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(54) COPPER ALLOY SHEET MATERIAL, CONNECTOR USING SAME, AND COPPER ALLOY SHEET MATERIAL PRODUCTION METHOD FOR PRODUCING SAME

(57) {Problems} To provide a copper alloy sheet material, which is excellent in the bending property, has an excellent mechanical strength, and is also excellent in the stress relaxation resistance, and which is thus suitable for lead frames, connectors, terminal materials, and the like, for 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, having a copper alloy composition containing 0.5 to 5.0 mass% in total of at least one of Ni and Co, and 0.1 to 1.2 mass% of Si, with the balance being Cu and inevitable impurities, wherein, in a crystal orientation analysis by an electron back scatter diffraction analysis, when an area ratio of the Cube orientation {0 0 1} <1 0 0> at a surface layer of the material is designated as W0, and an area ratio of the Cube orientation at a 1/4 position of the total depth of the material is designated as W4, a ratio of W0/W4 is 0.8 or more, W0 is 5% to 48%, and an average grain size is 12 to 100 µm, and wherein the copper alloy sheet material is excellent in 180° tight bending property and stress relaxation resistance.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy sheet material, and specially to a copper alloy sheet material that can be applied to lead frames, connectors, terminal materials, relays, switches, sockets, and the like, for parts to be mounted on automotives or for electrical/electronic equipments, the present invention also relates to a connector using the same, and to a method of producing a copper alloy sheet material for producing the same.

BACKGROUND ART

[0002] 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, are required to have, as characteristics, electrical conductivity, proof stress (yield stress), tensile strength, bending property, and stress relaxation resistance. In recent years, the demanded levels for those 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/electronic equipments. Some of representative examples will be shown.
Under the circumstances of reduction of mineral resources or weight reduction of parts, thickness reduction of materials is in progress. Further, in order to maintain the spring contact pressure, materials are used which have a higher mechanical strength than conventional cases. In this case, since a bending property is generally in a trade-off relationship with a mechanical strength, when a high mechanical strength material is worked at the bending radius as in conventional cases, there is a problem of occurrence of cracks. In particular, there are many occasions in which a design of bending the material 180° into a U-shape is needed in vehicle-mounted terminals, connectors for electronic equipment applications, and the like. However, since a large stress is imparted on the external side of the bent portion, cracks occur in a material poor in the bending property, causing a problem of conduction due to a decrease in the contact pressure of the connector. As a measure to be taken, a plurality of notches may be made in the inner side to be bent 180°, or a modification of design may be carried out such as adopting a large inner bending radius from the design of a tight bending. However, there is a problem that the design of bent parts cannot achieve a good balance with a reduction of press costs and a size reduction of the parts for electronic equipments.
Further, temperature elevation in the use environment is in progress. For example, in the parts to be mounted on automotives, a decrease in the vehicle weight is attempted, in order to reduce the amount of carbon dioxide to be generated. Thus, electronic equipments, such as ECUs for engine control, which have been conventionally provided in the door, are provided inside the engine room or in the vicinity of the engine, so that an attempt for shortening a wire harness between the electronic equipment and the engine is being made. Further, when the usage of high electric current is increased along with a trend for electric vehicles, the Joule heat causes a problem. When a contact material that is used in connectors is subjected to a high temperature, such as 100°C or higher, for a long time period, there is a problem that the displacement within the elastic limit becomes plastic displacement, and the contact pressure at the terminal fitting portion may decrease. Thus, there is a demand for the development of a copper alloy sheet material having excellent stress relaxation resistance.
In order to solve the problems described above, a copper alloy material is desired which is excellent in the stress relaxation resistance, and is enhanced in the bending property.

[0003] In regard to this demand for enhancement of the bending property of copper alloy materials, some proposals are already made to solve the problem by controlling crystal orientation.
It has been found in Patent Literature 1 that in regard to a Cu-Ni-Si-based copper alloy, bending property is excellent when the copper alloy has a crystal orientation such as that the grain size and the X-ray diffraction intensities obtained from {3 1 1}, {2 2 0} and {2 0 0} planes satisfy certain conditions. Further, it has been found in Patent Literature 2 that in regard to a Cu-Ni-Si-based copper alloy, bending property is excellent when the copper alloy has a crystal orientation in which the X-ray diffraction intensities obtained from {2 0 0} plane and {2 2 0} plane satisfy certain conditions. It has also been found in Patent Literature 3 that in regard to a Cu-Ni-Si-based copper alloy, excellent bending property is obtained by controlling the ratio of the Cube orientation {1 0 0} <0 0 1 >.
Further, in regard to the demand for enhancement of the stress relaxation resistance, there is a feature that generally as the grain size is larger, stress relaxation is more difficult. Accordingly, it is disclosed in Patent Literature 4 and the like that a balance is achieved between stress relaxation resistance and bending property in a Cu-Ni-Si-based copper alloy, by utilizing the feature.

CITATION LIST

PATENT LITERATURES

[0004]

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-2008-106356

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0005] However, in the inventions described in Patent Literatures 1, 2 and 4, the analysis of crystal orientation by X-ray diffraction from particular planes is related only to quite limited particular planes in the distribution of crystal orientations of a certain extent. Further, the analysis is related only to the crystal planes in the sheet plane direction, and it is not evaluated on which crystal face is oriented in the rolling direction or the sheet width direction. Thus, those techniques are often unsatisfactory for controlling the crystal orientations, with their effects of improving bending property being insufficient. Further, in the X-ray analysis of sheet surface as described these patent literatures, since the penetration depth of X-rays is a few ten micrometers, the crystal orientation in the deeper inside than that depth is not controlled. Further, in the invention described in Patent Literature 3, the effectiveness in the Cube orientation has been pointed out; however, the distribution in the sheet thickness direction, or the crystal orientation components other than that are not controlled. As such, in the conventional art, the improvement of bending property has been insufficient in some cases, and particularly, the improvement has been insufficient to reach the level of being capable of conducting bending without cracks under the high stress of 180° tight bending.

[0006] In view of the problems described above, an object of the present invention is to provide a copper alloy sheet material, which is excellent in the bending property, has an excellent mechanical strength, and is also excellent in the stress relaxation resistance, and which is thus suitable for lead frames, connectors, terminal materials, and the like, for electrical/electronic equipments, for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like. Another object is to provide a connector using the copper alloy sheet material, and to provide a method of producing a copper alloy sheet material, which preferably produces this connector.

SOLUTION TO PROBLEM

[0007] The inventors of the present invention extensively conducted investigations, and conducted a study on a copper alloy appropriate for electrical/electronic part applications. Thus, the inventors found that the 180° tight bending characteristics can be markedly enhanced, by controlling the Cube orientation area ratio at the surface layer of the sheet thickness and at the 1/4 position of the sheet thickness, and that the objects described above can be solved, by controlling the grain size to a specific range, in addition to the above orientation area ratio control. Furthermore, the inventors found that a reduction in the Brass orientation further contributes to the bending property. In addition to those, the inventors also found that when particular additive elements are contained in the copper alloy, the mechanical strength or the stress relaxation characteristics can be enhanced, without loosing electrical conductivity or the bending property. Thus, the inventors of the present invention have attained the present invention based on these findings.

[0008] That is, the present invention it to provide the following means:

(1) A copper alloy sheet material, having a copper alloy composition containing 0.5 to 5.0 mass% in total of at least one of Ni and Co, and 0.1 to 1.2 mass% of Si, with the balance being Cu and inevitable impurities,
wherein, in a crystal orientation analysis by an electron back scatter diffraction analysis, when an area ratio of the Cube orientation {0 0 1} <1 0 0> at a surface layer of the material is designated as W0, and an area ratio of the Cube orientation at a 1/4 position of the total depth of the material is designated as W4, a ratio of W0/W4 is 0.8 or more, W0 is 5% to 48%, and an average grain size is 12 to 100 μm, and
wherein the copper alloy sheet material is excellent in 180° tight bending property and stress relaxation resistance.
(2) The copper alloy sheet material according to the above item (1), which further contains at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf, in an amount of 0.005 to 2.0 mass% in total.
(3) The copper alloy sheet material according to the above item (1) or (2), wherein an area ratio of the Brass orientation {1 1 0} <1 1 2> is 20% or less.

(4) A connector, which is composed of the alloy sheet material according to claims 1 to 3.
(5) A method of producing a copper alloy sheet material, comprising the steps of:

providing a copper alloy ingot containing 0.5 to 5.0 mass% in total of at least one of Ni and Co, and 0.1 to 1.2 mass% of Si, with the balance being Cu and inevitable impurities; and
subjecting the ingot to at least treatments of steps I, III, and IV:
[Step I: a hot-rolling step at a working ratio per pass of 30% or less, with a retention time period between the respective passes of 20 to 100 seconds]
[Step III: an intermediate heat treatment step to be conducted between the hot-rolling step and the following solution heat treatment, at a temperature of 300 to 700°C for 10 seconds to 5 hours]
[Step IV: a solution heat treatment step at 800 to 1,000°C].

ADVANTAGEOUS EFFECTS OF INVENTION

[0009] The copper alloy sheet material of the present invention is excellent in the bending property, has an excellent mechanical strength, and is suitable for lead frames, connectors, terminal materials, and the like, for electrical/electronic equipments, and for connectors, for example, to be mounted on automotive vehicles, and for terminal materials, relays, switches, and the like. Further, according to the method of producing a copper alloy sheet material of the present invention, the copper alloy sheet material having excellent characteristics as described above can be favorably produced.

BRIEF DESCRIPTION OF DRAWINGS

[0010]

{Fig. 1} Fig. 1 is an explanatory diagram showing a method of calculating a rotation angle relative to the Cube orientation.
{Fig. 2} Figs. 2(a) and 2(b) are explanatory diagrams for the method of testing the stress relaxation resistance in the examples, in which Fig. 2(a) shows the state before heat treatment, and Fig. 2(b) shows the state after the heat treatment.

MODE FOR CARRYING OUT THE INVENTION

[0011] 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 base material 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. Herein, with regard to the sheet material, the term "surface layer of the material (or material surface layer)" means the "sheet surface layer," and the term "position of a depth of the material" means the "position in the sheet thickness direction." 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 8 to 800 μm, and more preferably 50 to 70 μm.
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, and it is noted that in the present invention, a tube material can also be construed and treated as a sheet material.

(Definition by EBSD analysis)

[0012] In order to clarify the cause of the occurrence of cracks upon bending of a material, the inventors of the present invention conducted a detailed investigation on the metal texture of the cross-section after bending deformation, through electron microscopy and electron back scatter diffraction (hereinafter, also referred to as EBSD). As a result, it was observed that the substrate material is not deformed uniformly, but non-uniform deformation proceeds, in which deformation is concentrated only in a region of a particular crystal orientation. Further, we found that, due to that non-uniform deformation, wrinkles of a depth of several micrometers or cracks occur, at the surface of the substrate material after bending.
Further, in 90° bending, strain is applied to the outermost layer of the sheet thickness direction, but, in 180° bending, large strain occurs not only in the outermost layer of the sheet thickness direction of a thin sheet but also in the region

extending to the 1/4 position of the sheet thickness. Thus, we found that, in the region of local deformation that develops from the surface layer, grains involved are not only the grains in the vicinity of the surface layer, but also the grains in the region extending to the depth of the 1/4 position of the sheet thickness. Further, the local deformation band is not often observed in the cube-oriented grains, and we found that the Cube orientation has an effect of suppressing non-uniform deformation. As a result, we found that wrinkles occurring at the sheet surface are reduced, and thus cracks are suppressed. Also, we found that the Brass orientation is frequently accompanied by local deformations after bending deformation, and that the Brass orientation has adverse affections on the bending property.

[0013] When the area ratio of the Cube orientation in the sheet surface layer, W0, is 5% to 48%, and the ratio thereof with the Cube orientation area ratio W4 at the 1/4 depth position of the sheet thickness, W0/W4, is 0.8 or greater, the 180° tight bending property is excellent. Preferably, W0 is 10% to 40%, and W0/W4 is 0.9 or greater. When W0/W4 is set to the range described above, particularly an enhancement of bending property can be achieved, and a balance between bending property and material strength can be favorably achieved.

The Brass orientation area ratio of the sheet surface layer is preferably 20% or less, more preferably 15% or less, and even more preferably 10% or less. It is preferable to set the Brass orientation area ratio to the range described above, similarly from the viewpoint of realizing high bending property, and achieving a balance between this bending property and the material strength.

[0014] Herein, the method of indicating the crystal orientation in the present specification is such that a Cartesian coordinate system is employed, representing the rolling direction (RD) of the material in the X-axis, the transverse direction (TD) in the Y-axis, and the direction normal to the rolling direction (ND) in the Z-axis, various regions in the 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) and the index [u v w] in the crystal direction parallel to the X-axis. 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 Cube orientation refers to the state in which the (1 0 0) plane is oriented in the direction normal to the rolling surface (ND), and the (1 0 0) plane is oriented in the rolling direction (RD). The Cube orientation is represented by the index of {0 0 1} <1 0 0>.

The Brass orientation refers to the state in which the (1 1 0) plane is oriented in the direction normal to the rolling surface (ND), and the (1 1 2) plane is oriented in the rolling direction (RD). The Brass orientation is represented by the index of {1 1 0} <1 1 2>.

[0015] The analysis of the crystal orientation in the present invention is conducted using the EBSD method. The EBSD method, which stands for Electron Back Scatter Diffraction, is a technique of crystal orientation analysis using reflected electron Kikuchi-line diffraction (Kikuchi pattern) that occurs when a sample is irradiated with an electron beam under a scanning electron microscope (SEM). In the present invention, a sample area measured 500 μm on each of the four sides and containing 200 or more grains, was subjected to an analysis of the orientation, by scanning in a stepwise manner at an interval of 0.5 μm.

The area ratio in the Cube orientation or the Brass orientation is a value calculated by dividing the area of a region in which the deviation angle from the respective ideal orientation (the Cube orientation or the Brass 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 is calculated with respect to all of the axes 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, and the number including up to the first decimal place is designated as the effective number. The area of grains having an orientation within 10° from the Cube orientation or the Brass orientation is divided by the total measured area, and the resultant value is designated as the ratio of the 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, the distribution of orientation is measured from the sheet surface.

[0016] In regard to the EBSD analysis, in order to obtain a clear Kikuchi-line diffraction image, it is preferable to mirror polish the substrate surface, with polishing particles of colloidal silica after mechanical polishing, and then to conduct the analysis.

In regard to the EBSD analysis at the 1/4 position of the sheet thickness, the surface layer region is dissolved by electrolytic polishing down to the 1/4 position, and the resultant surface was mirror-polished, and then the analysis is conducted in the same manner as in the case of the sheet surface layer as described above.

[0017] Herein, the features of the EBSD analysis will be explained in comparison with the X-ray diffraction analysis.

First, the first feature is that there are crystal orientations that cannot be measured by the X-ray diffraction analysis, and they are the S orientation and the BR orientation. In other words, information on the S orientation and the BR-orientation are obtained by employing EBSD, and the relationship between the metal texture to be specified by the orientations and the actions/effects thereof is elucidated for the first time. The second feature is that X-ray diffraction analyzes the quantity of the crystal orientation that is included in the range of about ±0.5° with respect to ND//{h k l), while EBSD analyzes the quantity of the crystal orientation that is included in the range of ±10° with respect to the relevant orientation. Therefore, when an EBSD analysis is conducted, a huge range of comprehensive information on the metal texture is obtained, and those states that cannot be easily specified by X-ray diffraction in the overall alloy material can be clarified. As explained above, the information obtainable by an EBSD analysis and the information obtainable by an X-ray diffraction analysis are different in the contents and the natures. Unless otherwise specified, in the present specification, the results of EBSD are results obtained in connection with the ND direction of a copper alloy sheet material.

(Alloy composition and the like)

[0018] Copper-based materials that are favorably used as materials for connectors can be divided into pure copper-based materials and high-mechanical strength copper-based materials, and the high-mechanical strength copper-based materials can be further divided into solid-solution-type materials and precipitate-type materials. According to the present invention, a precipitate-type copper alloy having the electrical conductivity, mechanical strength, and heat resistance that are required in connectors is preferred. Particularly, in order to achieve a balance between high mechanical strength and high electrical conductivity, a Cu-Ni-Si-based alloy, a Cu-Ni-Co-Si-based alloy, and a Cu-Co-Si-based alloy are preferred.

● Ni, Co, Si

[0019] In the present invention, when the respective amounts of addition of nickel (Ni), cobalt (Co), and silicon (Si), which form the first group of elements to be added to copper (Cu), are brought under control, Ni-Si, Co-Si, and/or Ni-Co-Si compounds can be precipitated, to thereby enhance the mechanical strength of the resultant copper alloy. The contents of any one of or two of Ni and Co are, in total, preferably from 0.5 to 5.0 mass%, more preferably 0.6 to 4.5 mass%, and still more preferably 0.8 to 4.0 mass%. The content of Si is preferably 0.1 to 1.5 mass%, and more preferably 0.2 to 1.2 mass%. If the amounts of addition of Ni, Co and Si are too large, the electrical conductivity is apt to be decreased, and if the amount of addition is too small, the mechanical strength is apt to be insufficient. In the case where it is desired to increase the electrical conductivity, it is preferable to essentially add Co, and in that case, the amount of addition of Co is 0.4 mass% to 1.5 mass%, and more preferably 0.6 mass% to 2.0 mass%. Since Co is a rare element, and since Co raises the solid solution temperature when added, if it is not necessary to significantly increase electrical conductivity depending on the use, it is preferable not to add Co.

● Average grain size

[0020] The average grain size is set to 12 to 100 μm. If the average grain size is too small, the stress relaxation resistance becomes poor, and if the size is too large, the bending property becomes poor, each of which is not preferable. Further, in order to control the grain size to a range smaller than 12 μm, it is necessary to control the end-point temperature in the final solution heat treatment that will be described below, to a relatively low temperature. However, in that case, solid solution of the solute element occurs insufficiently, and a reduction in aging precipitation hardening may be caused thereby. From that point of view as well, the average grain size is set to 12 μm or greater. The average grain size is more preferably 22 to 80 μm.
The average grain size according to the present invention refers to the value measured according to JIS H 0501 (cutting method).

● Other elements

[0021] The copper alloy sheet material of the present invention may contain at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf, together with the first group of additive elements. The average grain size and the preferred range thereof in this composition are also the same as those described above.
In order to sufficiently exhibit the effects of addition while not decreasing electrical conductivity, the content of at least one additive element selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf, as the total amount, is set to 0.005 to 2.0 mass%, preferably 0.1 to 1.5 mss%, and more preferably 0.7 to 1.2 mass%. If the total amount of these additive elements is too large, electrical conductivity is decreased. If the total amount is too small, the effects of adding these elements are hardly exhibited.

[0022] The effects of adding various elements will be described below. Mg, Sn, and Zn improve the stress relaxation resistance when added to Cu-Ni-Si-based, Cu-Ni-Co-Si-based, and Cu-Co-Si-based copper alloys. When these elements are added together, as compared with the case where any one of them is added, the stress relaxation resistance is further improved by synergistic effects. Further, an effect of remarkably improving solder brittleness is obtained. A preferred range of the total amount of Mg, Sn and Zn is 0.12 to 1.0 mass% in total.

[0023] Mn, Ag, B, and P, when added, improve hot workability, and at the same time, enhance the mechanical strength. A preferred range of the total amount of Mn, Ag, B and P is 0.12 to 0.5 mass% in total.

[0024] Cr, Fe, Ti, Zr, and Hf finely precipitate in the form of compounds with Ni, Co, and/or Si, which are main elements to be added, or in the form of simple elements, to contribute to precipitation hardening. Further, these elements precipitate in the form of compounds having a size of 50 to 500 nm, and suppress grain growth, thereby having an effect of making the grain size fine and making the bending property satisfactory. A preferred range of the total amount of Cr, Fe, Ti, Zr, and Hf is 0.12 to 0.5 mass% in total.

(Production method and the like)

[0025] Next, explanation will be made on the method of controlling the area ratios of the Cube orientation and the Brass orientation in the vicinity of the sheet thickness surface layer and at the 1/4 position of the sheet thickness. Herein, the explanation will be given by taking a sheet material (strip material) of a precipitate-type copper alloy as an example, but the method can be applied to solid-solution-type alloy materials, dilute-based alloy materials, and pure copper-based materials.

Generally, a precipitate-type copper alloy is produced by working an ingot that has been subjected to a homogenizing heat treatment into a thin sheet at the steps of hot-rolling and cold-rolling, conducting a final solution heat treatment at a temperature in the range of 700°C to 1,020°C to make the solute atoms into a solid solution again, and then conducting an aging precipitation heat treatment and finish cold-rolling, thereby to satisfy the required mechanical strength. The conditions for the aging precipitation heat treatment and the finish cold-rolling are adjusted, in accordance with the desired characteristics, such as mechanical strength and electrical conductivity. The texture is approximately determined by the recrystallization occurring in the final solution heat treatment in this series of steps, and is finally determined by the rotation of orientation occurring in the finish rolling.

The hot-rolling utilizes low deformation resistance at a high temperature and high deformability, and therefore has a notable advantage that the energy required for working is reduced as compared with cold-rolling. On the other hand, in a precipitation hardened-type alloy, precipitation may occur depending on the hot-rolling temperature; however, because the precipitate generated at this high temperature is generally coarse or giant, the precipitate is not completely made into a solid solution even in the final solution heat treatment, and consequently, precipitation hardening may occur insufficiently upon the aging precipitation heat treatment. Alternatively, when the final solution heat treatment is conducted at a high temperature, and the precipitate generated in hot-rolling is completely made into a solid solution, the grains become coarse or giant, and this time, the bending property may deteriorate. For such reasons, in order to suppress precipitation as far as possible upon hot-rolling, in a general design protocol for the hot-rolling process, hot-rolling is completed at a high temperature for a short time period by decreasing the total number of passes by increasing the one-pass working ratio (i.e. a working ratio per pass) as high as possible, and not taking any retention time period between one pass and another pass, and after the hot-rolling, the precipitate is quenched by a method, such as water cooling, to maintain in a state close to an oversaturated solid solution.

[0026] In general hot-rolling and a series of the production methods as described above, it is difficult to stably control the area ratios of the Cube orientation and the Brass orientation in the vicinity of the sheet thickness surface layer and at the 1/4 position of the sheet thickness, to the range defined in the present invention, and it is confirmed that the area ratios are achieved according to the production method shown below.

● Process condition I

[0027] Firstly, hot-rolling is preferably a rolling process in which the one-pass working ratio is set to 30% or less, and the rolling direction in the material is alternately changed in every single pass by reverse rolling. It can be presumed that this is caused by the effect in which, when the rolling direction is alternately changed every single cycle in the rolling on the surface layer where a large shear stress is imparted, the rotation of the crystals of the sheet surface layer is controlled by mutually canceling out the shear strain, and the formation of a texture that is different from the interior where compression stress is imparted is suppressed. Under the conditions described above, the variation of the texture in the sheet thickness direction can be reduced. Further, it is preferable to adjust the retention time period between one pass and another pass to 20 seconds to 100 seconds (preferably 20 to 50 seconds, and more preferably 20 to 30 seconds), and to adjust the temperature decrease between one pass and another pass to 5 to 100°C. As a result of the control of these time period and temperature between one pass and another pass, static recrystallization and recovery occur within the material, and the variation of the texture in the sheet thickness direction can be reduced. The temperature between one pass and another pass is measured with a radiation thermometer or a contact-type thermocouple thermometer. Upon the control of the temperature between one pass and another pass, heating is conducted using a burner or the like, and cooling is conducted by air cooling or water cooling.

[0028] When the retention time period between one pass and another pass is longer than 100 seconds, the material temperature drops too low, and therefore, plane cracks or edge cracks occurs upon rolling, which is not preferable.

● Process condition II

[0029] Secondly, hot-rolling, and cold-rolling that is conducted after scale removal after the hot-rolling, each are preferably conducted in a manner of lubrication rolling at a working ratio of 90% to 99%. If the working ratio is less than 90%, there may be an influence of the texture variation in the surface layer and the interior formed by hot-rolling. On the other hand, if the working ratio is greater than 99%, edge cracks may occur.

● Process condition III

[0030] Thirdly, it is preferable to introduce an annealing heat treatment (intermediate heat treatment) before the final solution heat treatment, and a cold-rolling with a low working ratio thereafter, and to conduct the said final solution heat treatment thereafter. This annealing heat treatment to be introduced may be conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and the cold-rolling may be conducted at a working ratio of 5 to 50%.

● Process condition IV

[0031] Fourthly, it is preferable to carry out the final solution heat treatment at a relatively high temperature at which the average grain size would become a size of 12 to 100 μm. This is because the precipitate generated between one pass and another pass of the hot-rolling process, and the precipitate generated in the annealing heat treatment before the final solution heat treatment, are made into a solid solution. In the general processes as described above, when the temperature of the final solution heat treatment is raised, the bending property is worsened as a result of the coarsening of grains. However, when the area ratio of the Cube orientation is increased as in the present invention, deterioration of the bending property is negligible due to the effect of the crystal orientation. The temperature for controlling the average grain size to 12 to 100 μm may vary depending on the alloy components, but a temperature of 800°C to 1,000°C is preferred.

[0032] Among the four conditions described above, the production steps described in the first (condition I), the third (condition III), and the fourth (condition IV) are different from the conventional general method of producing a precipitate-type copper alloy, and those are very important in the present invention. When the production step described in the second is used in combination with those, a more preferred state is obtained.

[0033] In regard to the hot-rolling of a Cu-Ni-Si-based alloy, the literatures published hitherto describe that precipitation upon hot-rolling is a phenomenon that should be suppressed as much as possible. Therefore, as a method of suppressing the precipitation of Ni and Si, which causes a lowering/decrease in bending property or mechanical strength, and the coarsening of the precipitate, for example, a method of shortening the hot-rolling time period is disclosed in Japanese Patent No. 4209749, paragraph 0025. Further, Japanese Patent No. 4444143 discloses a twin-roll casting method as a method which does not conduct the hot-rolling process itself.

In order to achieve the difficult subject of decreasing in the texture variation in the sheet thickness direction, the novel production method according to the present invention is to take a rather long retention time period between passes, as in the case of the process condition I, and to willingly employ a high temperature, as in the case of the process condition IV, as a measure against the precipitation that occurs between the passes.

[0034] When the matters described above are satisfied, for example, the characteristics required of a copper alloy sheet material for use in connectors can be satisfactorily exhibited. According to one preferred embodiment of the copper alloy sheet material of the present invention, the 0.2% proof stress is 500 MPa or greater, and the electrical conductivity is 30 %IACS or higher. Particularly preferred is a copper alloy sheet material which has a 0.2% proof stress of 700 MPa or greater, has a bending property that does not cause any cracks and is capable of being bent in a 180° tight bending test with a test specimen having a width of 1 mm, has an electrical conductivity of 35 %IACS or higher, and has satisfactory stress relaxation resistance of 30% or less when measured according to a measurement method of maintaining the test specimen at a temperature of 150°C for 1000 hours as will be described below. One advantage of the present invention is that such characteristics can be realized. According to the present invention, the 0.2% proof stress is a value obtained according to JIS Z 2241. Further, the term %IACS indicates the electrical conductivity, in which the resistivity 1.7241 $\times 10^{-8}$ Ωm of the International Annealed Copper Standard is designated as 100%IACS.

EXAMPLES

[0035] 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

[0036] As shown with the respective composition in the column of alloying elements in Tables 1-1 and 1-2, an alloy containing Ni, Co and Si, with the balance being Cu and unavoidable impurities, was melted in a high-frequency melting furnace, followed by casting, to obtain an ingot. The resultant ingots in this state were used as test materials, and test specimens of copper alloy sheet materials of Examples 1-1 to 1-12 according to the present invention and Comparative Examples 1-1 to 1-8 were produced in any of the following Steps A to G. It is indicated in Table 1-1 and Table 1-2 which of the Steps A to G was used. The thickness of the final alloy sheet material was set to 150 μm, unless otherwise specified. Although it is not shown in the Steps A to G, when the experimental production was conducted under the conditions in which the retention time period between one pass and another pass was longer than 100 seconds, the material temperature dropped too much, and plane cracks or edge cracks occurred upon rolling. Thus, the experimental production was stopped.

(Step A)

[0037] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 4 to 12 passes in total of reverse rolling at a one-pass working ratio of 10 to 30%, with the retention time period between one pass and another pass of 20 to 100 seconds. Then, a cold-rolling was conducted at a working ratio of 90 to 99%, a heat treatment was conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and a cold-rolling was conducted at a working ratio of 5 to 50%. Then, a solution heat treatment of maintaining at a temperature of 800°C or higher for 5 seconds or longer was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 5 to 40%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step B)

[0038] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 4 to 12 passes in total of reverse rolling at a one-pass working ratio of 10 to 30%, with the retention time period between one pass and another pass of 20 to 100 seconds. Then, a cold-rolling was conducted at a working ratio of 80 to 89%, a heat treatment was conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and a cold-rolling was conducted at a working ratio of 5 to 50%. Then, a solution heat treatment of maintaining at a temperature of 800°C or higher for 5 seconds or longer was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 5 to 40%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step C)

[0039] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 4 to 12 passes in total of reverse rolling at a one-pass working ratio of 10 to 30%, with the retention time period between one pass and another pass of 20 to 100 seconds. Then, a cold-rolling was conducted at a working ratio of 90 to 99%, a heat treatment was conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and a cold-rolling was conducted at a working ratio of 5 to 50%. Then, a solution heat treatment of maintaining at a temperature of 800°C or higher for 5 seconds or longer was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 40 to 50%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step D)

[0040] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 2 to 8 passes in total of tandem-type one-direction rolling at a one-pass working ratio of higher than 30%, with the retention time period between one pass and another pass of less than 20 seconds. Then, a cold-rolling was conducted at a working ratio of 80 to 89%, a heat treatment was conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and a cold-rolling was conducted at a working ratio of 5 to 50%. Then, a solution heat treatment of maintaining at a temperature of 800°C or higher for 5 seconds or longer was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 5 to 40%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step E)

[0041] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 2 to 8 passes in total of tandem-type one-direction rolling at a one-pass working ratio of higher than 30%, with the retention time period between one pass and another pass of less than 20 seconds. Then, a cold-rolling was conducted at a working ratio of 80 to 89%, a solution heat treatment of maintaining at a temperature of 800°C or higher for 5 seconds or longer was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 5 to 40%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step F)

[0042] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 4 to 12 passes in total of reverse rolling at a one-pass working ratio of 10 to 30%, with the retention time period between one pass and another pass of 20 to 100 seconds. Then, a cold-rolling was conducted at a working ratio of 90 to 99%, a heat treatment was conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and a cold-rolling was conducted at a working ratio of 5 to 50%. Then, a solution heat treatment of maintaining at a temperature of 650 to 750°C for 2 hours was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 5 to 40%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step G)

[0043] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at a temperature of 900 to 1,020°C for 3 minutes to 10 hours, followed by hot working, water cooling, and then surface milling to remove oxide scale. The hot-rolling was conducted via 4 to 12 passes in total of reverse rolling at a one-pass working ratio of 10 to 30%, with the retention time period between one pass and another pass of 20 to 100 seconds. Then, a cold-rolling was conducted at a working ratio of 80 to 89%, a heat treatment was conducted at a temperature of 300 to 700°C for 10 seconds to 5 hours, and a cold-rolling was conducted at a working ratio of 5 to 50%. Then, a solution heat treatment of maintaining at a temperature of 730 to 770°C for 5 to 30 seconds was conducted, and an aging precipitation heat treatment was conducted at a temperature of 350 to 600°C for 5 minutes to 20 hours. Then, a finish rolling was conducted at a working ratio of 5 to 40%, and a temper annealing of maintaining at a temperature of 300 to 700°C for 10 seconds to 2 hours was conducted.

(Step H)

[0044] Each of the test specimens was produced in the same manner as in the Step A, except that the intermediate heat treatment (for 10 seconds to 5 hours at a temperature of 300°C to 700°C) in the mid course of the cold-rolling steps was not conducted.

[0045]

Table A

		Step (1)							Step (2)			
		Homogenization treatment	Hot-working	Quenching (water cooling)	Cold-rolling	Intermediate heat treatment	Cold-rolling	Solution treatment	Cold-rolling	Aging	Cold-rolling	Temperannealing
Step A	Ex	o	o	o	o (Red ratio 90 to 99%)	o	o	o	-	o	o	o
Step B	Ex	o	o	o	o (Red ratio 80 to 89%)	o	o	o	-	o	o	o
Step C	Ex	o	o	-	o	o	o	o	-	o	o	o
Step D	C Ex	o	Δ over 30%/ pass less than 20 sec	-	o (Red ratio 90 to 99%)	o	o	o	-	o	o	o
Step E	C Ex	o	Δ over 30%/ pass less than 20 sec	-	o (Red ratio 80 to 89%)	o	o	o	-	o	o	o
Step F	C Ex	o	o	-	o	o	o	Δ Low temp.	-	o	o	o
Step G	C Ex	o	o	-	o	o	o	o Low temp.	-	o	o	o
Step H	C Ex	o	o	-	o	-	o	o	-	o	o	o

"Ex" means Example according to this invention, and "C Ex" means Comparative Example.
"Red ratio" means a working ratio.

[0046] After the respective heat treatment or rolling above, acid washing or surface polishing 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.

[0047] Various characteristics of those test specimens were analyzed and evaluated in the following manner. Herein, the thickness of the respective test specimen was set at 0.15 mm. The results are shown in Tables 1-1 and 1-2. a. Area ratio of the Cube orientation [W0, W0/W4]:

The measurement was conducted with the EBSD method in a measurement region of about 500 μm on each of the four sides, under the conditions of a scan step of 0.5 μm. The measured area was adjusted on the basis of the condition of inclusion of 200 or more grains.
As explained above, in regard to the deviation angle from the ideal orientation, the angle of rotation around the common axis of rotation was calculated, and the angle of rotation is designated as the deviation angle. The angle of rotation relative to the Cube orientation was calculated with respect to all of the axes of rotation. As for the axis of rotation, one that can be represented by the smallest deviation angle was employed. This deviation angle was calculated for all the measured points, and the number including up to the first decimal place is designated as the effective number. The area ratio was calculated, by dividing the area of grains having an orientation within 10° from the Cube orientation, by the total measured area. W0 represents the measured result from the sheet surface, and W4 represents the measured result at the 1/4 depth position in the sheet thickness direction. W0/W4 is the ratio thereof.

b. Area ratio of the Brass orientation [B0]:

[0048] The area ratio was measured from the sheet surface, in the same manner as in the case of the area ratio of the Cube orientation described above.

c. Average grain size [GS]:

[0049] The average grain size was measured according to JIS H 0501 (cutting method). Measurement was conducted for a cross-section parallel to the rolling direction, and a cross-section perpendicular to the rolling direction, and the average of both was taken. Observation of the metal texture was done by chemically edging a mirror polished material surface, with an optical microscope.

d. 180° tight bending property [bending property]:

[0050] A sample was taken, by pressing the respective test specimen perpendicularly to the rolling direction, into a size with width 1 mm and length 25 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 bending was conducted according to JIS Z 2248. Preliminary bending was conducted using a 0.4-mmR 90° bending mold, and then tight bending was conducted with a compression testing machine. The occurrence (i.e. presence or absence) of cracks in the outer side of the bent portion was examined, by observing the bent portion with the naked eye with an optical microscope with a magnification of 50. A sample which had no crack in the bent portion and had minor wrinkles is rated as "◎" (excellent), a sample which had no crack but had large wrinkles is rated as "o" (good), and a sample which had cracks is rated as "×" (poor).

e. 0.2% proof stress [YS]:

[0051] Three test specimens that were cut out from 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. Herein, a sample which had a YS value of 550 MPa or greater is judged to be excellent in the mechanical strength.

f: Electrical conductivity [EC]:

[0052] The electrical conductivity was calculated by using the four-terminal method to measure the specific resistance of the material in a thermostat bath that was maintained at 20°C (±0.5°C). The spacing between terminals was set to 100 mm. Herein, a sample which had an EC value of 35%IACS or higher is judged to be excellent in the electrical conductivity.

g. Stress relaxation ratio [SR]:

[0053] The stress relaxation ratio was measured, according to the provisional standard of the Japan Copper and Brass Association, JCBA T309:2001 (corresponding to the former Electronic Materials Manufacturer's Association of Japan Standard EMAS-3003), under the conditions of maintaining at 150°C for 1,000 hours, as shown in the below. An initial stress that was 80% of the yield stress (proof stress) was applied, by the cantilever method. Herein, a sample which had an SR value of 30% or less is judged to be excellent in the stress relaxation resistance.

[0054] 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 δ_0 from the reference position. This test specimen was kept in a thermostat at 150°C for 1,000 hours (which corresponds to the heat treatment at the state of the test specimen 1). 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: $SR(\%) = \{(H_t - H_1)/(\delta_0 - H_1)\} \times 100$. In the formula, δ_0 represents the distance from the reference position to the test specimen 1; H_1 represents the distance from the reference position to the test specimen 3; and H_t represents the distance from the reference position to the test specimen 2.

[0055]

Table 1-1

ID number	Alloying elements			Step	Cube orientation		Brass orientation	GS	Bending property		YS	EC	SR
	Ni	Co	Si		W0/W4	W0	B0						
	mass%	mass%	mass%			%	%	µm	GW BW		MPa	%IACS	%
Ex 1-1	2.27	-	0.66	A	1.1	22	6	25	⊙	o	725	40.3	25.1
Ex 1-2	3.05	-	0.70	B	0.9	30	8	32	⊙	⊙	788	39.8	21.7
Ex 1-3	3.05	-	0.70	C	1.1	15	9	30	o	o	812	39.2	22.2
Ex 1-4	3.86	-	0.93	A	1.3	32	7	15	⊙	⊙	806	38.2	19.8
Ex 1-5	-	0.82	0.23	C	1.2	45	8	62	o	o	585	35.6	23.6
Ex 1-6	-	1.41	0.39	B	1.5	21	7	28	⊙	o	620	56.7	24.0
Ex 1-7	-	1.86	0.56	A	1.1	15	6	25	⊙	o	665	52.1	23.3
Ex 1-8	0.98	0.51	0.39	A	0.9	8	9	26	⊙	o	635	51.0	23.5
Ex 1-9	0.98	1.02	0.49	B	1.2	26	6	35	o	⊙	714	49.7	23.6
Ex 1-10	1.32	1.17	0.62	C	1.1	16	8	46	o	o	789	45.2	24.3
Ex 1-11	1.32	1.17	0.62	B	0.9	8	3	42	o	o	808	43.2	22.5
Ex 1-12	3.14	1.84	1.12	B	1.3	32	5	15	⊙	o	807	46.2	19.2

"Ex" means Example according to the present invention.

[0056]

Table 1-2

ID number	Alloying elements			Step	Cube orientation		Brass orientation	GS	Bending property		YS	EC	SR
	Ni	Co	Si		W0/W4	W0	B0						
	mass%	mass%	mass%			%	%	µm	GW	BW	MPa	%IACS	%
C Ex 1-1	0.25	0.21	0.71	A	1	15	5	13	⊙	⊙	421	32.5	45.2
C Ex 1-2	3.52	1.64	1.15	A	1.1	6	6	24	o	o	768	28.3	26.3
C Ex 1-3	2.72	-	0.08	A	0.9	11	9	23	⊙	⊙	415	27.6	35.2
C Ex 1-4	2.68	-	1.33	A	1.1	12	7	16	o	o	769	25.5	23.2
C Ex 1-5	1.32	1.17	0.62	D	0.6	6	6	25	×	×	812	40.3	25.1
C Ex 1-6	1.32	1.17	0.62	E	0.7	1	8	32	×	×	794	39.8	21.7
C Ex 1-7	1.32	1.17	0.62	F	1.1	53	23	115	×	×	789	47.3	18.2
C Ex 1-8	1.32	1.17	0.62	G	1	6	18	7	o	o	776	45.6	33.2

"C Ex" means Comparative Example.
Underlined: values that are outside the specific range and conditions

[0057] As shown in Table 1-2, the samples of Comparative Examples gave results that were poor in any one of the characteristics.
That is, since Comparative Example 1-1 had a too small total amount of Ni and Co, the density of the precipitates that contributes to precipitation hardening was decreased, and the mechanical strength was poor. Further, Si that did not form a compound with Ni and/or Co, formed a solid solution in the metal texture excessively, and thus the electrical conductivity was poor. Further, the stress relaxation resistance was also poor. Comparative Example 1-2 had a too large total amount of Ni and Co, and thus the electrical conductivity was poor. Comparative Example 1-3 had a too small amount of Si, and thus the mechanical strength was poor. Comparative Example 1-4 had a too large amount of Si, and thus the electrical conductivity was poor.
Comparative Example 1-5 had a low value of W0/W4, and was poor in the 180° tight bending property. Comparative Example 1-6 had too low values of W0/W4 and W0, and was poor in the 180°C tight bending property. Comparative Example 1-7 had too high values of W0 and the average grain size, and was poor in the 180° tight bending property. Comparative Example 1-8 had a too small average grain size, and was poor in the stress relaxation resistance.
On the contrary, as shown in Table 1-1, Examples 1-1 to 1-12 were excellent in all of the 180° tight bending property, proof stress, electrical conductivity, and stress relaxation resistance. In particular, Examples 1-1, 1-2, 1-4, 1-6, 1-7, 1-8, 1-9, 1-11, and 1-12, each of which had the Brass orientation area ratio of the surface layer of 20% or less, exhibited a quite excellent bending property, without any cracks in at least one of GW and BW, and having only minor wrinkles.

Example 2

[0058] With respect to the copper alloys having the compositions shown in the column of alloying elements in Table 2, with the balance of Cu and unavoidable impurities, test specimens of copper alloy sheet materials of Examples 2-1 to 2-8 according to the present invention and Comparative Example 2-1 to 2-3 were produced in the same manner as in Example 1, and the test specimens were subjected to measurement and evaluation of the properties in the same manner as in Example 1. The results are shown in Table 2.
[0059]

Table 2

ID number	Alloying elements			Other elements	Step	Cube orientation		Brass orientation	GS	Bending property		YS	EC	SR
	Ni	Co	Si			W0/W4	W0	B0						
	mass%	mass%	mass%	mass%			%	%	µm	GW	BW	%	%IACS	%
Ex 2-1	-	0.90	0.25	0.05Mg, 0.21 Fe	A	1.0	25	5	22	⊙	⊙	565	52.2	21.6
Ex 2-2	0.50	1.50	0.35	0.2Ag, 0.05B, 0.1Mg	A	1.1	22	7	26	⊙	⊙	718	51.7	21.0
Ex 2-3	2.32	-	0.65	0.15Cr, 0.15Sn, 0.05Mg, 0.5Zn	A	1.0	19	4	18	⊙	⊙	782	40.2	17.5
Ex 2-4	0.90	1.70	0.61	0.04Zr, 0.42Ti, 0.05Mn	B	0.9	15	9	21	o	o	765	45.9	19.6
Ex 2-5	1.5	1.1	0.59	0.05P, 0.05Hf	C	1.0	12	7	31	o	o	770	43.7	19.2
Ex 2-6	-	1.40	0.35	0.11 Mg, 0.05Fe	B	1.2	35	8	25	⊙	o	632	42.8	20.3
Ex 2-7	2.50	0.50	0.71	0.23Cr, 0.11 Mg, 0.32Zn	A	1.2	30	8	30	⊙	o	791	42.1	20.0
Ex 2-8	3.85	-	0.92	0.20Cr, 0.2Sn, 0.2Mg, 0.5Zn	A	1.0	16	9	15	⊙	o	775	36.2	18.6
C Ex 2-1	2.32	-	0.65	1.24Hf, 1.11Zn	A	1.0	13	5	21	o	o	707	28.2	24.2

(continued)

ID number	Alloying elements			Other elements	Step	Cube orientation		Brass orientation	GS	Bending property		YS	EC	SR
	Ni	Co	Si			W0/W4	W0	B0						
	mass%	mass%	mass%	mass%			%	%	µm	GW	BW	%	%IACS	%
C Ex 2-2	1.35	1.15	0.61	0.42Mg, 1.52Sn, 0.53Zn	A	1.1	22	7	26	o	o	736	27.2	21.3
C Ex 2-3	-	1.82	0.55	0.82Mn, 0.89Cr, 0.42Ag	A	1.1	16	6	32	o	o	763	25.2	20.3

"Ex" means Example according to the present invention, and "C Ex" means Comparative Example.

Comparative Example 3

[0060] A copper alloy sheet material was produced by employing the alloy composition of Example 1-1, via the Step H. With respect to the resultant copper alloy sheet material, the results obtained by conducting the same evaluation as in the examples described above, are shown below.

[0061]

Table 3

Cube orientation		Brass orientation	GS	Bending property		YS	EC	SR
W0/W4	WO %	B0 %	μm	GW	BW	MPa	%IACS	%
0.9	3	12	10	×	×	721	41.3	31.2

[0062] The copper alloy sheet material which was produced without conducting the intermediate heat treatment as described above, had a small W0 value and was poor in the 180° tight bending property, even though the predetermined alloy composition, the hot-rolling conditions, and the solution heat treatment conditions were employed.

[0063] As shown in Table 2, Comparative Examples 2-1, 2-2, and 2-3 were poor in the electrical conductivity, because the total amounts of addition of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf, which are indicated as other elements, were too large.

On the contrary, Examples 2-1 to 2-8 were excellent in all of the bending property, proof stress, electrical conductivity, and stress relaxation resistance.

As described in the above, the copper alloy sheet material of the present invention has excellent characteristics that are suitable for connector materials

[0064] Next, 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 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) ••• Conditions described in JP-A-2009-007666

[0065] An alloy formed by blending the same metal elements as those in Example 1-1, with the balance of Cu and inevitable impurities, was melted in a high frequency melting furnace, followed by casting at a cooling speed of 0.1 to 100°C/sec, to obtain an ingot. The resultant ingot was maintained at 900 to 1,020°C for 3 minutes to 10 hours, followed by subjecting to hot working, quenching in water, and then surface milling to remove oxide scale. For the subsequent steps, use was made of the treatments/workings of the following steps A-3 and B-3, to produce a copper alloy c01. In regard to the hot working, the detailed conditions are not apparent from the publication, and thus, the hot working was conducted by employing the conditions that were usually used at the time of filing of the present application, that is, the conditions of temperature: 800°C to 1,020°C, one-pass working ratio: 35% to 40%, and the retention time period between the respective passes: 3 to 7 seconds.

The production steps included one, two times or more solution heat treatments. Herein, the steps were divided into those before and after the final solution heat treatment, so that the steps up to the intermediate solution treatment are designated as Step A-3, while the steps after the intermediate solution treatment are designated as Step B-3.

[0066] Step A-3: Cold working at a cross-sectional area reduction ratio of 20% or greater, a heat treatment at 350 to 750°C for 5 minutes to 10 hours, cold working at a cross-sectional area reduction ratio of 5 to 50%, and a solution heat treatment at 800 to 1,000°C for 5 seconds to 30 minutes.

Step B-3: Cold working at a cross-sectional area reduction ratio of 50% or less, a heat treatment at 400 to 700°C for 5 minutes to 10 hours, cold working at a cross-sectional area reduction ratio of 30% or less, and temper annealing at 200 to 550°C for 5 seconds to 10 hours.

[0067] Test specimen c01 thus obtained was different from the examples according to the present invention in terms of the hot working conditions in the production conditions, and resulted in not satisfying the required characteristics for the 180° tight bending property.

(Comparative Example 102) ••• Conditions described in JP-A-2006-009137

[0068] A copper alloy having the same composition as in Example 1-1 was melted in a high frequency melting furnace, followed by casting by a DC method into an ingot with thickness 30 mm, width 100 mm, and length 150 mm. Then, the

ingot was heated to 1,000°C, followed by maintaining at that temperature for one hour, hot rolling to thickness 12 mm, and rapid cooling. The conditions for the hot-rolling were set, by making reference to paragraph 0027 of the publication, such that the temperature was set to the range of 900 to 1,000°C, and the cold-rolling after the hot-rolling was conducted at a working ratio of 90% or higher. For the one-pass working ratio and the retention time period between the respective passes, the conditions employed were the one-pass working ratio of 35 to 40% and the retention time period of 3 to 7 seconds, which were usually used at the time of filing the present application.
Then, the thus-hot-rolled sheet was machined on each surface by 1.5 mm to remove the oxide layer, followed by working via cold-rolling (a) to thickness 0.15 to 0.25 mm, and heat treating for 15 seconds by changing the solution treatment temperature in a temperature range of 825 to 925°C, and then immediate cooling at a cooling speed of 15°C/sec or greater. Then, the resultant sheet was subjected to aging for 2 hours at 475°C in an inert gas atmosphere, followed by cold-rolling (c) as the final plastic working, to thereby control the final sheet thickness. After the final plastic working, the resultant sheet was subjected to low temperature annealing at 375°C for 2 hours, to produce a copper alloy sheet material (test specimen c02).

[0069] The test specimen c02 thus obtained was different from the examples according to the present invention in terms of the conditions of hot-rolling and the intermediate heat treatment whether conducted or not conducted, in connection with the production conditions, and resulted in not satisfying the 180° tight bending property.

(Comparative Example 103) ••• Conditions described in JP-A-11-335756

[0070] A copper alloy having the same composition as in Example 1-1 was melted in the air under charcoal coating in a kryptol furnace, followed by casting in a book mold, to produce an ingot with size 50 mm × 80 mm × 200 mm. The resultant ingot was heated to 930°C, followed by hot rolling to thickness 15 mm, and then immediate quenching in water. In order to remove the oxide scale at the surface of the hot-rolled sheet, the surface was machined with a grinder. The resultant sheet was cold rolled, followed by subjecting to a heat treatment at 750°C for 20 seconds, cold-rolling at 30%, and precipitation annealing at 480°C for 2 hours, to give a material adjusted in sheet thickness, which was supplied to the test (c02). In the hot-rolling, for the one-pass working ratio and the retention time period between the respective passes, the conditions employed were the one-pass working ratio of 35 to 40% and the retention time period between the respective passes of 3 to 7 seconds, which were usually used at the time of filing the present application.

[0071] The test specimen c02 thus obtained was different from the examples according to the present invention in terms of the conditions of hot-rolling and the intermediate heat treatment whether conducted or not conducted, in connection with the production conditions, and resulted in not satisfying the 180° tight bending property.

(Comparative Example 104) ••• Conditions described in JP-A-2006-283059

[0072] A copper alloy having the same composition as in Example 1-1 was melted in the air under a charcoal coating with an electric furnace, to judge whether the copper alloy was able to be cast or not. The resultant ingot produced by melting was hot rolled, to finish to thickness 15 mm. Then, this hot-rolled sheet was subjected to cold-rolling and a heat treatment (cold-rolling 1 → solution continuous annealing → cold-rolling 2 → aging → cold-rolling 3 → short-time annealing), to produce a thin copper alloy sheet (c04) with a predetermined thickness. The solution treatment was conducted, by making reference to paragraph 0027 of the publication, under the conditions of maintaining at a substantial temperature of 800 to 950°C for 30 seconds or less. The publication has no detailed disclosure on the hot-rolling, and the conditions employed were the one-pass working ratio of 35 to 40% and the retention time period between the respective passes of 3 to 7 seconds, which were usually used at the time of filing the present application.

[0073] The test specimen c04 thus obtained was different from Example 1 in terms of the conditions of hot-rolling and the intermediate heat treatment whether conducted or not conducted, in connection with the production conditions, and resulted in not satisfying the 180° tight bending property.

(Comparative Example 105) ••• Conditions described in JP-A-2006-152392

[0074] An alloy having the same composition as in Example 1-1 was melted in the air under charcoal coating in a kryptol furnace, followed by casting in a book mold made of cast iron, to produce an ingot with a size of thickness 50 mm, width 75 mm, and length 180 mm. Then, the surface of the ingot was surface milled, followed by hot rolling at a temperature of 950°C until that the thickness became 15 mm, and then quenching in water from a temperature of 750°C or higher. Then, oxide scale was removed, followed by cold-rolling, to give a sheet with a predetermined thickness. In the hot-rolling, for the one-pass working ratio and the retention time period between the respective passes, the conditions employed were the one-pass working ratio of 35 to 40% and the retention time period between the respective passes of 3 to 7 seconds, which were usually used at the time of filing the present application.

[0075] Then, the resultant sheet was subjected to a solution treatment by heating at a temperature for 20 seconds, in a salt bath furnace, followed by quenching in water, and then finish cold-rolling of the second half, to produce a cold-rolled sheet with any of various thicknesses. At that time, as shown below, cold-rolled sheets (c05) were obtained by changing the working ratio (%) in these cold-rollings. These cold-rolled sheets were subjected to aging by changing the temperature (°C) and the time period (hr) as shown below.

[0076]

Cold-working ratio: 95%
Solution treatment temperature: 900°C
Artificial age-hardening temperature × time period: 450°C × 4 hours
Sheet thickness: 0.6 mm

[0077] The test specimen c05 thus obtained was different from Example 1 in terms of the conditions of hot-rolling and the intermediate heat treatment whether conducted or not conducted, in connection with the production conditions, and resulted in not satisfying the 180° tight bending property.

(Comparative Example 106) ••• Conditions described in JP-A-2008-223136

[0078] The copper alloy shown in Example 1 was melted, followed by casting with a vertical continuous casting machine. From the thus-obtained ingot (thickness 180 mm), a sample with thickness 50 mm was cut out, and this sample was heated to 950°C, followed by extracting, and then starting hot-rolling. At that time, the rolling ratio in the temperature range of 950 to 700°C was 60% or higher, and the pass schedule was set so as to conduct rolling even in the temperature range of lower than 700°C. The final pass temperature of hot-rolling was between 600 and 400°C. The total hot-rolling ratio from the ingot was about 90%. After the hot-rolling, the oxide layer at the surface layer was removed by mechanical polishing (surface milling). The retention time period between the respective passes in the hot-rolling was set to 3 to 7 seconds, according to the conditions that were usually used at the time of filing the present application.

[0079] Then, after conducting cold-rolling, the sample was subjected to a solution treatment. The temperature change at the time of the solution treatment was monitored with a thermocouple attached to the sample surface, and the time period for temperature rise from 100°C to 700°C in the course of temperature rising was determined. The end-point temperature was adjusted in the range of 700 to 850°C, depending on the alloy composition, so that the average grain size (a twin boundary was not considered as the grain boundary) after the solution treatment would be 10 to 60 μm, and the retention time period in the temperature range of 700 to 850°C was adjusted in the range of 10 sec to 10 min. Then, the sheet material obtained after the solution treatment was subjected to intermediate cold-rolling at the rolling ratio, followed by aging. The aging temperature was set to a material temperature of 450°C, and the aging time period was adjusted to the time at which the hardness reached the maximum upon the aging at 450°C, depending on the alloy composition. The optimum solution treatment conditions and the optimum aging time period had been found by preliminary experiments in accordance with the alloy composition. Then, finish cold-rolling was conducted at the rolling ratio. Samples that had been subjected to the finish cold-rolling were then further subjected to low temperature annealing of placing the sample in a furnace at 400°C for 5 minutes. Thus, test specimens were obtained. Surface milling was conducted in the mid course, as necessary, and thus the sheet thickness of the test specimens was set to 0.2 mm. The principal production conditions are as described below.

[Conditions of Comparative Example 1 of JP-A-2008-223136]

[0080]

Hot-rolling ratio at below 700°C to 400°C: 17% (one pass)
Cold-rolling ratio before solution treatment: 90%
Cold-rolling ratio for intermediate cold-rolling: 20%
Cold-rolling ratio for finish cold-rolling: 30%
Time period for temperature rise from 100°C to 700°C: 10 seconds

[0081] The test specimen c05 thus obtained was different from Example 1 in terms of the conditions of hot-rolling and the intermediate heat treatment whether conducted or not conducted, in connection with the production conditions, and resulted in not satisfying the 180° tight bending property.

REFERENCE SIGNS LIST

[0082]

1 Test specimen with an initial stress applied thereon
2 Test specimen after removing the load
3 Test specimen without any stress applied thereon
4 Test bench

Claims

1. A copper alloy sheet material, having a copper alloy composition containing 0.5 to 5.0 mass% in total of at least one of Ni and Co, and 0.1 to 1.2 mass% of Si, with the balance being Cu and inevitable impurities,
   wherein, in a crystal orientation analysis by an electron back scatter diffraction analysis, when an area ratio of the Cube orientation {0 0 1} <1 0 0> at a surface layer of the material is designated as W0, and an area ratio of the Cube orientation at a 1/4 position of the total depth of the material is designated as W4, a ratio of W0/W4 is 0.8 or more, W0 is 5% to 48%, and an average grain size is 12 to 100 μm, and
   wherein the copper alloy sheet material is excellent in 180° tight bending property and stress relaxation resistance.

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, Fe, Ti, Zr, and Hf, in an amount of 0.005 to 2.0 mass% in total.

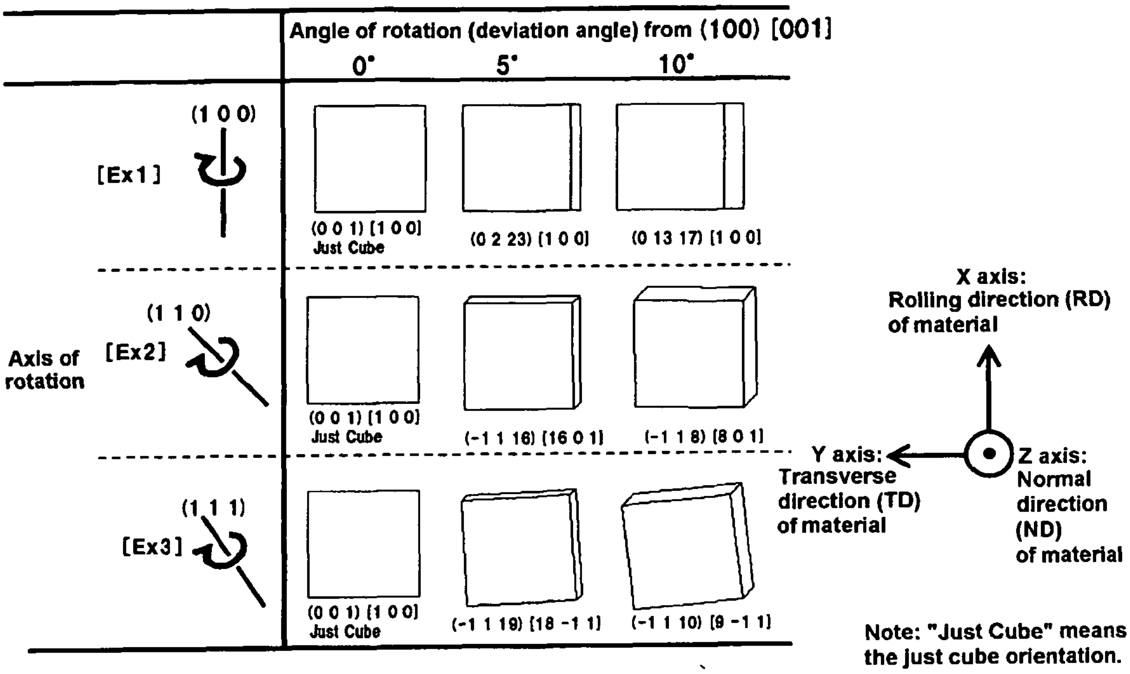
3. The copper alloy sheet material according to claim 1 or 2, wherein an area ratio of the Brass orientation {1 1 0} <1 1 2> is 20% or less.

4. A connector, which is composed of the alloy sheet material according to claims 1 to 3.

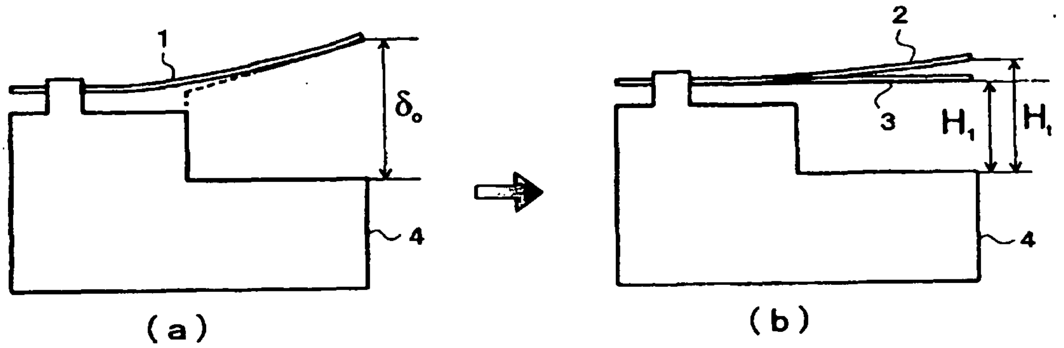
5. A method of producing a copper alloy sheet material, comprising the steps of:

   providing a copper alloy ingot containing 0.5 to 5.0 mass% in total of at least one of Ni and Co, and 0.1 to 1.2 mass% of Si, with the balance being Cu and inevitable impurities; and
   subjecting the ingot to at least treatments of steps I, III, and IV:
   [Step I: a hot-rolling step at a working ratio per pass of 30% or less, with a retention time period between the respective passes of 20 to 100 seconds]
   [Step III: an intermediate heat treatment step to be conducted between the hot-rolling step and the following solution heat treatment, at a temperature of 300 to 700°C for 10 seconds to 5 hours]
   [Step IV: a solution heat treatment step at 800 to 1,000°C].

{Fig. 1}


Angle of rotation (deviation angle) from (100) [001]
0°
5°
10°
Axis of rotation
(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)
[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
δ₀
4
(a)
2
3
H₁
Hₜ
4
(b)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071484

A. CLASSIFICATION OF SUBJECT MATTER
C22C9/06(2006.01)i, *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, *C22F1/08*(2006.01)i, *H01B1/02*(2006.01)i, *H01B5/02*(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)
C22C9/00-9/10, C22F1/08, H01B1/02, H01B5/02, 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	1996-2011
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 2008-75172 A (Nippon Mining & Metals Co., Ltd.), 03 April 2008 (03.04.2008), entire text; all drawings & US 2010/0000637 A1 & WO 2008/038593 A1 & KR 10-2009-0016485 A & CN 101512026 A	1-5
A	JP 11-222641 A (The Furukawa Electric Co., Ltd.), 17 August 1999 (17.08.1999), entire text; all drawings (Family: none)	1-5
A	JP 2006-283059 A (Kobe Steel, Ltd.), 19 October 2006 (19.10.2006), entire text; all drawings (Family: none)	1-5

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

*	Special categories of cited documents:	"T"	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
"A"	document defining the general state of the art which is not considered to be of particular relevance	"X"	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
"E"	earlier application or patent but published on or after the international filing date	"Y"	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"L"	document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	"&"	document member of the same patent family
"O"	document referring to an oral disclosure, use, exhibition or other means		
"P"	document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search 23 February, 2011 (23.02.11)	Date of mailing of the international search report 08 March, 2011 (08.03.11)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071484

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 2006-89763 A (Dowa Mining Co., Ltd.), 06 April 2006 (06.04.2006), claims; paragraph [0040] (Family: none)	1-5

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

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- JP 2008013836 A **[0004]**
- JP 2006283059 A **[0004]**
- JP 2008106356 A **[0004]**
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