellent mechanical strength, which is less in anisotropy in those characteristics in the parallel direction to rolling and the perpendicular direction to rolling, and which is suitable for lead frames, connectors, terminal materials, and the like in electrical or electronic equipments, for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like. Further, the present invention is also contemplated for providing a favorable method of producing the copper alloy sheet material.

SOLUTION TO PROBLEM

[0010] The inventors of the present invention, having keenly conducted investigations on copper alloys appropriate for electrical or electronic part applications, have found that there is a correlation between the accumulation ratio of the Cube orientation and the bending property, to largely improve the bending property, the mechanical strength, and the electrical conductivity, in Cu-Ni-Si-based copper alloy sheet materials. Further, the inventors have found a specific copper alloy composition to further enhance the mechanical strength, in copper alloy sheet materials having the above crystal orientation and characteristics. In addition, the inventors have also found copper alloy sheet materials to which are added additional alloying elements that act to enhance the mechanical strength, without impairing the electrical conductivity and the bending property in this alloy system. Further, the inventors have also found a production method comprising specific steps, based on the correlation between the accumulation ratio of the Cube orientation and the bending property, to attain the above specific crystal orientation. The present invention is attained, as a result of studies based on those findings.

[0011] That is, according to the present invention, there is provided the following means:

(1) A copper alloy sheet material, having a composition containing Ni in an amount of 1.0 mass% to 5.0 mass%, and Si in an amount of 0.1 mass% to 2.0 mass%, with the balance being copper and unavoidable impurities,
wherein, in a crystal orientation analysis by an electron backscatter diffraction method, an area ratio of grains having an orientation in which a deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 5% to 50%, and 40 to 100 grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° are dispersed within 60 μm square.

(2) A copper alloy sheet material, having a composition containing Ni in an amount of 1.0 mass% to 5.0 mass%, Si in an amount of 0.1 mass% to 2.0 mass%, and at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf, in an amount of 0.005 mass% to 1.0 mass% in total, with the balance being copper and unavoidable impurities,
wherein, in a crystal orientation analysis by an electron backscatter diffraction method, an area ratio of grains having an orientation in which a deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 5% to 50%, and 40 to 100 grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° are dispersed within 60 μm square.

(3) The copper alloy sheet material according to (1) or (2), wherein an average grain area of the grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 1.8 μm^2 to 45.0 μm^2.

(4) The copper alloy sheet material according to any one of (1) to (3), wherein an average grain area of grains in a matrix is 50 μm^2 or less.

(5) The copper alloy sheet material according to any one of (1) to (4), wherein a difference between a deflection coefficient in a parallel direction to rolling and a deflection coefficient in a perpendicular direction to rolling is 10 GPa or less in terms of an absolute value thereof, and wherein a difference between a proof stress in the parallel direction to rolling and a proof stress in the perpendicular direction to rolling is 10 MPa or less in terms of an absolute value thereof.

(6) A method of producing a copper alloy sheet material, containing: casting a copper alloy raw material into an ingot, followed by subjecting to a homogenization heat treatment, hot-rolling, cold-rolling to a thin sheet, and an intermediate solution heat treatment to form a solid solution of solute atoms in the thin sheet again,
wherein the copper alloy raw material has an alloy composition of the copper alloy sheet material according to (1) or (2), and
wherein the method contains the steps, in this order, of:

the homogenization heat treatment at 800°C to 1,020°C for 3 minutes to 10 hours;
the cold-rolling at a rolling reduction ratio of 80% to 99.8%;
an intermediate annealing at a temperature of 400°C to 700°C, which is lower than a recrystallization temperature, for 5 seconds to 20 hours;
heating to 100°C to 400°C, followed by intermediate warm-rolling in which a rolling reduction ratio is 5% to 50% at the temperature;
the intermediate solution heat treatment at 600°C to 1,000°C for 5 seconds to 1 hour; and
an aging-precipitation heat treatment at 400°C to 700°C for 5 minutes to 10 hours.

ADVANTAGEOUS EFFECTS OF INVENTION

[0012] According to the present invention, it is possible to provide a copper alloy sheet material, which is excellent in the bending property, which has an excellent mechanical strength, and which is less in anisotropy in those properties in the parallel direction to rolling and the perpendicular direction to rolling. Thus, according to the present invention, it is possible to provide a copper alloy sheet material, which has properties suitable for lead frames, connectors, terminal materials, and the like in electrical or electronic equipments, for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like.

[0013] Further, the production method of the present invention can favorably produce the above copper alloy sheet material.

[0014] 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 THE DRAWING

[0015] {Fig. 1} Fig. 1 is a diagram illustrating the homogeneous dispersibility in a case of at least four groups, each group including four blocks adjacent to each other.

MODE FOR CARRYING OUT THE INVENTION

[0016] A preferred embodiment of a copper alloy sheet material of the present invention will be described. Herein, in the present invention, the "sheet material" is construed to include a "strip material".

[0017] The copper alloy sheet material of the present invention has the composition containing 1.0 mass% to 5.0 mass% of Ni, and 0.1 mass% to 2.0 mass% of Si, with the balance being copper and unavoidable impurities. Preferably, Ni is set to 3.0 mass% to 5.0 mass%, and Si is set to 0.5 mass% to 2.0 mass%. Particularly preferably, Ni is set to 4.0 mass% or more, and Si is set to 1.0 mass% or more.

[0018] Further, in the crystal orientation analysis by the electron backscatter diffraction method, the area ratio of the Cube orientation {0 0 1} <1 0 0> (hereinafter, which may be referred to as a Cube orientation area ratio) is 5% to 50%, preferably 10% to 45%, more preferably 15% to 40%, and particularly preferably 20% to 35%.

[0019] Alternatively, the copper alloy sheet material may contain 1.0 mass% to 5.0 mass% of Ni, 0.1 mass% to 2.0 mass% of Si, and at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf in a total amount of 0.005 mass% to 1.0 mass%. The total amount of at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf is preferably 0.01 mass% to 0.9 mass%, more preferably 0.03 mass% to 0.8 mass%, and particularly preferably 0.05 mass% to 0.5 mass%. Even in this case, the preferable contents of Ni and Si, and particularly preferable contents thereof, and the preferable range of the Cube orientation area ratio, and particularly preferable range thereof are the same as described above.

[0020] Further, in each of the copper alloy sheet materials, the average grain area of the grains having the orientation in which deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is preferably 1.8 μm^2 to 45.0 μm^2, more preferably 3.8 μm^2 to 36.0 μm^2, still more preferably 6.0 μm^2 to 28.8 μm^2, and particularly preferably 10.0 μm^2 to 25.0 μm^2.

[0021] In this specification, the average grain area of the grains having the orientation in which deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° may be abbreviated to be referred to as a Cube orientation area ratio, an area ratio of the Cube orientation {0 0 1} <1 0 0>, or the like. Further, the grains having the orientation in which deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° may be abbreviated to be referred to as the Cube orientation grains, grains of the Cube orientation {0 0 1} <1 0 0>, or the like.

[0022] The average grain area of the matrix containing the Cube orientation grains is preferably 40 μm^2 or less, and more preferably 5 μm^2 to 30 μm^2. An average value of the grain area is calculated from EBSD measurement results within a range of $300\ \mu m \times 300\ \mu m$ on a plane of a sheet material, and the average value is set as the average grain area.

[0023] Further, in the crystal orientation analysis by the electron backscatter diffraction method, 40 to 100 grains of the Cube orientation {0 0 1} <1 0 0> are distributed within 60 μm square, to have the homogeneous dispersibility. With respect to the grains of the Cube orientation {0 0 1} <1 0 0>, within 60 μm square, preferably 45 to 95 grains are distributed, to have the homogeneous dispersibility, and particularly preferably 50 to 90 grains are distributed, to have the homogeneous dispersibility.

[0024] Furthermore, with regard to the bending property in the parallel direction to rolling and the perpendicular direction to rolling, it is preferable that no cracks occur on a bent surface upon 180° tight U-bending in bending of a narrow width of 1 mm width or less.

[0025] Furthermore, the difference between the deflection coefficient in the parallel direction to rolling (//) and the deflection coefficient in the perpendicular direction to rolling ($\perp$) is preferably 10 GPa or less, more preferably 8 GPa or less, and particularly preferably 5 GPa or less, in terms of an absolute value thereof. The difference between the proof stress in the parallel direction to rolling and the proof stress in the perpendicular direction to rolling is preferably 10 MPa or less, more preferably 8 MPa or less, and particularly preferably 5 MPa or less, in terms of an absolute value thereof. The smaller these differences are, the higher the resultant anisotropy becomes, which is preferable. Ideally, each of these differences is 0 (zero), that is, most preferably the values in the parallel direction to rolling and the perpendicular direction to rolling are the same as each other.

[0026] In the copper alloy sheet material of the present invention, when each of the area ratio of the Cube orientation {0 0 1} <1 0 0> and the average grain area thereof, more preferably the average grain area of the matrix in addition to those two, are within the above-described ranges, no cracks occur at the vertex of the bent portion upon the 180° tight U-bending and the favorable bending property can be obtained, and further the deflection anisotropy and the proof stress anisotropy becomes small. On the other hand, in a case where the area ratio is too small or the average grain area is too large, or in a case where the average grain area of the matrix is too large, cracks are apt to occur at the vertex of the bent portion, and thus any favorable bending property cannot be obtained, and the deflection anisotropy and the proof stress anisotropy becomes large.

[0027] The copper alloy sheet material of the present invention contains 1.0 mass% to 5.0 mass% of Ni, and 0.1 mass% to 2.0 mass% of Si. Due to those, a Ni-Si-based compound (Ni_2Si phase) precipitates in the Cu matrix, to enhance the mechanical strength and electrical conductivity. On the other hand, if the content of Ni is too small, the mechanical strength may not be obtained, and if the content is too large, precipitation, which does not contribute to enhancement of the mechanical strength, occurs upon casting or hot working, resulting in that any mechanical strength appropriate for an addition amount may not be obtained, and hot workability and bending property become worse. Furthermore, Si forms the Ni_2Si phase in combination with Ni, and thus when the content of Ni is determined, the addition amount of Si is determined. However, if the content of Si is too small, the mechanical strength may not be obtained, and if the content of Si is too large, the same problems as the case in which the content of Ni is large occur. Thus, it is preferable that the addition amounts of Ni and Si be set within the above-described ranges.

[0028] Next, the explanation is given on the area ratio of the Cube orientation {0 0 1} <1 0 0>.

[0029] In order to improve the bending property of the copper alloy sheet material, the inventors of the present invention conducted detailed investigation and analysis on the cause of cracks occurred at a bent portion. As a result, the inventors have found that the cause is that, upon bending, plastic deformation locally develops to form a shear deformation zone, to cause occurrence and connection of microvoids via local work-hardening, resulting in reaching the growth limitation. As a countermeasure therefor, the inventors have found that it is effective to increase the ratio of crystal orientation by which work hardening is difficult to occur in bending deformation. That is, as described above, the present inventors have found that in a case where the area ratio of the Cube orientation {0 0 1} <1 0 0> is 5% to 50%, a favorable bending property is exhibited.

[0030] In a case where the area ratio of the Cube orientation {0 0 1} <1 0 0> is within the above-described range, the above-described action and effect are sufficiently exhibited. Further, within the above-described range, even when cold-rolling after a recrystallization treatment is not conducted at a low rolling reduction ratio, the mechanical strength does not be lowered conspicuously, and thus the range is preferable. That is, the cold-rolling after the recrystallization treatment may be conducted at a high rolling reduction ratio, without significantly deteriorating the mechanical strength. On the other hand, when the area ratio of the Cube orientation {0 0 1} <1 0 0> is too low, the bending property deteriorates. On the contrary, when the area ratio of the Cube orientation {0 0 1} <1 0 0> is too high, the mechanical strength becomes worse. Thus, from the above-described viewpoints, the area ratio of the Cube orientation {0 0 1} <1 0 0> is set to 5% to 50%, a preferable range is 10% to 45%, a more preferable range is 15% to 40%, and a particularly preferable range is 20% to 35%.

[0031] Next, the explanation is given on orientations other than the Cube orientation of the above range. In the copper alloy sheet material of the present invention, the S orientation {3 2 1} <4 3 6>, the Copper orientation {1 2 1} <1 -1 1>, the D orientation {4 11 4} <11 -8 11>, the Brass orientation {1 1 0} <1 -1 2>, the Goss orientation {1 1 0} <0 0 1>, the RDW orientation {1 0 2} <0 1 0>, and the like are generated as crystal orientations, in addition to the Cube orientation. Any of these other orientation components may be present in the copper alloy sheet material of the present invention, as long as the area ratio of the Cube orientation is within the above-mentioned range to the areas of all of the observed orientations.

[0032] As described in above, the analysis of the crystal orientation 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 a reflected electron back-scattering pattern (EBSP) that occurs when one point of the surface of a sample is irradiated with an electron beam under a scanning electron microscope (SEM), to analyze a crystal orientation and a crystalline structure (texture) in a localized region of the sample.

[0033] A sample area, which is measured 1 mm on each of the four sides and which contains 200 or more grains, is subjected to an analysis of the crystal orientation, by scanning in a stepwise manner at an interval of 0.1 μm. A measurement area is set to 300 μm $\times$ 300 μm in consideration of the size of grains of the sample. The area ratio of the respective orientation is a ratio of the area of grains having the orientation in which the deviation (deviation angle) from the ideal orientation of the Cube orientation {0 0 1} <1 0 0> is within 15°, i.e. $\pm$15° or less, to the 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. In this application, a value measured in this way is referred to as an area ratio of a crystal plane having a certain crystal orientation, unless otherwise state.

[0034] Next, the explanation is given on the homogeneous dispersibility of the grains of the Cube orientation {0 0 1} <1 0 0>.

[0035] To examine the dispersibility of the Cube orientation grains, in the crystal orientation analysis by the EBSD method, a region of 300 μm $\times$ 300 μm is scanned in a stepwise manner at an interval of 0.1 μm, to analyze total 25 blocks, in which 60 μm square is set as one block. The area ratio, the number, and the average grain area of the Cube orientation grains per one block, and the average grain area of the matrix containing the Cube orientation grains are confirmed, to examine the dispersibility. As described above, a case in which, for one block, the Cube orientation area ratio is 5% to 50%, the number of Cube orientation grains is 40 to 100, the average grain area of each one of the Cube orientation grains is 1.8 μm^2 to 45.0 μm^2, and the average grain area of the matrix containing the Cube orientation grains is 50 μm^2 or less, is quantified as the homogeneous dispersibility of the Cube orientation grains for each visual field (300 μm $\times$ 300 μm) in the present invention. The homogeneous dispersibility is calculated by multiplying the area of one block (60 μm $\times$ 60 μm = 3,600 μm^2) by the Cube orientation area ratio of the corresponding block to obtain the total area of the Cube orientation grains per one block, and by dividing the value of the total area by the number of Cube orientation grains in one block, to obtain an average area per one Cube orientation grain in one block. The thus-obtained value is the average grain area. The "homogeneous dispersibility" referred to herein specifies the average grain area and the number of Cube orientation grains per one block. Even if a distribution state of the Cube orientation grains is uneven, the homogeneous dispersibility can be confirmed when seen in terms of the entirety of 300 μm $\times$ 300 μm in which 25 blocks are accumulated. For example, a bent portion of a narrow-width pin (0.25 mm = 250 μm) of an ultra-small connector is set to 250 μm $\times$ 250 μm, the Cube orientation groups are included in at least four or more blocks, and thus it can be said that the homogeneous dispersibility is present. As shown in Fig. 1, even if the Cube orientation grains are accumulated in corners of four blocks adjacent to each other, the dispersibility thereof is equivalent, and the anisotropy in the parallel direction to rolling and the perpendicular direction to rolling is small. Herein, with regard to the homogeneous dispersibility (of a case of at least four or more groups, in which adjacent four blocks are set as one group), more preferably, it can be specified that an area of one block is set to be further smaller. For example, in the case where the area of one block is set as 30 μm square, it is preferable that 10 to 25 grains of the Cube orientation {0 0 1} <1 0 0> be present within the one block, the area ratio of the grains of the Cube orientation {0 0 1} <1 0 0> be 5% to 50%, and the average grain area of the grains of the Cube orientation {0 0 1} <1 0 0> be 1.8 μm^2 to 45.0 μm^2. In this case, the average grain area of grains of the matrix is preferably 40 μm^2 or less.

[0036] In a case where the average grain area of the Cube orientation grains is too small, the solution heat treatment is insufficient, and thus non-crystallized structure remains. Thus, there is a possibility that the mechanical strength and the bending property may be deteriorated. On the other hand, in a case where the average grain area of the Cube orientation grains is too large, a possibility of occurrence of fracture (cracks) is high at a portion of grains having orientations other than the Cube orientation grains upon bending. Further, the anisotropy may occur depending on a bending direction in some cases. Thus, it is preferable that the average grain area of the Cube orientation grains be set within the above-described range.

[0037] Further, since 40 to 100 Cube orientation grains are distributed in 60 μm square, to have the homogeneous dispersibility, no crack occurs at the vertex of the bent portion, to give a favorable bending property, and to make the deflection anisotropy and the proof stress anisotropy small. On the other hand, when the number of Cube orientation grains that are distributed in 60 μm square is too less, cracks occur at the vertex of the bent portion, resulting in that any favorable bending property is not obtained, and that the deflection anisotropy and the proof stress anisotropy become conspicuously large. On the other hand, when the number of grains is too much, the bending property, the deflection anisotropy, and the proof stress anisotropy are excellent, but the mechanical strength is poor.

[0038] In particular, in a case of a narrow-width pin (for example, 0.25 mm width) for an ultra-small connector which is formed from the copper alloy sheet material, it is assumed when the area ratio is allowed to increase within the area ratio range of the grains of the Cube orientation {0 0 1} <1 0 0>, which is effective for improvement of the bending property. Even in that case, if the average grain area of the Cube orientation grains is large, and/or if the distribution of the Cube orientation grains is not uniform, a possibility of occurrence of cracks is high at a portion of grains having orientations other than the Cube orientation grains, upon bending. Further, in that case, the anisotropy may occur depending on a bending direction in some cases. Thus, in the crystal orientation analysis by the EBSD method, it is preferable that 40 to 100 Cube orientation grains be distributed in 60 μm square, to have the homogeneous dispersibility.

[0039] Thus, in the copper alloy sheet material of the present invention, the average grain area and the dispersibility of the Cube orientation grains are controlled. Specifically, in the intermediate warm-rolling before the recrystallization solution heat treatment, by heating to a temperature at which recrystallization does not occur, followed by rolling at a rolling reduction ratio of 5% or more under the temperature, it is possible to control introduction and release of a strain in the entirety of the thus-rolled material in an appropriate state. By conducting those, the homogeneous dispersibility of the Cube orientation can be realized. Further, the average grain area of each crystal orientation can be controlled simultaneously. By controlling the dispersibility, the bending property of the narrow-width pin enhances, and the strength anisotropy, such as the deflection anisotropy, and the proof stress anisotropy, are reduced.

[0040] Next, the explanation is given on the additional alloying elements, which may be added to the copper alloy sheet material of the present invention.

[0041] As described above, in one preferable embodiment of the copper alloy sheet material of the present invention, at least one additional alloying element selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf, may be contained, in addition to main alloying elements of Ni and Si. The content of the additional alloying elements is 0.005 to 1.0 mass%, preferably 0.01 to 0.9 mass%, more preferably 0.03 mass% to 0.8 mass%, particularly preferably 0.05 mass% to 0.5 mass%, in the total amount of the additional alloying elements. If the content of the additional alloying elements is 1.0 mass% or less in total, any adverse affection to lower the electrical conductivity is less likely to occur. If in the above range, the following effects of addition are sufficiently utilized, and it is possible to prevent conspicuously lowering of the electrical conductivity from occurring. If this total amount is in a particularly preferable range, a high additional effect and a high electrical conductivity can be obtained. If the content of the additional alloying elements is too small, an effect of addition is hardly expressed sufficiently. If, on the other hand, the content of the additional alloying elements is too high, the electrical conductivity is lowered, which is not preferable. The examples of the effects of adding various additional alloying elements will be described below.

[0042] Among the additional alloying elements, Mg, Sn, and Zn, when added, improve the stress relaxation resistance of the copper alloy sheet material. When these elements are added together, as compared with the case where any one of them is added singly, the stress relaxation resistance is further improved by synergistic effects. Further, an effect of remarkably improving solder brittleness is obtained. The stress relaxation resistance is measured, according to EMAS-3003, the former Technical Standard of the "Electronic Materials Manufacturer's Association of Japan", under the conditions of retaining the sample specimen at 150°C for 1,000 hours. An initial stress that is 80% of a yield stress (proof stress) is applied thereto, by a cantilever method, and an amount of displacement after the test at 150°C for 1,000 hours is determined as an index of the stress relaxation resistance.

[0043] Among the additional alloying elements, Mn, Ag, B, and P, when added, improve hot workability, and at the same time, enhance the mechanical strength, of the copper alloy sheet material.

[0044] Among the additional alloying elements, Cr, Zr, Fe, and Hf each finely precipitate, in the matrix, in the form of a compound thereof or in the form of a simple elementary substance. As the simple elementary substance, Cr, Zr, Fe, and Hf precipitate in a size of preferably 75 nm to 450 nm, more preferably 90 nm to 400 nm, and particularly preferably 100 nm to 350 nm, to contribute to precipitation hardening. Further, as the compound, Cr, Zr, Fe, and Hf precipitate in a size of 50 nm to 500 nm. In any case, those elements each have an effect of making the grain size fine, by suppressing the grain growth, and an effect of improving the bending property favorably, by making the dispersion state of the Cube orientation {0 0 1} <1 0 0> grains better.

[0045] Next, the explanation is given on the bending property of the copper alloy sheet material of the present invention.

[0046] With regard to the bending property, a test specimen subjected to the 90° W-bending is subjected to 180° tight bending by a compression test machine. At this test, it is preferable that cracks do not occur at the vertex of the resultant bent portion.

[0047] In other words, in the copper alloy sheet material of the present invention, with regard to the bending property in the parallel direction to rolling and the perpendicular direction to rolling, it is preferable that no crack occur in the bent surface at the 180° tight U-bending upon bending of a narrow width of 1 mm or less.

[0048] Next, the explanation is given on the anisotropy in the deflection coefficient and the anisotropy in the proof stress.

[0049] A difference between the deflection coefficient in the parallel direction to rolling (//) and the deflection coefficient in the perpendicular direction to rolling (⊥) is preferably 10 GPa or less in terms of an absolute value thereof, and in that case, the anisotropy in the deflection coefficient is small. Further, a difference between the proof stress in the parallel direction to rolling and the proof stress in the perpendicular direction to rolling is preferably 10 MPa or less in terms of an absolute value thereof, and in that case, the anisotropy in the proof stress is small.

[0050] Next, the explanation is given on a preferred embodiment of a method of producing the copper alloy sheet material of the present invention.

[0051] The production method of the copper alloy sheet material of the present invention, contains, in this order, the steps of: casting a copper alloy raw material to give an ingot, followed by subjecting to a heat treatment (homogenization treatment) and hot-rolling, cold-rolling to roll into a thin sheet, intermediate annealing at a temperature lower than the recrystallization temperature of the thin sheet, heating to 100°C to 400°C and warm-rolling (hereinafter, referred to as intermediate warm-rolling) at a rolling reduction ratio of 5% or more at the temperature, and then an intermediate solution heat treatment to form a solid solution of solute atoms in the thin sheet again, to produce the copper alloy sheet material.

[0052] The copper alloy raw material has a composition containing 1.0 mass% to 5.0 mass% of Ni, 0.1 mass% to 1.0 mass% of Si, and optionally at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf in a total amount of 0.005 mass% to 1.0 mass%, with the balance being copper and unavoidable impurities.

[0053] The rolling reduction ratio referred to herein means a value expressed in percentage by dividing a value, which is obtained by subtracting a cross-sectional area after rolling from a cross-sectional area before rolling, by the cross-sectional area before the rolling, and by multiplying the thus-divided value by 100. That is, the rolling reduction ratio is expressed by the following expression.

$$[\text{Rolling reduction ratio}] = \{([\text{cross-sectional area before rolling}] - [\text{cross-sectional area after rolling}])/[\text{cross-sectional area before rolling}]\} \times 100\ (\%)$$

[0054] Specifically, the following production method may be exemplified as a preferred example.

[0055] The above copper alloy raw material is subjected to casting [Step 1], to give an ingot. The resultant ingot is subjected to homogenization heat treatment [Step 2], followed by hot rolling [Step 3], and immediately cooling [Step 4] (for example, water cooling, water quenching). Then, the resultant sheet is subjected to face milling [Step 5], to remove an oxide layer on the surface thereof. Then, the resultant sheet is subjected to cold-rolling [Step 6], to roll at a rolling reduction ratio of 80% or more, to give a thin sheet.

[0056] Then, the resultant thin sheet is subjected to intermediate annealing [Step 7] at a temperature of 400°C to 700°C, at which the thin sheet is partially recrystallized, for 5 seconds to 20 hours, followed by heating to 100°C to 400°C and intermediate warm-rolling [Step 8] under the temperature at a rolling reduction ratio of 5% to 50%.

[0057] Then, the resultant thin sheet is subjected to the intermediate solution heat treatment [Step 9], to form a solid solution of solute atoms again. In a recrystallized texture of the thin sheet in the intermediate solution heat treatment, the Cube orientation area ratio increases.

[0058] After the intermediate solution heat treatment [Step 9], the aging-precipitation heat treatment [Step 10] is conducted, and then a finish cold-rolling [Step 11], and a temper annealing [Step 12] may be conducted, in this order.

[0059] Contrary to the above, in a conventional method of producing a precipitation-type copper alloy, a copper alloy raw material is subjected to: casting [Step 1] to give an ingot, and the resultant ingot is subjected to homogenization heat treatment [Step 2], followed by hot rolling [Step 3], cooling (water cooling) [Step 4], face milling [Step 5], and cold-rolling [Step 6], in this order, to give a thin sheet. Then, the resultant thin sheet is subjected to: intermediate solution heat treatment [Step 9] at a temperature in the range of 700 to 1,000°C, to thereby form a solid solution of solute atoms again, followed by aging-precipitation heat treatment [Step 10], finish cold-rolling [Step 11], and, if necessary, temper annealing [Step 12], to satisfy the required mechanical strength. In these series of steps, the texture in the copper alloy sheet material is determined on the most thereof, by the recrystallization, which occurs upon the intermediate solution heat treatment, and is finally determined, by the rotation of the orientations, which occurs upon the finish rolling.

[0060] In comparison with the production method of the present invention, two steps of: the intermediate annealing [Step 7] and the intermediate warm-rolling [Step 8], are not conducted in the conventional art.

[0061] Next, the explanation is given on an embodiment in which conditions of each step of the production method of the present invention are set in more detail.

[0062] In the casting [Step 1], the copper alloy raw material, containing at least Ni in an amount of 1.0 to 5.0 mass%, and Si in an amount of 0.1 to 1.0 mass%, and optionally containing other element(s) such that any of the additional alloying elements would be suitably contained, with the balance being Cu and unavoidable impurities, is melted in a high-frequency melting furnace, followed by cooling at a cooling speed of 0.1 to 100°C/sec, to obtain an ingot. This ingot is subjected to the homogenization heat treatment [Step 2] at 800 to 1,020°C for 3 minutes to 10 hours, followed by the hot rolling [Step 3], and water quenching (this corresponds to the cooling [Step 4]). Further, the surface oxide layer is removed by the face milling [Step 5]. Then, the cold-rolling [Step 6] is conducted at a rolling reduction ratio of 80% to 99.8%, to obtain the thin sheet.

[0063] Then, the intermediate annealing [Step 7] is conducted at 400°C to 700°C for 5 seconds to 20 hours, followed by heating under the condition of 100°C to 400°C, and the intermediate warm-rolling [Step 8] under the temperature at a rolling reduction ratio of 5% to 50%. Herein, the warm-rolling means that rolling is conducted at the temperature of 100°C to 400°C.

[0064] Then, the intermediate solution heat treatment [Step 9] is conducted at 600 to 1,000°C for 5 seconds to 1 hour. Then, the aging-precipitation heat treatment [Step 10] at 400 to 700°C for 5 minutes to 10 hours, preferably under an inert gas atmosphere, such as Ni and Ar, is conducted, and then, the finish cold-rolling [Step 11] at a rolling reduction ratio of 3 to 25%, and the temper annealing [Step 12] at 200 to 600°C for 5 seconds to 10 hours may be conducted, in this order, to obtain the copper alloy sheet material of the present invention.

[0065] In the production method of the present invention, in a case where there is no particular necessity for the properties or state of the resultant sheet material, one or more of the steps of the face milling [Step 5], the finish cold-rolling [Step 11], and the temper annealing [Step 12] may be omitted and may not be conducted.

[0066] In this embodiment, the hot-rolling [Step 3] is to conduct, at the temperature region from 700°C to the reheated temperature (1,020°C), working for breaking the cast structure and segregation to form a homogeneous structure, and working for making grains fine by dynamic recrystallization.

[0067] In the intermediate annealing [Step 7], a heating is conducted such that the microstructure of the resultant alloy would not be recrystallized in the whole. Then, heating at a temperature range at which recrystallization does not occur is conducted preferably at 100°C to 400°C, more preferably 120°C to 380°C, and particularly preferably 140°C to 360°C, and the intermediate warm-rolling [Step 8] is conducted under the temperature, at a rolling reduction ratio of preferably 5% to 50%, more preferably 7% to 45%, and particularly preferably 10% to 40%, to control introduction and release of a working strain.

[0068] When the rolling reduction ratio in this intermediate warm-rolling [Step 8] is too low, the working strain is small, and the grains are coarsened in the subsequent intermediate solution heat treatment [Step 9], resulting in that bending wrinkles become large, to make the characteristics poor. On the other hand, when the rolling reduction ratio in the intermediate warm-rolling [Step 8] is too high, the Cube orientation which is grown in the recrystallization solution heat treatment [Step 9] rotates to other orientations, resulting in lowering of the Cube orientation area ratio. Further, when the heating temperature in the intermediate warm-rolling [Step 8] is lower than 100°C, the release of working strain is less, and on the contrary, when this heating temperature is higher than 400°C, recrystallization is apt to progress along with the progress of the release of the working strain. Thus, in each case, in the subsequent intermediate solution heat treatment [Step 9], the homogeneous dispersibility of the Cube orientation grains at strain-induced grain boundary migration becomes not sufficient. As a result, in any case in which the heating temperature is too high or too low in the intermediate warm-rolling [Step 8], the resultant copper alloy sheet material is caused with the deflection anisotropy as the anisotropy in bending, and the proof stress anisotropy as the anisotropy in mechanical strength.

[0069] In the intermediate solution heat treatment [Step 9], the Cube orientation area ratio increases in the resultant recrystallized texture. Herein, when the heat treatment temperature in the intermediate annealing [Step 7] before the intermediate solution heat treatment [Step 9] is set to be higher than a temperature within the above-described range, the surface oxide layer is formed, which is not preferable. Thus, the heat treatment temperature in the intermediate annealing [Step 7] is preferably set to 400°C to 700°C. In particular, although it is difficult to make an ambiguous determination, when the heat treatment temperature in the intermediate annealing [Step 7] is set within the above-described temperature range, the Cube orientation area ratio has a tendency to increase in the intermediate solution heat treatment [Step 9].

[0070] After the intermediate solution heat treatment [Step 9], the aging-precipitation heat treatment [Step 10] is conducted, and then the finish cold-rolling [Step 11] and the temper annealing [Step 12] may be conducted. With regard to the recrystallized texture formed upon the intermediate solution heat treatment [Step 9], it is effective to conduct a predetermined working in the intermediate warm-rolling [Step 8], to increase the Cube orientation area ratio, due to the strain-induced grain boundary migration. Further, when a crystal orientation is controlled to a certain direction in the intermediate warm-rolling [Step 8], this control contributes to development of the Cube orientation grains. Further, by allowing the alloying elements to precipitate from solid solution by conducting the aging-precipitation heat treatment [Step 10], the mechanical strength can be enhanced, due to precipitation hardening. Furthermore, the sheet thickness may be finally adjusted, by conducting the finish cold-rolling [Step 11]. Furthermore, the temper of the sheet material may be finally adjusted, by conducting the temper annealing [Step 12].

[0071] Further, when a further working strain is introduced by the cold-rolling [Step 6], a heat treatment is conducted in the intermediate annealing [Step 7] at 400°C to 700°C for 5 seconds to 20 hours, and the intermediate warm-rolling [Step 8] is further conducted, the Cube orientation area ratio in the recrystallized texture in the intermediate solution treatment [Step 9] remarkably increases.

[0072] The object of the intermediate annealing [Step 7] is to obtain a sub-annealed structure, which is partially recrystallized without being completely recrystallized. The object of the intermediate warm-rolling [Step 8] is to allow introduction and release of a microscopically nonuniform strain to progress, by rolling under the conditions of a heating temperature of 100°C to 400°C and a rolling reduction ratio of 5% or more.

[0073] Due to the actions and effects of the intermediate annealing [Step 7] and the intermediate warm-rolling [Step 8], it becomes possible to grow the Cube orientation grains, and to make the Cube orientation grains fine and homogeneous dispersion thereof in the intermediate solution treatment [Step 9]. In the intermediate warm-rolling [Step 8], introduction of a strain by rolling and release of the strain by heating are carried out. By controlling both of the introduction and the release appropriately, it becomes possible to develop the Cube orientation grains by the strain-induced grain boundary migration in the intermediate solution heat treatment [Step 9], to make the Cube orientation grains fine, and to make the homogeneous dispersibility of the Cube orientation grains higher. That is, the Cube orientation grains can be developed, by the introduction of the strain, and the Cube orientation grains can be made fine and the homogeneous dispersibility of the Cube orientation grains can be made higher, by the release of the strain. In the usual method in the conventional art, the primary object of the heat treatment, such as the intermediate solution treatment [Step 9], is to recrystallize a material so as to reduce a load in the subsequent step, thereby lowering the strength, but the object of the said heat treatment in the present invention is completely different from the above object in the conventional art.

[0074] The sheet thickness of the copper alloy sheet material of the present invention is not particularly limited, and the sheet thickness is generally 0.03 mm to 0.50 mm, and preferably 0.05 mm to 0.35 mm.

[0075] When the copper alloy sheet material of the present invention satisfies the conditions described above, the following characteristics, for example, which are required for a copper alloy sheet material for use in connectors, can be satisfactorily exhibited, which is preferable.

[0076] With regard to the bending property as one of the characteristics, it is preferable that no crack be present in the bent surface portion in a 180° tight U-bending test. Detailed conditions of the test are set as described in the Examples section.

[0077] The deflection coefficient as one of the characteristics is preferably 130 GPa or less. Detailed conditions thereof are set as described in the Examples section. The lower limit of the deflection coefficient exhibited by the copper alloy sheet material of the present invention is not particularly limited, but the lower limit is generally 90 GPa or more.

[0078] The proof stress as one of the characteristics is preferably 700 MPa or more, and more preferably 750 MPa or more. Detailed measurement conditions thereof are set as described in the Examples section. The upper limit of the proof stress exhibited by the copper alloy sheet material of the present invention is not particularly limited, but the upper limit is generally 900 MPa or less.

[0079] As one of the characteristics, the copper alloy sheet material has an electrical conductivity of preferably 5%IACS or more, more preferably 10%IACS or more, and particularly preferably 20%IACS or more. Herein, the term IACS is an abbreviation of international annealed copper standard. Unless otherwise specified, the specific measurement conditions are set as described in the Examples section. Although the upper limit value of the electrical conductivity of the copper alloy sheet material of the present invention is not particularly limited, it is generally 50%IACS or less.

EXAMPLES

[0080] 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.

(Examples 1 to 14 and Comparative Examples 1 to 4)

[0081] The respective alloy containing Ni, Si, and optionally any of additional alloying elements, in the amounts as shown in Table 1, with the balance being Cu and unavoidable impurities, was melted in a high-frequency melting furnace, followed by the casting [Step 1] by cooling at a cooling speed of 0.1 to 100°C/sec, to obtain the respective ingot.

[0082] This resultant respective ingot was subjected to the homogenization heat treatment [Step 2] at 800 to 1,020°C for 3 minutes to 10 hours, followed by the hot rolling [Step 3] as a hot working at 700°C or higher and a reheated temperature of 1,020°C or lower, and then the water quenching (this corresponds to the water cooling [Step 4]), to obtain a hot-rolled sheet. Then, the hot-rolled sheet was subjected to the face milling [Step 5] of the surface, so as to remove an oxide layer. Then, the respective resultant sheet was subjected to the cold-rolling [Step 6] at a rolling reduction ratio of 80 to 99.8%, to obtain a thin sheet.

[0083] Then, the thin sheet was subjected to the intermediate annealing [Step 7] in heating for 5 seconds to 20 hours at 400°C to 700°C, followed by subjected to further heating to 100°C to 400°C and the intermediate warm-rolling [Step 8] at a rolling reduction ratio of 5 to 50% under the temperature.

[0084] Then, the intermediate solution treatment [Step 9] was conducted at 600 to 1,000°C for 5 seconds to 1 hour. Then, the respective resultant sheet was subjected to the aging-precipitation heat treatment [Step 10] at 400°C to 700°C for 5 min to 1 hours, under an inert gas atmosphere, followed by the finish cold-rolling [Step 11] at a rolling reduction ratio of 3% to 25%, and the temper annealing [Step 12] at 200°C to 600°C for 5 seconds to 10 hours, to give the respective sample specimen (Examples 1 to 14 and Comparative Examples 1 to 4) of the copper alloy sheet material. The final sheet thickness of the respective sample specimen was set to be 0.08 mm.

[0085] The compositions and characteristics of the resultant Examples 1 to 14, and Comparative Examples 1 to 4, are shown in Tables 1 and 2.

[0086] After the respective heat treatment or rolling, pickling or surface grinding was conducted according to the state of oxidation or roughness of the material surface, and correction with a tension leveler was conducted according to the shape. The working temperature in the hot working [Step 3] was measured, by a radiation thermometer that was installed on the entry side and exit side of the rolling machine.

[0087] The thus-obtained sample specimens were subjected to examination of the properties as described below.

(a) Cube orientation area ratio

[0088] The measurement was conducted with the EBSD method in a measurement region of 0.09 μm^2 (300 μm × 300 μm), under the conditions of a scan step of 0.1 μm. Further, with regard to the measurement area, 60 μm × 60μ m was set as one block, and the measurement area was set to measure total 25 blocks (5 blocks × 5 blocks) at one visual field. In this case, the scanning step was set to 0.1 μm step as described above, to measure fine grains. In analysis, EBSD measurement results in the measurement area of 300 μm × 300 μm were divided to the above-described 25 blocks. The Cube orientation area ratio, the average grain area, the number of grains, and the average grain area of the matrix containing the Cube orientation grains in each block were confirmed. With regard to electron rays, a thermo-electron from a tungsten filament of a scanning electron microscope was utilized as a generation source.

(b) 180° Tight U-bending test

[0089] Test specimens with width 0.25 mm and length 1.5 mm were taken out, by press punching in a direction perpendicular to the rolling direction. With respect to the test specimens, a W-bent test specimen in which a bending axis was perpendicular to the rolling direction was set as GW (Good Way), and a W-bent test specimen in which the bending axis was parallel to the rolling direction was set as BW (Bad Way). The test specimens were subjected to 90° W-bending according to the Technical Standard JCBA-T307 (2007) by the Japan Copper and Brass Association, followed by 180° tight U-bending by a compression test machine without any inner radius. The resultant bent-surface was observed with a scanning electron microscope with a magnification of 100x, to examine whether or not cracking occurred. A test specimen without any cracks was indicated by "o (good)", and a test specimen having cracks was indicated by "x (poor)". In a size of cracks, the maximum width was 30 μm to 100 μm, and the maximum depth was 10 μm or more.

(c) Deflection coefficient

[0090] The test specimen was taken out, by press punching to have a width of 0.25 mm in a direction perpendicular to the rolling direction, and a length of 1.5 mm in a direction parallel to the rolling direction. The front surface and backing surface of the test specimen was measured ten times, respectively, by a cantilever beam, and an average value thereof is shown.

[0091] The deflection coefficient E (GPa) is expressed by the following expression (1):

$$E=4a/b\times(L/t)^3 \qquad (1)$$

wherein "a" represents a gradient between a displacement "f' and a stress "w", "b" represents a width of the specimen, "L" represents a distance between a fixed end and a loading point, and "t" represents the sheet thickness of the sample specimen.

[0092] In this test, the anisotropy in deflection between the parallel direction to rolling and the perpendicular direction to rolling was confirmed.

(d) Proof stress [Y]

[0093] In the measurement of the deflection coefficient, a proof stress Y (MPa) was calculated from a pushed amount (displacement) to the elastic limit of each test specimen, by the following expression (2):

$$Y=\{(3E/2)\times t\times(f/L)\times 1{,}000\}/L \qquad (2)$$

wherein "E" represents the deflection coefficient, "t" represents the sheet thickness, "L" represents the distance between the fixed end and the loading point, and "f" represents the displacement (pushed depth).

[0094] In this test, the anisotropy in the proof stress between the parallel direction to rolling and the perpendicular direction to rolling was confirmed.

(e) Electrical conductivity [EC]

[0095] 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.

[0096] With respect to Examples 1 to 14 according to the present invention, and Comparative Examples 1 to 4, Cu, Ni, Si, as main raw alloying materials, and optional additional alloying elements were blended in a composition shown in Table 1, followed by melting, and then casting.

[0097] As shown in Table 2, with the production conditions of Example 1 to 14, the intermediate warm-rolling [Step 8] was carried out by heating to 100°C to 400°C, followed by rolling at a rolling reduction ratio at 5% or more. In the resultant microstructure (texture) of Examples 1 to 14, the Cube orientation area ratio was 5% to 50%, the average grain area of the Cube orientation grains was 1.8 μm^2 to 45.0 μm^2, the number of Cube orientation grains per one block (60 μm × 60 μm) was 40 to 100, and the average grain area of the matrix containing the Cube orientation grains was 50 μm^2 or less. In the properties of Example 1 to 14, all of the results of the 180° tight U-bending, the deflection anisotropy, and the proof stress anisotropy were excellent.

[0098] In Comparative Examples 1 to 4, any of the requirements in the production method of the present invention was not satisfied, and thus the Cube orientation area ratio, and the number of Cube orientation grains per one block were not satisfied.

[0099]

Table 1

ID No.	Alloying elements			
	mass%			
	Ni	Si	Others	Cu
Ex 1	3.0	0.5	Sn=0.2, Zn=0.4, P=0.005	Balance
Ex 2	1.5	0.7	Mn=0.1, Cr=0.05, Fe=0.01	Balance
Ex 3	4.5	1.0	Ag=0.2, B=0.1, Mg=0.06	Balance
Ex 4	1.0	0.5	Sn=0.4, Mg=0.1, Cr=0.05, Fe=0.01	Balance
Ex 5	2.2	0.3	Zn=0.1, Hf=0.005	Balance
Ex 6	5.0	0.1	Cr=0.005	Balance
Ex 7	1.1	0.4	Sn=0.1, Zr=0.01	Balance
Ex 8	2.3	0.6	Zn=0.5, Cr=0.15, Sn=0.15, Mg=0.1	Balance
Ex 9	4.8	2.0	Zn=0.2, B=0.05, P=0.01	Balance
Ex 10	3.8	1.4	Zn=0.5, Cr=0.2, Sn=0.2, Mg=0.1	Balance
Ex 11	1.2	1.8	None	Balance
Ex 12	1.0	0.5	None	Balance
Ex 13	4.9	0.2	None	Balance
Ex 14	4.8	1.9	None	Balance
C Ex 1	4.0	0.4	Sn=0.1, Mg=0.05, Fe=0.01	Balance
C Ex2	3.0	0.6	Ag=0.3, Cr=0.2	Balance
C Ex 3	1.0	0.2	Zn=0.4	Balance
C Ex 4	2.0	0.1	Mn=0.3, B=0.1	Balance
"Ex" means Example according to this invention; and "C Ex" means Comparative Example. (The same will be applied in below.)				

{0060}

Table 2

ID No.	Production step: Intermediate warm-rolling [Step 8]		Texture			
	Heating temp. (°C)	Rolling reduction ratio (%)	Area ratio of Cube orientation {0 0 1} <1 0 0> (%)	Av. area of Cube orientation grains (μm²)	The number of Cube orientation grains per block of 60 μm square (number)	Av. area of grains of the matrix (μm²)
Ex 1	350	10	20	14.4	50	45
Ex 2	200	5	34	14.6	84	18
Ex 3	400	15	10	4.0	90	10
Ex 4	100	20	5	1.8	100	5
Ex 5	160	8	26	21.3	44	29
Ex 6	220	40	13	7.2	65	9
Ex 7	380	25	50	45.0	40	50
Ex 8	270	18	15	7.3	74	22
Ex 9	120	22	9	4.1	80	30
Ex 10	330	30	30	11.4	95	12
Ex 11	180	10	11	7.2	55	42
Ex 12	250	15	20	17.1	42	25
Ex 13	300	7	23	16.6	50	19
Ex 14	120	18	36	16.8	77	33
C Ex 1	200	4	10	90.0	4	100
C Ex 2	500	20	15	108.0	5	75
C Ex 3	None	None	1	4.0	9	4
C Ex 4	50	35	18	81.0	8	47

Table 2 *(continued)*

ID No.	Properties: 180°tight U-bending		Deflection coefficient (GPa)			Proof stress (MPa)			Electrical conductivity (%IACS)
	GW	*BW*	*GW*	*BW*	Deflection *coefficient* anisotropy	*GW*	*BW*	Proof stress anisotropy	
Ex 1	○	○	111	120	9	773	765	-8	32
Ex 2	○	○	109	113	4	760	756	-4	40
Ex 3	○	○	114	115	1	782	774	-8	30
Ex 4	○	○	120	123	3	790	781	-9	35
Ex 5	○	○	103	106	3	711	710	-1	39
Ex 6	○	○	109	110	1	730	725	-5	31
Ex 7	○	○	101	104	3	725	720	-5	40
Ex 8	○	○	128	126	-2	790	789	-1	38
Ex 9	○	○	130	129	-1	751	745	-6	33
Ex 10	○	○	100	103	3	700	710	10	30
Ex 11	○	○	113	118	5	760	755	-5	32
Ex 12	○	○	120	115	-5	800	794	-6	30
Ex 13	○	○	105	109	4	736	736	0	36
Ex 14	○	○	116	118	2	701	705	4	32
C Ex 1	○	×	130	146	16	730	680	-50	36
C Ex 2	○	×	115	138	23	715	644	-71	28
C Ex 3	×	×	142	155	13	695	603	-92	37
C Ex 4	○	×	123	147	24	704	650	-54	32

[0100] As shown in Tables 1 and 2, in a case of satisfying the ranges according to the present invention, that is, having a composition containing 1.0 mass% to 5.0 mass% of Ni, 0.1 mass% to 2.0 mass% of Si, and optionally at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf in a total amount of 0.005 mass% to 1.0 mass%, with the balance being copper and unavoidable impurities, and satisfying the conditions in which, in the crystal orientation analysis by the electron backscatter diffraction method, the area ratio of the Cube orientation {0 0 1} <1 0 0> was 5% to 50%, in addition to those, preferably the average grain area of grains having the Cube orientation was 1.8 μm^2 to 45.0 μm^2, and further the average grain area of the grains of the matrix was 50 μm^2 or less, all of the bending property, the deflection coefficient property, and the proof stress property were favorable. In the bending property, no cracks occurred at the bent vertex. Further, in the deflection coefficient property, the deflection coefficient anisotropy was 10 GPa or less, and in the proof stress property, the proof stress anisotropy was 10 MPa or less. Both of the deflection coefficient anisotropy and the proof stress anisotropy were small.

[0101] Thus, the copper alloy sheet material of the present invention can be provided as a copper alloy sheet material suitable for lead frames, connectors, terminal materials, and the like for electrical or electronic equipments, and for connectors, for example, to be mounted on automotive vehicles, for terminal materials, relays, switches, and the like.

[0102] Further, as shown in Table 2, in the samples of the Comparative Examples, at least one property was poor.

[0103] That is, in Comparative Examples 1, 2, and 4, since the average grain area of the Cube orientation grains was too large, the bending property of BW, the deflection coefficient anisotropy and the proof stress anisotropy were poor. In Comparative Example 3, since the Cube orientation area ratio was too small, the bending property (GW, BW), the deflection anisotropy, and the proof stress anisotropy were poor.

[0104] Further, electrical conductivity of 30%IACS to 45%IACS was exhibited in each case.

(Conventional examples)

[0105] Copper alloy sheet materials were prepared with the respective alloy composition as shown in Table 3 (the balance was copper (Cu)) in the same manner as in the above Example 1, except for not conducting the intermediate annealing [Step 7] and the heating in the intermediate warm-rolling [Step 8]. Sample specimens of the thus-obtained copper alloy sheet materials were evaluated in the same manner as in the above Example 1. The results are shown in Table 4.

Table 3

ID No.	Alloying elements mass%			
	Ni	Si	Others	Cu
Conv. Ex 1	3.2	0.7	Zn=1.0, Sn=0.2	Balance
Conv. Ex 2	2.0	0.5	Zn=1.0, Sn=0.2, Mn=0.2	Balance
Conv. Ex 3	3.6	1.0	Zn=0.5, Sn=0.2	Balance
"Conv. Ex " means Conventional Example				

Table 4

ID No.	Production step: Intermediate warm-rolling [Step 8]		Texture			
	Heating temp. (°C)	Rolling reduction ratio (%)	Area ratio of Cube orientation {0 0 1} <1 0 0> (%)	Av. area of Cube orientation grains (μm^2)	The number of Cube orientation grains per block of 60 μm square (number)	Av. area of grains of the matrix (μm^2)
Conv. Ex 1	None	95	15	60.0	9	95
Conv. Ex 2	None	95	18	92.6	7	177
Conv. Ex 3	None	95	16	96.0	6	113

Table 4 (continued)

ID No.	Properties								
	180°U tight bending		Deflection coefficient (GPa)			Proof stress (MPa)			Electrical conductivity (%IACS)
	GW	BW	GW	BW	Deflection coefficient anisotropy	GW	BW	Proof stress anisotropy	
Conv. Ex 1	○	×	113	131	18	740	726	-14	40
Conv. Ex 2	○	×	116	133	17	715	698	-17	39
Conv. Ex 3	○	×	117	135	18	705	680	-25	35

[0106] As is clear from Tables 3 and 4, in the copper alloy sheet materials in Conventional Examples 1 and 2, which did not satisfy the alloy composition defined in the present invention, and which were produced without conducting the intermediate annealing [Step 7] and without conducting heating in the intermediate warm-rolling [Step 8], even if the production conditions (respective steps and conditions) other than those two steps were employed, the average grain area of the Cube orientation was conspicuously large, the number of cube grains per one block was conspicuously small, and the anisotropy in the deflection coefficient and the anisotropy in the proof stress each were conspicuously large.

[0107] Further, in the copper alloy sheet material in Conventional Example 3, which satisfied the alloy composition defined in the present invention, but which was produced without conducting the intermediate annealing [Step 7] and without conducting heating in the intermediate warm-rolling [Step 8], even if the production conditions (respective steps and conditions) other than those two steps were employed, the average grain area of the Cube orientation was conspicuously large, the number of cube grains per one block was conspicuously small, the bending property (BW) was poor, and the anisotropy in the deflection coefficient and the anisotropy in the proof stress each were conspicuously large.

[0108] Apart from these, in order to clarify the difference between copper alloy sheet materials produced under the conventional production conditions and the copper alloy sheet material according to the present invention, copper alloy sheet materials were produced under the conventional production conditions, and evaluations of the same characteristic items as described above were conducted. The working ratio was adjusted so that, unless otherwise specified, the thickness of the respective sheet material would be the same as the thickness in the Examples described above.

(Comparative Example 101) ••• The conditions of Example 1 in JP-A-2011-162848

[0109] A copper alloy having a composition containing 3.2 mass% of Ni, 0.7 mass% of Si, 1.0 mass% of Zn, and 0.2 mass% of Sn was melted and casted. The resultant ingot was subjected to face milling, followed by a homogenization heat treatment, and hot-rolling in which a termination temperature was set to 550°C to 850°C. After quenching with water cooling, an oxide layer on the surface was removed by mechanical grinding (face milling). Then, rolling to a predetermined sheet thickness was conducted by cold-rolling, followed by subjecting to cold-rolling at a working ratio of 90% or more. Then, heating was conducted to a temperature of 800°C to 900°C at a temperature rising speed of 0.1°C/s or less, followed by subjecting to a solution treatment.

[0110] Then, an aging treatment was conducted at 500°C. The time period for the aging treatment was adjusted to a time period in which the hardness reached a peak by aging at 460°C, depending on the composition of the copper alloy. With respect to this time period for the aging treatment, an optimal time period for the aging treatment was obtained by a preliminary experiment depending on the composition of the alloy of this Example 1 of JP-A-2011-162848.

[0111] Then, the sheet material after the above aging treatment was further subjected to finish cold-rolling at a rolling reduction ratio of 40%. Further, the resultant sheet material was subjected to low-temperature annealing at 480°C for 30 seconds. Where necessary, grinding and face milling were conducted in the mid course, and the sheet thickness was set to 0.10 mm.

[0112] This was utilized as Sample specimen c01.

[0113] With regard to the resultant Sample specimen c01, as compared to the Examples according to the present invention with respect to production conditions, the intermediate annealing [Step 7] was not conducted, and the intermediate warm-rolling [Step 8] under a heating temperature before the solution heat treatment [Step 9] was also not conducted. Further, since the temperature rising speed in the solution heat treatment was slow, grain growth in the vicinity of the reached temperature was significant, to coarsen grains. In the resultant texture, the area of the Cube orientation grains was as conspicuously large as 150 μm^2 or more. Further, the anisotropy in the deflection coefficient was as conspicuously large as more than 10 GPa, and the anisotropy in the strength was as conspicuously large as more than 15 MPa. Thus, Sample specimen c01 in Comparative Example 101 was poor in the results, in which the characteristics required for the present invention were not satisfied.

(Comparative Example 102) ••• The conditions of Examples 1 and 4 in JP-A-2011-12321

[0114] A copper alloy (Example 1 of the publication, JP-A-2011-12321) having a composition containing 2.8 mass% of Ni and 0.9 mass% of Si, and a copper alloy (Example 4 of the publication, JP-A-2011-12321) having a composition containing 2.8 mass% of Ni, 0.9 mass% of Si, 0.1 mass% of Zn, 0.1 mass% of Mg, and 0.1 mass% of Sn, each were melted in a coreless furnace (high-frequency electrically-induction melting furnace) in the air in a state of being coated with charcoal, and the resultant respective molten metal was casted in a casting mold of which four sides were surrounded by a copper mold, to prepare an ingot with thickness 250 mm, width 620 mm, and length 2,500 mm, respectively.

[0115] Then, an SUS rod with a diameter of 3 mmϕ was inserted in a vertical direction from a molten metal surface located at an upper end portion of the casting mold, at an intersection position between a width 155-mm position and a thickness 125-mm position of the casting mold, to measure the depth of a non-solidified portion. A value obtained by subtracting the length of the casting mold (the length of the copper mold) from the depth of the thus non-solidified portion, was defined as a distance from a lower end depth of the casting mold to a solidification termination depth. Specifically, the distance was 300 mm (Example 1 of JP-A-2011-12321) and 260 mm (Example 4 of JP-A-2011-12321), respectively. In order to set the distance to be 250 mm or more, the casting was conducted, by adjusting a casting speed within a range of 50 mm/min/ to 200 mm/min, to obtain the ingots, respectively.

[0116] From the thus-obtained ingot, a block of 250 mm × 620 mm × 300 mm of a constant region was cut to take out, and a slice (250 mm × 15 mm × 300 mm) of a cross-section parallel with the casting direction was collected at the central portion of the width of 620 mm. The slice was immersed and etched in nitric acid for 0.5 hours to 1 hour, and a columnar crystal in a [100] axis direction was obtained from the macro structure that was obtained after etching. An angle made by a face perpendicular to the casting direction and the direction of the [100] axis of the columnar crystal was measured. Specifically, the angle was 13° (Example 1 of JP-A-2011-12321) and 11° (Example 4 of JP-A-2011-12321), respectively.

[0117] Further, after subjecting the ingot to a homogenization treatment, a temperature of the resultant ingot was adjusted to 500°C to 1,000°C, followed by rolling at a total working ratio of 60% to 96%, and then directly cooling the rolled material with water, to obtain a coil with thickness approximately 10 mm. The surface of the rolled material was subjected to face-milling, to remove oxide scale. A proportion of the Cube orientation of the rolled material at this point of time was 5% to 95%. Then, to the rolled material, cold-rolling at a working ratio of 85% to 99.8%, a solution heat treatment at 700°C to 1,020°C for 5 sec to 1 hour, finish cold-rolling at a working ratio of 1% to 60%, and temper annealing at 200°C to 600°C for 5 sec to 10 hours, were conducted in this order, to obtain specimens with thickness 0.15 mm, respectively.

[0118] The specimens were indicated as a sample d01 (Example 1 of JP-A-2011-12321) and a sample d02 (Example 4 of JP-A-2011-12321), respectively.

[0119] With regard to the resultant Sample specimens d01 and d02, as compared to the Examples according to the present invention with respect to production conditions, the intermediate annealing [Step 7] was not conducted, and the intermediate warm-rolling [Step 8] under a heating temperature before the solution heat treatment [Step 9] was also not conducted. In the thus-obtained microstructure/texture, the area ratio of the Cube orientation grains was 35% for the sample d01 (Example 1 of JP-A-2011-12321), and 7% for the sample d02 (Example 4 of JP-A-2011-12321). However, grain growth was significant in each case, and thus the average grain area of the matrix containing the Cube orientation grains was 254 μm^2 for the sample d01 (Example 1 of JP-A-2011-12321) and 201 μm^2 for the sample d02 (Example 4 of JP-A-2011-12321), and the grains were coarsened, respectively. Further, the anisotropy in the deflection coefficient was as large as more than 10 GPa, and the anisotropy in the strength was as large as more than 15 MPa, resulting in that the characteristics required for the present invention were not satisfied.

[0120] 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.

[0121] This application claims priority on Patent Application No. 2011-102996 filed in Japan on May 2, 2011, which is entirely herein incorporated by reference.

Claims

1. A copper alloy sheet material, having a composition containing Ni in an amount of 1.0 mass% to 5.0 mass%, and Si in an amount of 0.1 mass% to 2.0 mass%, with the balance being copper and unavoidable impurities,
   wherein, in a crystal orientation analysis by an electron backscatter diffraction method, an area ratio of grains having an orientation in which a deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 5% to 50%, and 40 to 100 grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° are dispersed within 60 μm square.

2. A copper alloy sheet material, having a composition containing Ni in an amount of 1.0 mass% to 5.0 mass%, Si in an amount of 0.1 mass% to 2.0 mass%, and at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Fe, and Hf, in an amount of 0.005 mass% to 1.0 mass% in total, with the balance being copper and unavoidable impurities,
   wherein, in a crystal orientation analysis by an electron backscatter diffraction method, an area ratio of grains having an orientation in which a deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 5% to 50%, and 40 to 100 grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° are dispersed within 60 μm square.

3. The copper alloy sheet material according to Claim 1 or 2, wherein an average grain area of the grains having the orientation in which the deviation from the Cube orientation {0 0 1} <1 0 0> is within 15° is 1.8 μm^2 to 45.0 μm^2.

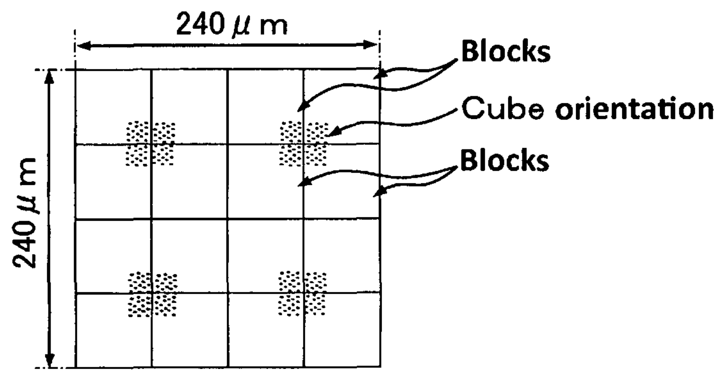
4. The copper alloy sheet material according to any one of Claims 1 to 3, wherein an average grain area of grains in a matrix is 50 μm^2 or less.

5. The copper alloy sheet material according to any one of Claims 1 to 4, wherein a difference between a deflection coefficient in a parallel direction to rolling and a deflection coefficient in a perpendicular direction to rolling is 10 GPa or less in terms of an absolute value thereof, and wherein a difference between a proof stress in the parallel direction to rolling and a proof stress in the perpendicular direction to rolling is 10 MPa or less in terms of an absolute value thereof.

6. A method of producing a copper alloy sheet material, containing: casting a copper alloy raw material into an ingot, followed by subjecting to a homogenization heat treatment, hot-rolling, cold-rolling to a thin sheet, and an intermediate solution heat treatment to form a solid solution of solute atoms in the thin sheet again,
wherein the copper alloy raw material has an alloy composition of the copper alloy sheet material according to Claim 1 or 2, and
wherein the method contains the steps, in this order, of:

the homogenization heat treatment at 800°C to 1,020°C for 3 minutes to 10 hours;
the cold-rolling at a rolling reduction ratio of 80% to 99.8%;
an intermediate annealing at a temperature of 400°C to 700°C, which is lower than a recrystallization temperature, for 5 seconds to 20 hours;
heating to 100°C to 400°C, followed by intermediate warm-rolling in which a rolling reduction ratio is 5% to 50% at the temperature;
the intermediate solution heat treatment at 600°C to 1,000°C for 5 seconds to 1 hour; and
an aging-precipitation heat treatment at 400°C to 700°C for 5 minutes to 10 hours.

Fig. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/061479

A. CLASSIFICATION OF SUBJECT MATTER
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, *C22F1/00*(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
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.
X A	WO 2009/148101 A1 (The Furukawa Electric Co., Ltd.), 10 December 2009 (10.12.2009), claims; paragraphs [0024], [0033], [0037] & JP 4875768 B & US 2011/0073221 A1 & EP 2298945 A1 & CN 102105610 A	1-4 5,6
X A	JP 2011-12321 A (The Furukawa Electric Co., Ltd.), 20 January 2011 (20.01.2011), claims; paragraph [0020] (Family: none)	2-4 1,5,6
A	JP 2006-152392 A (Kobe Steel, Ltd.), 15 June 2006 (15.06.2006), entire text (Family: none)	1-6

[X] Further documents are listed in the continuation of Box C. [ ] See patent family annex.

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Date of the actual completion of the international search 25 July, 2012 (25.07.12)	Date of mailing of the international search report 07 August, 2012 (07.08.12)
Name and mailing address of the ISA/ Japanese Patent Office	Authorized officer
Facsimile No.	Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/061479

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2011-52316 A (Kobe Steel, Ltd.), 17 March 2011 (17.03.2011), entire text (Family: none)	1-6
A	JP 2006-16687 A (Hitachi Cable, Ltd.), 19 January 2006 (19.01.2006), entire text (Family: none)	1-6

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

REFERENCES CITED IN THE DESCRIPTION

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- JP 2005350695 A **[0008]**
- JP 2011162848 A **[0008] [0110]**
- JP 2011012321 A **[0008] [0114] [0115] [0116] [0118] [0119]**
- JP 2011102996 A **[0121]**