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

(57) {Problems} To provide a copper alloy sheet material and a method of producing the same, which sheet material is excellent in a bending property, and has an excellent mechanical strength, and which is suitable for lead frames, connectors, terminal materials, and the like in electrical/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, containing Ti in an amount of 1.0 to 5.0 mass%, with the balance being copper and unavoidable impurities, wherein an area ratio of Cube orientation {0 0 1} <1 0 0> is 5 to 50%, in crystal orientation analysis by an EBSD analysis in the sheet thickness of the sheet material; and a method of producing the same.

EP 2 612 934 A1

## Description

TECHNICAL FIELD

**[0001]** The present invention relates to a copper alloy sheet material and a method of producing the same, and specifically 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, motors, and the like, for parts to be mounted on automotives or for parts in electrical/electronic equipments.

BACKGROUND ART

**[0002]** Characteristics required for copper alloy sheet materials that are used in applications, such as lead frames, connectors, terminal materials, relays, switches, and sockets, for parts to be mounted on automotives or for electrical/ electronic equipments, include, electrical conductivity, proof stress (yield stress), tensile strength, bending property, and stress relaxation resistance. In recent years, the demanded levels for the characteristics to those parts 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/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 cold-working ratio high.

**[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. In a conventional Cu-Ti-based alloy, in order to obtain high mechanical strength, high work hardening was obtained by increasing a rolling working ratio, but this method deteriorates the bending property as described above, and thus a good balance between high mechanical strength and favorable bending property cannot be achieved.

**[0005]** In order to improve the bending property, there are some proposals based on controlling of crystal orientation. For example, the following disclosures were made on Cu-Ni-Si-based copper alloys. Patent Literature 1 proposed, 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 proposed, 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 proposed, 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 Cube orientation {1 0 0} <0 0 1>.

**[0006]** Further, the following disclosures were made for Cu-Ti-based copper alloys. In Patent Literature 4, the (3 1 1) plane is developed so as to adjust: $I(3\ 1\ 1)/I(11\ 1) \geq 0.5$, to thereby improve the press property. Patent Literature 5 proposed a copper alloy sheet material, which has a given average grain size and a given crystal orientation in which the X-ray diffraction intensity at the sheet plane of the copper alloy sheet material satisfy: $I\{4\ 2\ 0\}/I_0\{4\ 2\ 0\} > 1.0$, and which is high in the mechanical strength and excellent in the bending property after notching, by controlling the addition amounts of Ti and third elements other than Ti, the temperatures and rolling ratios at the respective stages of the hot-rolling that are conducted in two stages, the working ratio in the cold-rolling, the conditions in the solution treatment, and the conditions in the aging precipitation. Patent Literature 6 proposed a copper alloy having high mechanical strength, excellent bending property and high size stability, by controlling the conditions in homogenization, the final pass temperature in the hot-rolling, and the average working degrees of the respective passes in the hot-rolling, as well as the conditions in the solution treatments that are conducted in two stages, the working degree in the cold-rolling that is conducted after the respective solution treatments, and the conditions in aging. Patent Literature 7 tried to balance the mechanical strength and the bending property, by obtaining a recrystallized texture comprising {2 0 0} crystal plane as a main orientation component.

**[0007]** Further, a low Young's modulus (modulus of longitudinal elasticity) is required, as one of the characteristics required for copper alloy sheet materials for use in electrical/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 sheet material, the effects of variation in size, which affect to a contact pressure, can be decreased, and thus the designing of parts becomes readily.

**[0008]**

Patent Literature 1: JP-A-2006-009137 ("JP-A" means unexamined published Japanese patent application)
Patent Literature 2: JP-A-2008-013836
Patent Literature 3: JP-A-2006-283059
Patent Literature 4: JP-A-2006-249565
Patent Literature 5: JP-A-2010-126777
Patent Literature 6: JP-A-2007-270267
Patent Literature 7: JP-A-2011-26635

SUMMARY OF INVENTION

TECHNICAL PROBLEM

**[0009]** However, 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 specific planes. Further, in the invention described in Patent Literature 3, the mechanical strength and the bending property are balanced, by increasing the area ratio of Cube orientation to 50% or more in the Cu-Ni-Si-based alloy. In this technique, the control of the crystal orientations was attained, by decreasing the rolling working ratio after the solution heat treatment. In the invention described in Patent Literature 4, the (3 1 1) plane is developed by conducing cold-rolling in a state that the solute atoms are completely solidified, and the press property is improved by adjusting: I(3 1 1)/I(1 1 1) $\geq$ 0.5. In the production steps, the orientation is controlled by cold-rolling, recrystallization annealing, and the subsequent steps. In Patent Literature 5, the bending property after notching is improved, by controlling the average grain size to 5 to 25 $\mu$m and controlling the texture containing {4 2 0} crystal plane as a main orientation component. In the production method, Patent Literature 5 has descriptions on the conditions in hot-rolling, the conditions in cold-rolling, the conditions in solution heat treatment, and the conditions in aging precipitation, but the hot-rolling is conducted by two stages, and the solution treatment is conducted without conducting any intermediate annealing before the solution treatment and any subsequent cold-rolling. In Patent Literature 6, the wavelength and amplitude of the concentration wave (a so-called modulated structure) of titanium formed in the matrix, by having a group of the third elements precipitate as second phase particles. Further, the mechanical strength and the bending property are balanced, and the size accuracy of press working is also increased, by controlling the number density of the second phase particles. In the production method, the cold-rolling working ratio before the final solution is as high as 70 to 99%, and each thermal history in the solution treatments conducted in the two stages, the first and final stages, are completely different from those defined in the present invention. In Patent Literature 7, the mechanical strength and the bending property are balanced, by controlling the average grain size of the recrystallized grains in the solution heat treatment, to give a recrystallized texture containing {2 0 0} crystal plane as a main orientation component. In the steps, the retention is conducted at 450 to 600°C for 1 to 20 hours in the intermediate annealing after the cold-rolling, and these conditions are largely different from those in the present invention. Further, the bending property is improved by increasing the diffraction intensity of I{2 0 0}, but Patent Literature 7 has no description on decreasing of bending wrinkles, on a Young's modulus and a deflection coefficient.

On the other hand, along with the recent further downsizing, enhancement of the performance, high-density packaging, and the like of electrical or electronic equipments, the copper alloy materials for the electrical or electronic equipments have been required to have a bending property higher than the bending property assumed in the inventions described in the above patent literatures, and also to decrease bending wrinkles on a bent surface part.

**[0010]** It is necessary to cast Cu-Ti in an inert gas or a vacuum melting furnace so as to prevent oxidation of Ti, but coarse crystallized products and precipitates formed of oxides are present in a resultant ingot. It is assumed that there is a possibility that dislocation and/or strain are introduced on the periphery of those crystallized products and precipitates upon strong working (cold-rolling) at 80% or more, to thereby inhibit the rotation of the orientation in a recrystallization solution heat treatment by which Cube orientation is grown.

**[0011]** In view of the problems described above, the present invention is contemplated for providing a copper alloy sheet material, which is excellent in the bending property, and has an excellent mechanical strength, and which is suitable for lead frames, connectors, terminal materials, and the like in electrical/electronic equipments, for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like. The present invention is also contemplated for providing a method of producing the copper alloy sheet material.

## SOLUTION TO PROBLEM

**[0012]** The inventors of the present invention, having conducted investigations on copper alloy sheet materials appropriate for electrical/electronic part applications, found that there is a correlation between the accumulation ratio of Cube orientation and the bending property, to largely improve the bending property, the mechanical strength, the electrical conductivity, and the stress relaxation resistance, in Cu-Ti-based copper alloys. The inventors, having conducted an extensively study, found that these desired properties can be remarkably improved, by controlling a specific orientation texture of a specific copper alloy composition. Further, the inventors also found additive alloying elements that act to further enhance the mechanical strength in the copper alloy sheet material having that crystal orientation and properties, and also found additive 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 also found a production method comprising specific steps, to attain the above specific crystal orientation. The present invention was attained based on those findings.

**[0013]** That is, according to the present invention, there is provided the following means:

(1) A copper alloy sheet material, containing Ti in an amount of 1.0 to 5.0 mass%, with the balance substantially being copper and unavoidable impurities,
wherein an area ratio of Cube orientation {0 0 1} <1 0 0> is 5 to 50%, in crystal orientation analysis by an EBSD analysis;
(2) The copper alloy sheet material described item (1), which further contains at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Si, Fe, and Hf, in an amount of 0.005 to 1.0 mass% in total;
(3) The copper alloy sheet material described in item (1) or (2),
wherein the copper alloy sheet material has a 0.2% proof stress of 850 MPa or more; and
wherein the copper alloy sheet material has a bending property, to causes no crack in a 90° W bending test, and to give a value (r/t) of 1 or less, which value is obtained by dividing a minimum bending radius (r, mm) enabling bending with small bending wrinkles by a sheet thickness (t, mm);
(4) The copper alloy sheet material described in any one of items (1) to (3), wherein the copper alloy sheet material has a Young's modulus of 90 to 120 GPa, which is measured by a tensile test, and which shows an amount of displacement when a given stress is applied to the sheet material, and
wherein the copper alloy sheet material has a deflection coefficient of 80 to 110 GPa, which is measured by a deflection test;
(5) A method of producing the copper alloy sheet material described in any one of items (1) to (4), comprising: subjecting a copper alloy raw material having an alloy composition to give the copper alloy sheet material, to the steps of:

casting [Step 1]; homogenization heat treatment [Step 2]; hot-rolling [Step 3]; water-cooling [Step 4]; cold-rolling [Step 6]; intermediate annealing [Step 7]; cold-rolling [Step 8], and intermediate solution heat treatment [Step 9], in this order;

(6) The method of producing the copper alloy sheet material described in item (5), wherein aging-precipitation heat treatment [Step 10]; finish cold-rolling [Step 11]; and temper annealing [Step 12] are conducted in this order, after the intermediate solution heat treatment [Step 9];
(7) A copper alloy part, comprising the copper alloy sheet material described in any one of items (1) to (4); and
(8) A connector, comprising the copper alloy sheet material described in any one of items (1) to (4).

## ADVANTAGEOUS EFFECTS OF INVENTION

**[0014]** The copper alloy sheet material of the present invention is excellent in the bending property, has an excellent mechanical strength, and has properties suitable for lead frames, connectors, terminal materials, and the like in electrical/electronic equipments, for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like. Further, the production method of the present invention can favorably produce the above copper alloy sheet material.

**[0015]** Since the copper alloy sheet material of the present invention has a composition containing Ti in an amount of 1.0 to 5.0 mass%, with the balance being copper and unavoidable impurities, and has an area ratio of Cube orientation {0 0 1} <1 0 0> of 5 to 50%, in crystal orientation analysis by an EBSD analysis, it can provide a copper alloy, which is excellent in properties of the mechanical strength, the bending property, the electrical conductivity, and the stress relaxation resistance, and which is preferable for the uses in parts to be mounted on automotives or in parts in electrical/electronic equipments.

**[0016]** Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

**[0017]**

{Fig. 1}
Fig. 1 is a schematic view showing examples in which the declination angle (deviation angle) from Cube orientation {0 0 1} <1 0 0> is within 10°.
{Fig. 2}
Fig. 2(a) and 2(b) are explanatory diagrams for the method of testing the stress relaxation properties, in which Fig. 2(a) shows the state before heat treatment, and Fig. 2(b) shows the state after the heat treatment.
{Fig. 3}
Fig. 3 is an explanatory diagram for the method of testing the stress relaxations according to JCBA T309:2001 (provisional).

MODE FOR CARRYING OUT THE INVENTION

**[0018]** Preferable embodiments of the copper alloy sheet material of the present invention will be described in detail. Herein, the term "copper alloy material" means a product obtained after a copper alloy raw material (before working, having a predetermined alloy composition) is worked into a predetermined shape (for example, sheet, strip, foil, rod, or wire). Among them, a sheet material refers to a material which has a specific thickness, is stable in the shape, and is extended in the plane direction, and in a broad sense, the sheet material is meant to encompass a strip material. In the present invention, there are no particular limitations on the thickness of the sheet material, but when it is considered that the thickness should well exhibit the effects of the present invention and should be suitable for practical applications, the thickness is preferably 0.01 to 1.0 mm, more preferably 0.05 to 0.5 mm.
In the copper alloy sheet material of the present invention, the characteristics are defined by the accumulation ratio of the atomic plane in a predetermined direction of a rolled sheet, but this will be considered enough if the copper alloy sheet material has such characteristics. The shape of the copper alloy sheet material is not intended to be limited to a sheet material or a strip material. It is noted that, in the present invention, a tube material can also be construed and treated as a sheet material.

[Area ratio of Cube orientation]

**[0019]** 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 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 found that it is effective to increase the ratio of crystal orientation in which work hardening is difficult to occur in bending deformation. Specifically, the inventors found that favorable bending property is exhibited, when an area ratio of Cube orientation {0 0 1} <1 0 0> is 5% to 50%, in crystal orientation analysis by an EBSD analysis conducted in the thickness direction of the sheet material, to attain the present invention based on this finding. When the area ratio of Cube orientation is equal to the lower limit value or more, the above effects are sufficiently exhibited. An area ratio of the upper limit value or less is preferable, since it is not necessary to conduct the cold-rolling after the recrystallization treatment at a low working ratio, without largely lowering the mechanical strength. From those viewpoints, the area ratio of Cube orientation {0 0 1} <1 0 0> is preferably within the range of 7 to 47%, more preferably 10 to 45%.

[Orientations other than Cube orientation]

**[0020]** In addition to Cube orientation in the above-mentioned range, S orientation {2 3 1} <3 4 6>, Copper orientation {1 2 1} <1 1 1>, D orientation {4 11 4} <11 8 11>, Brass orientation {1 1 0} <1 1 2>, Goss orientation {1 1 0} <0 0 1>, R1 orientation {3 5 2} <3 5 8>, RDW orientation {1 0 2} <0 1 0>, and the like are generated as other crystal orientations. Any of these orientation components may be present in the copper alloy sheet material of the present invention, as long as the area ratio of Cube orientation is within the above-mentioned range to the areas of all of the observed orientations.

[EBSD method]

**[0021]** Herein, the method of indicating the crystal orientation in the present specification is such that a Cartesian coordinate system is employed, representing the longitudinal direction (LD) of the copper alloy sheet material {which equals to the rolling direction (RD) of the sheet material} in the X-axis, the transverse direction (TD) in the Y-axis, and the thickness direction of the sheet material {which equals to the direction (ND) normal to the rolling direction of the sheet material} in the Z-axis, various regions in the copper alloy sheet material are indicated in the form of (h k l) [u v w], using the index (h k l) of the crystal plane that is perpendicular to the Z-axis (parallel to the rolled plane (XY plane)) and the index [u v w] of the crystal direction that is perpendicular to the X-axis (parallel to YZ plane). Further, the orientation that is equivalent based on the symmetry of the cubic crystal of a copper alloy is indicated as {h k l} <u v w>, using parenthesis symbols representing families, such as in (1 3 2) [6 -4 3], and (2 3 1) [3 -4 6].
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 reflected electron Kikuchi-line diffraction that occurs when a sample is irradiated with an electron beam under a scanning electron microscope (SEM). A sample area, which is measured 1 $\mu$m 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 $\mu$m. The measurement area and the scan-step are adjusted depending on the size of the grains of the sample. The area ratio of the respective orientation is a ratio of the area of a region, in which the deviation angle from the ideal orientation of Cube orientation {0 0 1} <1 0 0> is ± 10° 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.
The area ratio of the respective orientation is a value calculated by dividing the area of a region in which the deviation angle from the respective ideal orientation is 10° or less, by the measured area.
In regard to the deviation angle from the ideal orientation, an angle of rotation around the axis of common rotation is calculated, and the angle of rotation is designated as the deviation angle. Fig. 1 presents examples of the orientations in which the deviation angle from the Cube orientation is 10° or less. This diagram shows orientations in which the deviation angle is within 10°, on the axes of rotation of the planes (1 0 0), (1 1 0), and (1 1 1), but the angle of rotation relative to the Cube orientation can be calculated with respect to any axis of rotation. As for the axis of rotation, one that can be represented by the smallest deviation angle is employed. This deviation angle is calculated for all measurement points. The sum of the area of grains having an orientation within 10° from the respective orientation is divided by the total measured area, and the resultant value is designated as the ratio of the area (i.e. the area ratio).
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. The orientation distribution is measured from the sheet material surface of the copper alloy sheet material, and in the case where the orientation distribution changes in the sheet thickness direction, the orientation analysis by EBSD refers to a value that is obtained, by taking arbitrary several points in the sheet thickness direction, and obtaining the average thereof.

**[0022]** Herein, the features of the EBSD analysis will be explained in comparison with the X-ray diffraction analysis.
Firstly, an X-ray diffractometry can measure only five kinds of planes: i.e. ND//(1 1 1), (2 0 0), (2 2 0), (3 1 1), and (4 2 0) planes, each of which satisfy the Bragg's diffraction conditions and can provide a sufficient diffraction intensity. However, the X-ray diffractometry cannot measure any crystal orientations that are expressed by a high index, such as ND//(511) plane and ND//(951) plane, which correspond to an angle formed with (i.e. the deviation angle or a misorientation angle from) the Cube orientation from 15 to 30°. Namely, utilizing the EBSD analysis, information relating to those crystal orientations expressed by a high index can be obtained, for the first time, which makes it to possible to clarify the relationships between the metal microstructure specified by this way and the action thereof.
Secondly, the X-ray diffraction measures the content of a crystal orientation included in about ±0.5° of ND//{hkl). On the other hand, since a Kikuchi pattern is utilized in the EBSD analysis, incomparably broader information on metal microstructures can be cyclopedically obtained with the EBSD analysis, which is not limited to specific crystal planes, to clarify a state of the whole alloy material, which state is difficult to specify with the X-ray diffraction.
As explained above, the information obtainable via the EBSD analysis and the information obtainable via the X-ray diffraction analysis differ from each other in the points of the contents and the natures.
Unless otherwise specified, in the present specification, the results of EBSD analysis are results obtained in connection with the ND direction of a copper alloy sheet material.

[X-ray diffraction intensity]

**[0023]** In the present invention, when the X-ray diffraction intensity from {2 0 0} plane on the alloy sheet surface is represented by I{2 0 0} and the X-ray diffraction intensity from {2 0 0} plane of a pure copper standard powder is represented by $I_0$\{2 0 0}, it is preferable to satisfy the relationship of formula (a), and more preferable to have a crystal orientation that satisfies the relationship of formula (b).

$$I\{200\}/I_0\{200\} \geq 1.3 \qquad \text{Formula (a)}$$

$$I\{200\}/I_0\{200\} \geq 2.5 \qquad \text{Formula (b)}$$

[Ti]

**[0024]** In the present invention, by controlling the addition amount of titanium (Ti) to be added to copper (Cu), to precipitate a Cu-Ti compound, the mechanical strength of the resultant copper alloy can be enhanced. The content of Ti is 1.0 to 5.0 mass%, preferably 2.0 to 4.0 mass%. When the addition amount of this element is more than this prescribed range, the electrical conductivity is lowered, whereas the addition amount is smaller than the range, the mechanical strength becomes insufficient. A copper alloy containing Ti as a second alloy component as in the copper alloy according to the present invention is sometimes referred to as a "Ti-based copper alloy".

[Additional alloying elements]

**[0025]** Next, the effects of the additional alloying elements on this alloy will be shown. Examples of preferable additional alloying elements, include Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Si, Fe, and Hf. The content of these additional alloying elements is preferably 1 mass% or less in the total amount of at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Si, Fe, and Hf, since any adverse affection to lower the electrical conductivity is not occurred. In order to sufficiently utilize the effects of addition and to prevent lowering of the electrical conductivity from occurring, this total amount is preferably 0.005 to 1.0 mass%, more preferably 0.01 to 0.9 mass%, particularly preferably 0.03 mass% to 0.8 mass%. The examples of the effects of adding various elements will be described below.

(Mg, Sn, Zn)

**[0026]** Mg, Sn, and Zn, when added, improve the stress relaxation resistance. 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.

(Mn, Ag, B, P)

**[0027]** Mn, Ag, B, and P, when added, improve hot workability, and at the same time, enhance the mechanical strength.

(Cr, Zr, Si, Fe, Hf)

**[0028]** Cr, Zr, Si, Fe, and Hf each finely precipitate in the form of a compound or in the form of a simple elementary substance, to contribute to precipitation hardening. Further, these elements each precipitate in the form of a compound with a size of 50 to 500 nm, to suppress grain growth. Thus, those elements each have an effect of making the grain size fine and making the bending property favorable.

[Method of producing the copper alloy sheet material]

**[0029]** Next, preferable conditions of producing the copper alloy sheet material of the present invention will be explained. 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], 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 rang of 700 to 1,000°C, to thereby form a solid solution of solute atoms again, followed by aging-precipitation heat treatment [Step 10], and finish cold-rolling [Step 11], 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 [Step 9], and is finally determined by the rotation of the orientations, which occurs upon the finish rolling [Step 11].

**[0030]** Contrary to the above-mentioned conventional method, in an embodiment of the present invention, the area ratio of Cube orientation is increased in the recrystallized texture upon the intermediate solution heat treatment [Step 9], after the hot-rolling [Step 3], by conducting the water cooling [Step 4], the face milling [Step 5], the cold-rolling [Step 6] by rolling at a rolling ratio of 80% to 99.8%, then the intermediate annealing [Step 7] by heating to 600 to 800°C at a heating speed of 10 to 30°C/sec so that no recrystallization would occur, and then quenching at 200°C/sec or more, and further the cold-rolling [Step 8] at a working ratio of 2 to 50%. Further, the aging-precipitation heat treatment [Step 10], the finish cold-rolling [Step 11], and the temper annealing [Step 12] may be conducted, after the intermediate solution heat treatment [Step 9].

**[0031]** Hereinafter, a preferable embodiment, in which the conditions in the respective steps are set in detail, is described.

A copper alloy raw material at least containing Ti in 1.0 to 5.0 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 casting [Step 1] at a cooling speed of 0.1 to 100°C/sec, to obtain an ingot. This ingot is subjected to the homogenization heat treatment at 800 to 1,020°C for 3 minutes to 10 hours [Step 2], followed by the hot working [Step 3] at 1,020 to 700°C, and water quenching (this corresponds to the water cooling [Step 4]). Then, if necessary, the face milling [Step 5] may be conducted so as to remove oxide scale. Then, the cold-rolling [Step 6] at a working ratio of 80 to 99.8% is conducted, followed by the intermediate annealing [Step 7] by heating at a heating speed of 10 to 30°C/sec to 600 to 800°C, and quenching at 200°C/sec or more; the cold-rolling [Step 8] at a working ratio of 2 to 50%, and the intermediate solution heat treatment [Step 9] 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, the finish cold-rolling [Step 11] at a working 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. By the above method, the copper alloy sheet material of the present invention can be obtained.

**[0032]** In this embodiment, the hot-rolling [Step 3] is to conduct, at the temperature region from the reheat temperature to 700°C, working for breaking the cast structure and segregation to form a homogeneous structure, and working for making grains fine by dynamic recrystallization. Then, after subjecting to a heating in the intermediate annealing [Step 7] such that the structure of the resultant alloy would not be recrystallized in the whole, the cold-rolling [Step 8] at a working ratio of 2 to 50% is conducted, followed by the intermediate solution [Step 9], to increase the area ratio of Cube orientation in the thus-recrystallized texture. When the (highest) temperature reached by the heating in the intermediate annealing [Step 7] before the intermediate solution [Step 9] is higher than the value defined in the present invention, oxide scale is formed, which is not preferable, and thus the temperature reached by the heating in this intermediate annealing [Step 7] is set to 600 to 800°C. Specifically, although it is difficult to unambiguously determine, the area ratio of Cube orientation tends to increase, by specifying the temperature reached in the intermediate annealing [Step 7] and adjusting the working ratio in the cold-rolling [Step 8]. That is, in the intermediate annealing [Step 7], the sheet is not kept at the temperature reached in the annealing, and the heating is conducted at a predetermined heating speed, and when reaching the target temperature reached in the annealing, cooling is immediately conducted at a predetermined cooling speed.

When the heating speed in the intermediate annealing [Step 7] is slower than 10°C/sec, the growth of grains proceeds and the grains are coarsened, resulting in that bending wrinkles become large. When the heating speed is faster than 30°C/sec, Cube orientation is not sufficiently developed, resulting in that the bending property becomes poor. When the temperature to reach is lower than 600°C, Cube orientation is not developed, resulting in that the bending property is poor; and when the temperature to reach is higher than 800°C, the growth of the grains proceeds, and the grains are coarsened, resulting in that bending wrinkles become large, to make the characteristics poor. Further, as mentioned above, it is presumed that, by conducting strong working, such as the cold-rolling [Step 6] at a working ratio of 80 to 99.8%, there is a possibility that dislocation and strain are introduced around the coarse crystallized product and precipitate generated by casting, to thereby inhibit the rotation of the orientation in the intermediate solution heat treatment [Step 9] upon which Cube orientation is grown. However, by conducting the intermediate annealing [Step 7], the dislocation and strain are released via this annealing, and thus the inhibition of the growth of Cube orientation is suppressed in the intermediate solution heat treatment [Step 9].

**[0033]** Then, the cold-rolling [Step 8] is conducted at a working ratio of 2 to 50%. When the working ratio is lower than 2%, the working strain is small, and the grain size is coarsened in the intermediate solution heat treatment [Step 9], resulting in that bending wrinkles become large, to make the characteristics poor. When the working ratio is higher than 50%, Cube orientation is not sufficiently developed, resulting in that the bending property becomes poor.

The aging-precipitation heat treatment [Step 10], the finish cold-rolling [Step 11], and the temper annealing [Step 12]

are conducted, after the intermediate solution heat treatment [Step 9]. The treatment temperature in the aging precipitate heat treatment [Step 10] is lower than that in the intermediate solution heat treatment [Step 9]. Further, the treatment temperature in the temper annealing [Step 12] is lower than that in the intermediate solution heat treatment [Step 9].
In order to increase the area ratio of Cube orientation in the recrystallized texture, the finish cold working [Step 11] is conducted. Further, controlling of the crystal orientation in a predetermined direction contributes to the development of Cube orientation.
By conducting the cold-rolling [Step 6] to introduce a further work strain, and conducting the intermediate annealing [Step 7] of heating at a heating speed of 10 to 30°C/sec, to a temperature to reach of 600 to 800°C, in which quenching is conducted after reaching the temperature, the area ratio of Cube orientation increases in the recrystallized texture that is generated in the intermediate solution treatment [Step 9]. The purpose of the intermediate annealing [Step 7] is to obtain a subannealed structure that is not completely recrystallized but partially recrystallized. The purpose of the cold-rolling [Step 8] is to introduce microscopically-uneven strain, by rolling at a working ratio of 2 to 50%. The actions and effects of the intermediate annealing [Step 7] and the cold-rolling [Step 8] enable the growth of Cube orientation in the intermediate solution treatment [Step 9]. Generally, the main purpose of a heat treatment such as the intermediate solution treatment [Step 9] is to recrystallize the copper alloy sheet material so as to decrease the loading in the subsequent step, thereby to lower the mechanical strength, but the purpose in the present invention is different from such a purpose.

**[0034]** The working ratio in the above respective rolling step (this is also referred to as a rolling reduction ratio or cross-section reduction ratio. The rolling ratio mentioned in the following Comparative Examples has the same meaning.), refers to a value calculated as in the following formula, by using the sheet thickness $t_1$ before the rolling step and the sheet thickness $t_2$ after the rolling step.

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

Scalping (face milling) for scale on the surface of the material, and dissolution by pickling or the like may be introduced as necessary. In the case where the shape after the rolling is not fine, correction by a tension leveler or the like may be introduced as necessary.
After the respective heat treatment or rolling, a pickling or surface-polishing may be conducted depending on the state of the oxidation or roughness of the surface of the sheet material, or a correction by a tension leveler may be conducted depending on the shape, and it is no problem as long as the area ratio of Cube orientation {0 0 1} <1 0 0> is within the range according to the present invention.

[Characteristics of the copper alloy sheet material]

**[0035]** When the conditions described above are satisfied, the characteristics, for example, which are required for a copper alloy sheet material for use in connectors, can be satisfactorily exhibited. In the present invention, it is preferable that the copper alloy sheet material has the following properties.

- The copper alloy sheet material has a 0.2% proof stress of preferably 850 MPa or more, more preferably 950 MPa or more. Although the upper limit value of the 0.2% proof stress is not particularly limited, it is generally 1,000 MPa or less. Unless otherwise specified, the specific measurement conditions are set as described in the Examples section.
- It is preferable that the copper alloy sheet material has a bending property, which causes no crack in a 90° W bending test, and which gives a value (r/t) of 1 or less, which value is obtained by dividing a minimum bending radius (r), at which bending with small bending wrinkles is possible, by a sheet thickness (t). With respect to bending wrinkles, the bending wrinkles preferably have wrinkle intervals of 20 μm or less in GW (Good Way) and 25 μm or less in BW (Bad Way). More preferably, the bending wrinkles have wrinkle intervals of 15 μm or less in GW and 20 μm or less in BW. Unless otherwise specified, the specific measurement conditions are set as described in the Examples section. As used herein, in a sample specimen that is cut out perpendicularly to the rolling direction, GW refers to that the specimen is bent by W bending so that the bending axis would become perpendicular to the rolling direction, and BW refers to that the specimen is bent by W bending so that the bending axis would be parallel to the rolling direction.

- The copper alloy sheet material has an electrical conductivity of preferably 5%IACS or more, more preferably 10%IACS or more. Although the upper limit value of the electrical conductivity is not particularly limited, it is generally 30%IACS or less. Unless otherwise specified, the specific measurement conditions are set as described in the Examples section.

- The copper alloy sheet material preferably has a Young's modulus of 90 to 120 GPa and a deflection coefficient of 80 to 110 GPa. Further, the copper alloy sheet material more preferably has a Young's modulus of 100 to 110 GPa and a deflection coefficient of 90 to 100 GPa. Unless otherwise specified, the specific measurement conditions are set as described in the Examples section.
- According to the present invention, a favorable property of a stress relaxation resistance of 5% or less can be attained. Unless otherwise specified, the specific measurement conditions are set as described in the Examples section.

EXAMPLES

**[0036]** 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)

**[0037]** With respect to Examples 1 to 21 according to the present invention and Comparative Examples 1 to 17, main raw materials: Cu and Ti, and any of other additional alloying elements for some test examples, were blended so as to give the respective composition as shown in Table 1, followed by melting and casting.
That is, the respective alloy containing Ti and the like 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] at a cooling speed of 0.1 to 100°C/sec, to obtain an ingot. This 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 working [Step 3] at 1,020 to 700°C, then the water quenching (this corresponds to the water cooling [Step 4]) and the face milling [Step 5] so as to remove oxide scale. Then, the respective resultant sheet was subjected to the cold-rolling [Step 6] at a working ratio of 80 to 99.8%, followed by the intermediate annealing [Step 7] of heating at a heating speed of 10 to 30°C/sec, to reach a temperature of 600 to 800°C, and quenching at 200°C/sec or more, further the cold-rolling [Step 8] at a working ratio of 2 to 50%, and the intermediate solution treatment [Step 9] 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 10 hours, the finish cold-rolling [Step 11] at a working 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. In some of Comparative Examples, as shown in Table 2, the intermediate annealing [Step 7] and the cold-rolling [Step 8] were conducted under conditions outside of the above-mentioned conditions. With respect to these sample specimens, the compositions, the conditions in the intermediate annealing [Step 7] and the cold-rolling [Step 8], and the obtained properties are shown on those Examples and Comparative Examples in Table 1 and Table 2. 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.
**[0038]** The thus-obtained sample specimens were subjected to examination of the properties as described below. The thickness of each of the sample specimens was set to 0.15 mm. The evaluation results are shown in Table 2.

a. Area ratios of Cube orientation and S orientation

**[0039]** The measurement was conducted with the EBSD method in a measurement region of 0.08 to 0.15 $\mu m^2$, under the conditions of a scan step of 0.5 to 1 μm. The measured area was adjusted on the basis of the condition of containing 200 or more grains. The scan step was adjusted according to the grain size, such that when the average grain size was 15 μm or less, scanning was conducted at a step of 0.5 μm, or alternatively when the average grain size was 30 μm or less, scanning was conducted at a step of 1 μm. The electron beam was generated by using thermoelectrons from a W filament of a scanning electron microscope as the source of generation.
As an EBSD analyzer, OIM 5.0 (trade name) manufactured by TSL Solutions, Ltd., was used.

b. Bending property

**[0040]** A sample was taken, by cutting out from the respective sample specimen perpendicularly to the rolling direction, into a size with width 10 mm and length 35 mm. The respective sample 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 50x. A sample which had no crack was judged as "○" (good), and a sample which had cracks was judged as "x" (poor). The bending angle at the respective bent portion was set at 90°, and the inner radius of the respective bent portion was set at 0.15 mm. Specifically, under the conditions of, the minimum bending radius (r) was 0.15 mm, the sheet thickness (t) was 0.15 mm, and the ratio thereof (r/t) was 1.

c. Examination of bending wrinkles

**[0041]** Bending wrinkles were examined, which were occurred on the surface of the bent portion of the sample that had been subjected to a 90° W bending test and a 180° tight bending test, respectively. The respective sample was embedded with a resin, and the bent cross-section was observed by an SEM. The size of the wrinkle was measured based on the size between the grooves of the wrinkles, which were seen in the observation of the cross-section. The bending wrinkles were judged as acceptable when they had wrinkle intervals of 20 μm or less in GW and 25 μm or less in BW.

d. 0.2% proof stress [YS]

**[0042]** Each three test pieces that were cut out from the respective sample specimen in the direction parallel to the rolling direction, according to JIS Z2201-13B, were measured according to JIS Z2241, and the 0.2% proof stress (yield stress) is shown as an average value of the results.

e. Electrical conductivity [EC]

**[0043]** 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.

f. Young's modulus

**[0044]** A test piece was cut out from the respective sample specimen in the direction parallel to the rolling direction, followed by working so as to have a width of 20 mm, a length of 150 mm and a degree of parallelism of 0.05 mm or less per 50 mm. The Young's modulus was a value calculated from the inclination of an elastic region in the respective stress-strain curve by a tensile test.

g. Deflection coefficient

**[0045]** A test piece was cut out from the respective sample specimen in the direction parallel to the rolling direction, so that the size would be the width 10 mm, the sheet thickness 0.1 to 0.65 mm, and the length 100 or more times of the sheet thickness, according to the Technique Standard of the Japan Copper and Brass Association. The inclination of an elastic region in the respective stress-strain curve when a beam (a cantilever) underwent deflection was measured twice for each of the top and backing surfaces of each test piece, according to JIS H 3130, and the average value thereof is shown.

h. X-ray diffraction intensity

**[0046]** Diffraction intensity around one rotation axis of the sample was measured by a reflection method. Copper was used as a target, and X-ray of Kα was used. The measurement was conducted under conditions of a tube current of 20 mA and a tube voltage of 40 kV, a background of a diffraction intensity was removed from a profile of diffraction angle and diffraction intensity, and an integrated diffraction intensity was obtained, which is a combination of Kα1 and Kα2 of the respective peak, to determine I{2 0 0} and $I_0${2 0 0}, and the diffraction intensity ratio of I{2 0 0}/$I_0${2 0 0}.

i. Stress relaxation ratio [SRR]

**[0047]** The stress relaxation ratio was 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, as shown below. An initial stress that was 80% of the yield stress (proof stress) was applied thereto, by the cantilever method.
Figs. 2(a) and 2(b) each are a drawing explaining the method of testing the stress relaxation resistance, in which Fig. 2 (a) shows the state before heat treatment, and Fig. 2(b) shows the state after the heat treatment. As shown in Fig. 2(a),

the position of a test specimen 1 when an initial stress of 80% of the proof stress was applied to the test specimen 1 cantilevered on a test bench 4, is defined as the distance $\delta_0$ from the reference position. This test specimen was kept in a thermostat at 150°C for 1,000 hours. The position of the test specimen 2 after removing the load, is defined as the distance $H_t$ from the reference position, as shown in Fig. 2(b). The reference numeral 3 denotes the test specimen to which no stress was applied, and the position of the test specimen 3 is defined as the distance $H_1$ from the reference position. Based on the relationships between those positions, the stress relaxation ratio (%) was calculated as: $(H_t - H_1)/\delta_0 \times 100$.

The following methods are also applicable as similar test methods: "JCBA T309: 2001 (provisional); Stress relaxation testing method based on bending of copper and copper alloy thin sheets and rods", which is in a Technical Standard proposal, published by the Japan Copper and Brass Association (JCBA); "ASTM E328; Standard Test Methods for Stress Relaxation Tests for Materials and Structures", which is a test method, published by the American Society for Testing and Materials (ASTM); and the like.

Fig. 3 is an explanatory diagram for the stress relaxation testing method using a test jig for deflection displacement loading of a lower deflection-type and cantilever screw-type, based on the above-mentioned JCBA T309:2001 (provisional). Since the principle of this testing method is similar to that of the testing method using the test bench of Fig. 2, an almost same value of stress relaxation ratio is obtained as well.

In this testing method, first, a test specimen 11 was mounted on a test jig (testing apparatus) 12, and the resultant test specimen was imparted with a predetermined displacement at room temperature, followed by maintaining for 30 seconds. After removing the load, the bottom face of the test jig 12 was designated as a reference plane 13, and the distance between this plane 13 and the point of deflection loading of the test specimen 11, was measured as $H_i$. After a lapse of the predetermined time period, the test jig 12 was taken out at normal temperature from a thermostat bath or heating furnace, and a bolt 14 for deflection loading was made loose to remove the load. The test specimen 11 was cooled to normal temperature, and then the distance $H_t$ between the reference plane 13 and the point of deflection loading of the test specimen 11 was measured. After the measurement, a deflection displacement was applied thereto again. In the figure, reference numeral 11 represents the test specimen after removing the load, and reference numeral 15 represents the test specimen with deflection loading. The permanent deflection displacement $\delta_t$ is determined by formula.

$$\delta_t = H_i - H_t$$

From this relationship, the stress relaxation ratio (%) is calculated by:

$$\delta_t/\delta_0 \times 100$$

Herein, $\delta_0$ represents the initial deflection displacement of the test specimen required to obtain a predetermined stress, and is calculated by formula:

$$\delta_0 = \sigma l_s^2/1.5Eh$$

wherein $\sigma$ is the maximum surface stress of test specimen (N/mm$^2$), h is the sheet thickness (mm), E is a coefficient of deflection (N/mm$^2$), and $l_s$ is a span length (mm).

[0048]

Table 1

| | Ti | Sn | Zn | Ag | Mn | B | P | Mg | Cr | Zr | Si | Fe | Hf | Total amount of element other than Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Ex 1 | 1.00 | 0.01 | | | | 0.60 | | | | | | | | 0.61 |
| Ex 2 | 1.15 | | 0.01 | | | | 0.50 | | | | | | | 0.51 |
| Ex 3 | 1.30 | | | 0.01 | | | | 0.90 | | | | | | 0.91 |
| Ex 4 | 1.55 | | | | 0.02 | | | | 0.40 | | | | | 0.42 |
| Ex 5 | 1.95 | | | | | 0.12 | | | | 0.60 | | | | 0.72 |
| Ex 6 | 2.10 | | | | | | 0.50 | | | | 0.50 | | | 1 |
| Ex 7 | 2.30 | | | | | | | 0.01 | | | | 0.16 | | 0.17 |
| Ex 8 | 2.65 | | | | | | | | 0.05 | | | | 0.10 | 0.15 |
| Ex 9 | 2.80 | 0.30 | | | | | | | | 0.01 | | | | 0.31 |
| Ex 10 | 2.95 | | 0.05 | | | | | | | | 0.75 | | | 0.8 |
| Ex 11 | 3.10 | | | | | | | | | | | 0.20 | | 0.2 |
| Ex 12 | 3.20 | | | | 0.05 | | | | | | | | 0.10 | 0.15 |
| Ex 13 | 3.55 | | | | | 0.09 | | | | | | | | 0.09 |
| Ex 14 | 3.70 | | | | | | 0.20 | | | | | | | 0.2 |
| Ex 15 | 3.85 | | | | | | | 1.00 | | | | | | 1 |
| Ex 16 | 4.10 | | | | | | | | 0.40 | | | | | 0.4 |
| Ex 17 | 4.35 | 0.05 | | | | | | | | 0.01 | | | | 0.06 |
| Ex 18 | 4.50 | | 0.60 | | | | | | | | 0.10 | | | 0.7 |
| Ex 19 | 4.80 | | | 0.30 | | | | | | | | 0.05 | | 0.35 |
| Ex 20 | 5.00 | | | | 0.50 | | | | | | | | 0.20 | 0.7 |
| Ex 21 | 3.00 | | | | | | | | | | | | | 0 |
| C Ex 1 | 3.000 | 1.000 | | | | | | | | | | | | 1 |

(continued)

| | Ti | Sn | Zn | Ag | Mn | B | P | Mg | Cr | Zr | Si | Fe | Hf | Total amount of element other than Ti |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| C Ex 2 | 3.000 | | 0.500 | | | | | | | | | | | 0.5 |
| C Ex 3 | 3.000 | | | 0.005 | | | | | | | | | | 0.005 |
| C Ex 4 | 3.000 | | | | 0.009 | | | | | | | | | 0.009 |
| C Ex 5 | 0.850 | | | | | 0.350 | | | | | | | | 0.35 |
| C Ex 6 | 5.400 | | | | | | 0.540 | | | | | | | 0.54 |
| C Ex 7 | 3.000 | | | | | | | 0.150 | | | | | | 0.15 |
| C Ex 8 | 3.000 | | | | | | | | 0.800 | | | | | 0.8 |
| C Ex 9 | 3.000 | | | | | | | | | 0.900 | | | | 0.9 |
| C Ex 10 | 3.000 | 1.000 | | | | | | | | | 0.400 | | | 1.4 |
| C Ex 11 | 3.000 | | | | | | | | | | | 1.000 | | 1 |
| C Ex 12 | 3.000 | 0.003 | | | | | | | | | | | 0.400 | 0.403 |
| C Ex 13 | 3.000 | | 0.900 | | | | | | | | | | | 0.9 |
| C Ex 14 | 3.000 | | | 0.003 | | | | | | | | | | 0.003 |
| C Ex 15 | 2.310 | | | | | | | | | | | 0.150 | | 0.15 |
| C Ex 16 | 0.900 | | | | | | | | | | | | | 0 |
| C Ex 17 | 5.200 | | | | | | | | | | | | | 0 |

Unit: mass%, the balance was copper (Cu) (the same will be applied in below)
"Ex" means Example according to this invention (the same will be applied in below).
"C Ex" means Comparative Example (the same will be applied in below).

[0049]

Table 2

| ID Number | Alloying element | Intermediate annealing [7] | | Cold-rolling [8] | Area ratio of Cube orientation | Integrated intensity ratio of X-ray diffraction | Bending property Cracks | |
|---|---|---|---|---|---|---|---|---|
| | Ti | Heating speed | Temp. reached | Working ratio | | | | |
| | mass% | °C/sec | °C | % | % | $I200/I_0200$ | GW | BW |
| Ex 1 | 1.00 | 25 | 650 | 20 | 5 | 1.34 | o | o |
| Ex 2 | 1.15 | 10 | 710 | 12 | 32 | 8.58 | o | o |
| Ex 3 | 1.30 | 15 | 740 | 35 | 17 | 4.56 | o | o |
| Ex 4 | 1.55 | 20 | 610 | 40 | 5 | 1.34 | o | o |
| Ex 5 | 1.95 | 26 | 760 | 5 | 21 | 5.63 | o | o |
| Ex 6 | 2.10 | 14 | 600 | 45 | 50 | 13.41 | o | o |
| Ex 7 | 2.30 | 18 | 690 | 18 | 19 | 5.10 | o | o |
| Ex 8 | 2.65 | 21 | 780 | 25 | 44 | 11.80 | o | o |
| Ex 9 | 2.80 | 11 | 800 | 50 | 10 | 2.68 | o | o |
| Ex 10 | 2.95 | 30 | 730 | 10 | 18 | 4.83 | o | o |
| Ex 11 | 3.05 | 20 | 640 | 31 | 23 | 6.17 | o | o |
| Ex 12 | 3.20 | 22 | 700 | 24 | 24 | 6.44 | o | o |
| Ex 13 | 3.55 | 30 | 780 | 9 | 8 | 2.15 | o | o |
| Ex 14 | 3.70 | 14 | 620 | 14 | 20 | 5.36 | o | o |
| Ex 15 | 3.85 | 19 | 645 | 41 | 21 | 5.63 | o | o |
| Ex 16 | 4.10 | 14 | 755 | 28 | 29 | 7.78 | o | o |
| Ex 17 | 4.35 | 25 | 720 | 2 | 25 | 6.71 | o | o |
| Ex 18 | 4.50 | 13 | 660 | 17 | 36 | 9.66 | o | o |
| Ex 19 | 4.80 | 17 | 795 | 29 | 22 | 5.90 | o | o |
| Ex 20 | 5.00 | 26 | 680 | 43 | 19 | 5.10 | o | o |
| Ex 21 | 3.00 | 15 | 700 | 30 | 25 | 6.71 | o | o |

Table 2 (continued)

| ID number | Wrinkles on bent surface (R/t=0) | | YS | EC | Young's modulus | Deflection coefficient | SRR |
|---|---|---|---|---|---|---|---|
| | GW (μm) | BW (μm) | MPa | %IACS | GPa | GPa | % |
| Ex 1 | 20 | 20 | 911 | 17 | 100 | 90 | 3.3 |
| Ex 2 | 20 | 25 | 867 | 15 | 90 | 85 | 2.5 |
| Ex 3 | 15 | 20 | 870 | 13 | 110 | 80 | 4.9 |
| Ex 4 | 20 | 25 | 906 | 16 | 120 | 110 | 2.0 |
| Ex 5 | 15 | 20 | 890 | 14 | 105 | 91 | 1.0 |
| Ex 6 | 10 | 20 | 955 | 15 | 92 | 89 | 4.0 |
| Ex 7 | 15 | 20 | 871 | 17 | 114 | 98 | 2.0 |
| Ex 8 | 15 | 20 | 866 | 15 | 93 | 88 | 3.0 |
| Ex 9 | 20 | 20 | 903 | 18 | 116 | 98 | 4.6 |
| Ex 10 | 10 | 15 | 894 | 13 | 107 | 87 | 2.0 |
| Ex 11 | 10 | 15 | 875 | 16 | 100 | 94 | 3.5 |
| Ex 12 | 15 | 20 | 868 | 18 | 98 | 97 | 3.8 |
| Ex 13 | 10 | 15 | 869 | 14 | 95 | 90 | 4.1 |
| Ex 14 | 10 | 15 | 893 | 13 | 110 | 83 | 2.4 |
| Ex 15 | 10 | 20 | 898 | 11 | 112 | 110 | 3.0 |
| Ex 16 | 10 | 15 | 865 | 14 | 99 | 83 | 4.5 |
| Ex 17 | 15 | 10 | 874 | 10 | 101 | 96 | 3.8 |
| Ex 18 | 10 | 15 | 866 | 12 | 100 | 86 | 2.8 |
| Ex 19 | 20 | 20 | 963 | 11 | 112 | 105 | 3.6 |
| Ex 20 | 10 | 15 | 900 | 10 | 111 | 90 | 3.8 |
| Ex 21 | 15 | 20 | 880 | 11 | 100 | 92 | 4.0 |

Table 2 (continued)

| ID number | Alloying element | Intermediate annealing [7] | | Cold-rolling [8] | Area ratio of Cube orientation | Integrated intensity ratio of X-ray diffraction | Bending property Cracks | |
|---|---|---|---|---|---|---|---|---|
| | Ti | Heating speed | Temp. reached | Working ratio | | | | |
| | Mass% | °C/sec | °C | % | % | $I200/I_0200$ | GW | BW |
| C Ex 1 | 3.00 | 8 | 700 | 30 | 4 | 0.56 | × | × |
| C Ex 2 | 3.00 | 19 | 620 | 1 | 2 | 0.54 | × | × |
| C Ex 3 | 3.00 | 15 | 830 | 28 | 4 | 0.52 | × | × |
| C Ex 4 | 3.00 | 31 | 820 | 13 | 2 | 0.54 | × | × |
| C Ex 5 | 0.85 | 29 | 590 | 10 | 1 | 0.27 | × | × |
| C Ex 6 | 5.40 | 32 | 560 | 55 | 3 | 0.80 | × | × |
| C Ex 7 | 3.00 | 11 | 640 | 1 | 4 | 1.07 | × | × |
| C Ex 8 | 3.00 | 6 | 730 | 40 | 55 | 14.75 | ○ | ○ |
| C Ex 9 | 3.00 | 12 | 670 | 55 | 4 | 1.07 | × | × |
| C Ex 10 | 3.00 | 23 | 570 | 34 | 3 | 0.80 | × | × |
| C Ex 11 | 3.00 | 9 | 810 | 10 | 51 | 13.68 | ○ | ○ |
| C Ex 12 | 3.00 | 34 | 700 | 52 | 4 | 1.07 | × | × |
| C Ex 13 | 3.00 | 27 | 750 | 1 | 2 | 0.54 | × | × |
| C Ex 14 | 3.00 | 28 | 850 | 41 | 4 | 1.07 | × | × |
| C Ex 15 | 2.31 | 10 | 520 | 86 | 4 | 1.07 | ○ | ○ |
| C Ex 16 | 0.90 | 8 | 560 | 57 | 3 | 0.80 | × | × |
| C Ex 17 | 5.20 | 9 | 535 | 52 | 4 | 1.07 | × | × |

Table 2 (continued)

| ID number | Wrinkles on bent surface (R/t=0) | | YS | EC | Young's modulus | Deflection coefficient | SRR |
|---|---|---|---|---|---|---|---|
| | GW (µm) | BW (µm) | MPa | %IACS | GPa | GPa | % |
| C Ex 1 | 60 | 40 | 880 | 17 | 130 | 111 | 4.5 |
| C Ex 2 | 30 | 40 | 780 | 12 | 120 | 110 | 4.5 |
| C Ex 3 | 40 | 50 | 832 | 15 | 123 | 111 | 5.6 |
| C Ex 4 | 60 | 30 | 845 | 10 | 121 | 114 | 6.0 |
| C Ex 5 | 55 | 50 | 839 | 28 | 119 | 115 | 7.0 |
| C Ex 6 | 75 | 80 | 890 | 5 | 118 | 113 | 5.8 |
| C Ex 7 | 20 | 15 | 850 | 17 | 121 | 120 | 4.9 |
| C Ex 8 | 15 | 10 | 770 | 12 | 87 | 78 | 3.8 |
| C Ex 9 | 60 | 50 | 874 | 15 | 122 | 109 | 9.0 |
| C Ex 10 | 10 | 20 | 845 | 4 | 120 | 116 | 4.8 |
| C Ex 11 | 20 | 25 | 750 | 16 | 88 | 79 | 4.5 |
| C Ex 12 | 75 | 80 | 890 | 14 | 118 | 110 | 3.8 |
| C Ex 13 | 15 | 20 | 836 | 15 | 124 | 114 | 3.5 |
| C Ex 14 | 75 | 80 | 765 | 14 | 125 | 116 | 5.4 |
| C Ex 15 | 80 | 90 | 928 | 12 | 135 | 126 | 6.0 |
| C Ex 16 | 50 | 60 | 820 | 10 | 126 | 115 | 10.0 |
| C Ex 17 | 40 | 45 | 815 | 11 | 121 | 114 | 8.0 |

**[0050]** As shown in Table 2, in the production methods of Examples 1 to 21 according to the present invention, the heat treatment in the intermediate annealing [Step 7] was conducted at a heating speed of 10 to 30°C/sec, a temperature reached of 600 to 800°C, and rapid cooling by water quenching after reaching the temperature (cooling speed 200°C/sec or more). Then, the sample was subjected to a working of the cold-rolling [Step 8] at a working ratio of 2 to 50%. Comparative Examples 1 to 17 show the cases when any of the definitions in the production method of the present invention was not satisfied. In Comparative Examples 5, 6, 16, and 17, the Ti component was outside of the range; and, in the intermediate annealing [Step 7] of Comparative Examples 1 to 17, the heating speed was outside of the range in Comparative Examples 1, 4, 6, 8, 11, 12, 16, and 17, and the reached temperature was outside of the range in Comparative Examples 3 to 6, 10, 11, and 14 to 17. Further, in Comparative Examples 2, 6, 7, 9, 12, 13, 15, and 16, the working ratio in the cold-rolling [Step 8] was outside of the range. In addition, as shown in Table 1, in Comparative Example 10, the addition amount of the third elements was too large over the range of the defined value of 0.005 to 1.0%.

**[0051]** As shown in Table 2, Examples 1 to 21 according to the present invention were excellent in the bending property and the proof stress. However, as shown in Comparative Examples 1 to 17, when any of the definitions of the present invention was not satisfied, the results were poor in any of the properties. In Examples 1 to 21, by conducting the heat treatment at a temperature region lower than the solid-solution temperature, the rotation of the crystal orientation of the titanium-copper proceeded, and finally, the area ratio of Cube orientation was remarkably increased, to thereby improve the bending property. In all of Examples 1 to 21, Cube orientation was 5% or more. In Examples 1 to 21, the wrinkles on the bent surface part each had a size of GW $\leq$ 20 µm and BW $\leq$ 25 µm, no crack was observed, and bending wrinkles were small, and thus the bending property was excellent. Further, the Young's modulus and the deflection coefficient were also within the prescribed ranges.

**[0052]** Contrary to the above, in Comparative Examples 1 to 7, 9, 10, 12 to 14, 16, and 17, cracks occurred on the bent surface. In all of Comparative Examples 1 to 17, the area ratio of Cube orientation was outside of the range of the defined value of 5 to 50%. Among those, Comparative Example 5 that had a too small area ratio of Cube orientation was poor in the bending property, and Comparative Example 8 that had a too large area ratio of Cube orientation was poor in the proof stress.

The X-ray diffraction integration intensity ratio I{2 0 0}/$I_0${2 0 0} was within the prescribed value of 1.3 or less, in all of Comparative Examples 1 to 17, except for Comparative Examples 8 and 11; and Comparative Examples 8 and 11 showed 1.3 or more, but were poor in the proof stress.

In Comparative Examples 5, 6, 16, and 17, the Ti content was outside of the range of the defined value of 1.0 to 5.0%. In Comparative Examples 1 to 17, any of the heating speed and the reached temperature in the intermediate annealing, and the cold-rolling working ratio was outside of the range of the defined value, and the properties were also outside of the prescribed ranges. In Comparative Examples 1, 3, 4, 7 to 9, 11, and 13 to 17, the Young's modulus was outside of the range of the prescribed value of 90 to 120 GPa. Further, in Comparative Examples 1, 3 to 8, 10 to 11, and 13 to 17, the deflection coefficient was outside of the range of the prescribed value of 80 to 110 GPa. In addition, in Comparative Example10, the addition amount of the third elements was too large over the prescribed value, and the electrical conductivity was lowered; and in Comparative Example 14, since the reached temperature in the intermediated annealing was too high, despite that the addition amount of the third elements was smaller than the prescribed value, cracks and wrinkles were occurred by the bending, the proof stress (mechanical strength) was too low, and the Young's modulus and the deflection coefficient were too high. In Comparative Example 15, the sample was bent without cracks in both GW and BW, and the proof stress satisfied the prescribed value, but the wrinkles on the bent surface part were large, the Young's modulus and the deflection coefficient were too large over the upper limits of the prescribed values, and the properties were poor. In Comparative Examples 16 and 17, the content of Ti and the production steps each were outside of the prescribed ranges, and both of the area ratio of Cube orientation and the I{2 0 0} diffraction intensity were outside of the prescribed ranges.

In Comparative Examples 3 to 6, 9, and 14 to 17, the area ratio of Cube orientation was outside of the range, and further, since an element (that improves the stress relaxation resistance) was not added, the stress relaxation resistance was poor, as compared to Examples 1 to 21.

**[0053]** In the present invention, by controlling the heating speed and the reached temperature in the intermediate annealing [Step 7], and the working ratio in the cold-rolling [Step 8], the target texture can be obtained, and a titanium-copper alloy sheet material can be obtained, which has balanced bending property and mechanical strength, which satisfies the size of the wrinkles on the bent surface part, and which satisfies the Young's modulus and the deflection coefficient.

(Conventional examples)

**[0054]** Copper alloy sheet materials were prepared with the respective alloy composition 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 subsequent cold-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 also shown in Table 3.

**[0055]**

Table 3

| ID number | Alloying element | Intermediate annealing [7] | | Cold-rolling [8] | Area ratio of Cube orientation | Integrated intensity ratio of X-ray diffraction | Bending property Cracks | |
|---|---|---|---|---|---|---|---|---|
| | Ti | Heating speed | Temp. reached | Working ratio | | | GW | BW |
| | mass% | °C/sec | °C | % | % | $I200/I_0200$ | | |
| Conv. Ex 1 | 3.10 | None | | None | 3 | 0.80 | × | × |
| Conv. Ex 2 | 3.00 | None | | None | 2 | 0.54 | × | × |
| Conv. Ex 3 | 3.00 | None | | None | 4 | 1.07 | × | × |

"Conv. Ex" means Conventional Example (the same will be applied in below).

Table 3 (continued)

| ID number | Wrinkles on bent surface (R/t=0) | | YS | EC | Young's modulus | Deflection coefficient | SRR |
|---|---|---|---|---|---|---|---|
| | GW (µm) | BW (µm) | MPa | %IACS | GPa | GPa | % |
| Conv. Ex 1 | 65 | 40 | 856 | 14 | 113 | 111 | 6.8 |
| Conv. Ex 2 | 55 | 50 | 830 | 13 | 112 | 107 | 7.0 |
| Conv. Ex 3 | 40 | 45 | 829 | 13 | 100 | 109 | 5.5 |

**[0056]** As is apparent from Table 3, in each of the copper alloy sheet materials of Conventional Examples 1 to 3 that were prepared without undergoing the intermediate annealing [Step 7] and the subsequent cold-rolling [Step 8], the area ratio of Cube orientation was too small, and the bending property was poor, and thus cracks were occurred or conspicuously large wrinkles were occurred, even the predetermined alloy composition and the predetermined production conditions (respective steps and conditions) other than these two steps were employed.

**[0057]** 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-2011-26635

**[0058]** A copper alloy having a composition containing Ti 3.25 mass%, with the balance being copper, was melted, followed by casting by using a vertical-type semi-continuous casting machine.

The thus-obtained slab was heated to 950°C, subjected to hot-rolling while the temperature was lowered from 950°C to 400°C, to form a sheet material with a thickness of about 9 mm, followed by water quenching by water cooling, and then removing the oxidized layer on the surface layer by mechanical polishing (face milling). The thickness of the sheet material was determined based on the relationship of the rolling ratios in the subsequent respective cold-rolling and the final sheet thickness. Then, the first cold-rolling was conducted at a rolling ratio of 84%, followed by subjecting to an intermediate annealing treatment. The intermediate annealing (heat treatment) was conducted at 550°C for 6 hours. When the electrical conductivities before and after the intermediate annealing are defined as Eb and Ea, respectively, and the Vickers hardnesses before and after the intermediate annealing are defined as Hb and Ha, respectively, Ea/Eb was 3.3, and Ha/Hb was 0.72. The second cold-rolling was then conducted at a rolling ratio of 86%.

Then, a solution treatment was conducted, by retaining the resultant alloy at 900°C for 15 seconds depending on the composition of the alloy, so that the average grain size on the surface of the rolled sheet (according to the cutting method of JIS H0501) would be more than 5 μm and not more than 25 μm.

The subsequent intermediate rolling was omitted and not conducted.

Then, an aging treatment was conducted at 450°C. The time period for the aging treatment was adjusted to a time period in which the hardness reached a peak by aging at 450°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-2011-26635.

Then, the sheet material after the above aging treatment was further subjected to finish cold-rolling at a rolling ratio of 15%. Further, the resultant sheet material was subjected to low-temperature annealing in an annealing furnace at a furnace temperature of 450°C for a retention time period of 1 minute. Where necessary, grinding and face milling were conducted in the mid course, and the sheet thickness was set to 0.10 mm.

This was utilized as Sample specimen c01.

The thus-obtained Sample specimens c01 was different from those in the above Examples according to the present invention in the production conditions, in that the treatment temperature was too low and the treatment time period was too long in the intermediate annealing treatment, and that the rolling ratio in the second cold-rolling after the intermediate annealing treatment was too high. The results were that the Sample specimen c01 had the area ratio of Cube orientation of lower than 5%, and that it did not satisfy the properties required in the present invention on the bending property in the direction perpendicular to the rolling direction.

**[0059]** (Comparative Example 102) ··· The conditions of Example 1 in JP-A-201 0-126777

A copper alloy containing 3.18 mass% of Ti, with the balance being Cu, was melted, followed by casting by using a vertical-type semi-continuous casting machine, to give an ingot with thickness 60 mm.

The thus-obtained ingot was heated to 950°C, followed by subjecting to extraction, and hot-rolling was started. In the hot-rolling, the pass schedule was set so that the rolling ratio in a temperature region of 750°C or more would become 60% or more, and that the rolling would be conducted even in a temperature region of lower than 700°C. The hot-rolling ratio in a temperature region of lower than 700°C but not lower that 500°C was set to 42%, and the final pass temperature of the hot-rolling was from 600°C to 500°C. The total hot-rolling ratio from the ingot was about 95%. After the hot-rolling, the oxidized layer on the surface layer was removed by mechanical polishing (face milling).

Then, the resultant sheet was subjected to cold-rolling at a rolling ratio of 98%, followed by subjecting to solution treatment. In this solution treatment, the heat treatment was conducted, by setting the temperature to a temperature that was higher by 30°C or more than the solidus line of the alloy composition in a temperature region of 750 to 1,000°C depending on the alloy composition, and adjusting the retention time period within the range of 5 seconds to 5 minutes, so that the average grain size (a twin boundary was not deemed as a grain boundary) after the solution treatment would be 5 to 25 μm. Specifically, the heat treatment was conducted at 900°C for 15 seconds.

Then, the resultant sheet material after the solution treatment was subjected to cold-rolling at a rolling ratio of 15%.

With respect to the thus-obtained sheet material, aging experiments at a temperature range of 300 to 550°C up to 24 hours at the highest were conducted as preliminary experiments, to figure out the aging conditions to give the maximum hardness (the aging temperature therefor is defined as $T_M$ (°C), the aging time period thereof is defined as $t_M$ (min), and the maximum hardness is defined as $H_M$ (HV)) depending on the alloy composition. Further, the aging temperature was set to a temperature within the range of $T_M \pm 10$°C, and the aging time period was set to a time period that was shorter than $t_M$ and that would give a hardness after the aging within the range of 0.90 $H_M$ to 0.95 $H_M$.

Then, the resultant sheet material after the aging was subjected to finish cold-rolling at a rolling ratio of 10%, followed by low-temperature annealing in which the resultant sheet material was maintained in an annealing furnace at 450°C for 1 minute.

In the above manner, a copper alloy sheet material was obtained. Where necessary, face milling was conducted in the mid course, to set the sheet thickness of the copper alloy sheet material to 0.15 mm. This was utilized as Sample specimen c02.

The thus-obtained Sample specimens c02 was different from those in the above Examples according to the present invention in the production conditions, in that the hot-rolling was conducted by two stages, that the solution treatment was conducted without conducting the intermediate annealing [Step 7] and the cold-rolling [Step 8] before the solution treatment, and that the steps of heat treatments and cold-rollings after the cold-rolling [Step 6] were different from those in the above Examples. The results were that the Sample specimen c02 had the area ratio of Cube orientation of lower than 5%, and that it did not satisfy the properties required in the present invention on the bending property in the direction perpendicular to the rolling direction.

**[0060]** 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.

**[0061]** This application claims priority on Patent Application No. 2010-195120 filed in Japan on August 31, 2010, which is entirely herein incorporated by reference.

REFERENCE SIGNS LIST

**[0062]**

1 Test specimen with an initial stress applied thereto
2 Test specimen after removing the load
3 Test specimen without any stress applied thereto
4 Test bench
11 Test specimen (after removing the load)
12 Test jig
13 Reference plane
14 Bolt for deflection loading
15 Test specimen (with the deflection loading applied thereto)

## Claims

1. A copper alloy sheet material, containing Ti in an amount of 1.0 to 5.0 mass%, with the balance being copper and unavoidable impurities,
wherein an area ratio of Cube orientation {0 0 1} <1 0 0> is 5 to 50%, in crystal orientation analysis by an EBSD analysis.

2. The copper alloy sheet material according to claim 1, which further contains at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Zr, Si, Fe, and Hf, in an amount of 0.005 to 1.0 mass% in total.

3. The copper alloy sheet material according to claim 1 or 2,
wherein the copper alloy sheet material has a 0.2% proof stress of 850 MPa or more; and
wherein the copper alloy sheet material has a bending property, to causes no crack in a 90° W bending test, and to give a value (r/t) of 1 or less, which value is obtained by dividing a minimum bending radius (r, mm) enabling bending with small bending wrinkles by a sheet thickness (t, mm).

4. The copper alloy sheet material according to any one of claims 1 to 3,
wherein the copper alloy sheet material has a Young's modulus of 90 to 120 GPa, which is measured by a tensile test, and which shows an amount of displacement when a given stress is applied to the sheet material, and
wherein the copper alloy sheet material has a deflection coefficient of 80 to 110 GPa, which is measured by a deflection test.

5. A method of producing the copper alloy sheet material according to any one of claims 1 to 4, comprising: subjecting a copper alloy raw material having an alloy composition to give the copper alloy sheet material, to the steps of:

   casting [Step 1]; homogenization heat treatment [Step 2]; hot-rolling [Step 3]; water-cooling [Step 4]; cold-rolling [Step 6]; intermediate annealing [Step 7]; cold-rolling [Step 8], and intermediate solution heat treatment [Step 9], in this order.

6. The method of producing the copper alloy sheet material according to claim 5, wherein aging-precipitation heat treatment [Step 10]; finish cold-rolling [Step 11]; and temper annealing [Step 12] are conducted in this order, after the intermediate solution heat treatment [Step 9].

**7.** A copper alloy part, comprising the copper alloy sheet material according to any one of claims 1 to 4.

**8.** A connector, comprising the copper alloy sheet material according to any one of claims 1 to 4.

*Fig. 1*

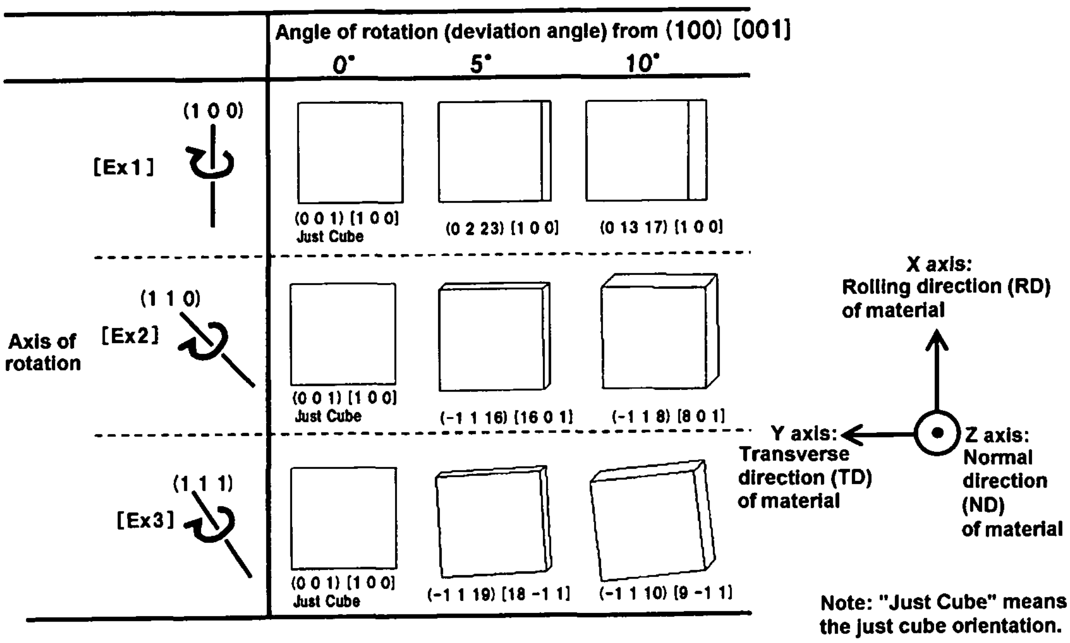
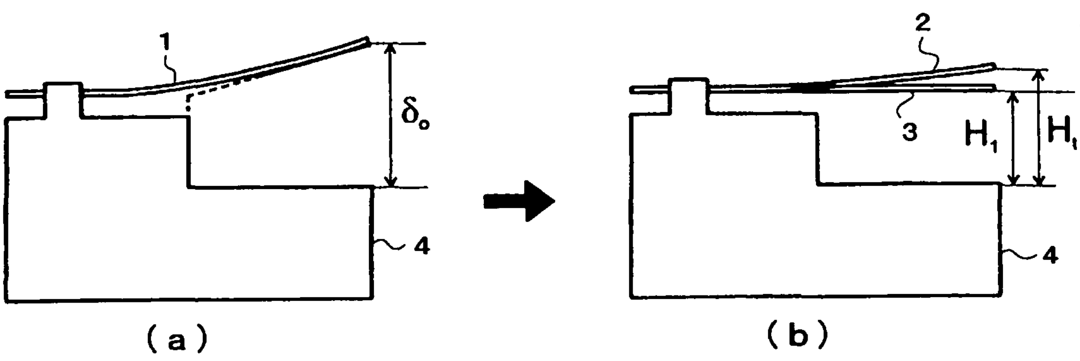
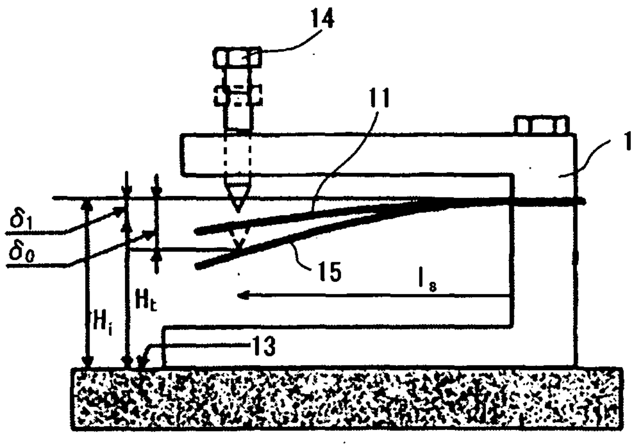

Angle of rotation (deviation angle) from (100) [001]
0°
5°
10°
(1 0 0)
[Ex1]
(0 0 1) [1 0 0]
Just Cube
(0 2 23) [1 0 0]
(0 13 17) [1 0 0]
(1 1 0)
Axis of rotation
[Ex2]
(0 0 1) [1 0 0]
Just Cube
(-1 1 16) [16 0 1]
(-1 1 8) [8 0 1]
(1 1 1)
[Ex3]
(0 0 1) [1 0 0]
Just Cube
(-1 1 19) [18 -1 1]
(-1 1 10) [9 -1 1]
X axis:
Rolling direction (RD) of material
Y axis:
Transverse direction (TD) of material
Z axis:
Normal direction (ND) of material
Note: "Just Cube" means the just cube orientation.

*Fig. 2*


1
δo
4
(a)
2
3
H1
Ht
4
(b)

## *Fig. 3*



## INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2011/069467

A. CLASSIFICATION OF SUBJECT MATTER
*C22C9/00*(2006.01)i, *C22C9/02*(2006.01)i, *C22C9/04*(2006.01)i, *C22C9/05*(2006.01)i, *C22C9/10*(2006.01)i, *C22F1/00*(2006.01)n, *C22F1/08*(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)
C22C9/00, C22C9/02, C22C9/04, C22C9/05, C22C9/10, C22F1/00, C22F1/08

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

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1922-1996 | Jitsuyo Shinan Toroku Koho | 1996-2011 |
| Kokai Jitsuyo Shinan Koho | 1971-2011 | Toroku Jitsuyo Shinan Koho | 1994-2011 |

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 2005-314779 A (Nikko Metal Manufacturing Co., Ltd.), 10 November 2005 (10.11.2005), entire text (Family: none) | 1-8 |
| A | JP 53-15217 A (Tokyo Shibaura Electric Co., Ltd.), 10 February 1978 (10.02.1978), entire text (Family: none) | 1-8 |
| A | JP 2004-27257 A (Nippon Mining & Metals Co., Ltd.), 29 January 2004 (29.01.2004), entire text & US 2004/0003878 A1 & CN 1470660 A | 1-8 |

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

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"&" document member of the same patent family

| Date of the actual completion of the international search | Date of mailing of the international search report |
|---|---|
| 15 November, 2011 (15.11.11) | 22 November, 2011 (22.11.11) |

| Name and mailing address of the ISA/ | Authorized officer |
|---|---|
| Japanese Patent Office | |
| Facsimile No. | Telephone No. |

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

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2011/069467

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | WO 2009/148101 A1 (The Furukawa Electric Co., Ltd.), 10 December 2009 (10.12.2009), entire text & US 2011/0073221 A1 & EP 2298945 A1 & CN 102105610 A | 1-8 |

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## REFERENCES CITED IN THE DESCRIPTION

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- JP 2008013836 A **[0008]**
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- JP 2006249565 A **[0008]**
- JP 2010126777 A **[0008] [0059]**
- JP 2007270267 A **[0008]**
- JP 2011026635 A **[0008] [0058]**
- JP 2010195120 A **[0061]**


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- ASTM E328; Standard Test Methods for Stress Relaxation Tests for Materials and Structures. American Society for Testing and Materials **[0047]**