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(54) COPPER ALLOY SHEET AND PROCESS FOR PRODUCING SAME

(57) {Problems} To provide a copper alloy sheet material, which is excellent in the bending property, and has an excellent mechanical strength, 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; and to provide a production method of the same.

{Means to solve} A copper alloy sheet material, wherein, in crystal orientation analysis by an EBSD (electron back scatter diffraction) analysis, in connection with accumulation of atomic planes oriented toward the transverse direction (TD) of a rolled sheet, an area ratio of a region having atomic planes in which the angle formed by the normal direction of (1 1 1) plane and the TD is 20° or less, is 50% or less, a proof stress is 500 MPa or greater, and an electrical conductivity is 30 %IACS or higher; and a production method of the same.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy sheet material and a method of producing the same, and specifically the present invention relates 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, and to a method of producing the same.

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, for example, 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.
Thus, under the circumstances where the copper alloy sheet materials are used, changes, such as shown below, may be mentioned.
Firstly, since multipolarization of connectors is in progress, along with the functional enhancements of automobiles and electrical/electronic equipments, size reduction of an individual terminal or contact part is in progress. For example, there is an ongoing movement to reduce the size of a terminal having a tab width of about 1.0 mm to 0.64 mm.
Secondly, under the circumstances of reduction of mineral resources or weight reduction of parts, thickness reduction of substrate materials is in progress. Further, in order to maintain the spring contact pressure, substrate materials are used which have a higher mechanical strength than conventional cases.
Thirdly, 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.
[0003] Further, along with the changes described above, copper alloy materials have problems such as described below.
Firstly, along with the size reduction of terminals, the bending radius in bending that is applied to the contact portion or spring portion is decreased, and the material is subjected to bending that is more severe than conventional cases. Thus, there is a problem that cracks or/and wrinkles occur in the material.
Secondly, there is a problem that cracks occur in the material, along with an enhancement in the mechanical strength of the material. This is because the bending property of a material is generally in a trade-off relation with mechanical strength.
Thirdly, when cracks occur at a bent portion that is applied to the contact portion or spring portion, the contact pressure at the contact portion decreases. In that case, the contact resistance at the contact portion is enhanced, and the electrical connection is insulated, to result in that the function as a connector is lost. Thus, this causes a serious problem.
[0004] In regard to this demand for enhancement of the bending property, 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 the grain size and a crystal orientation in which 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>. In addition to those, Patent Literatures 4 to 8 also proposed materials which are excellent in bending property that is defined by X-ray diffraction intensities with respect to various atomic planes. It has been found in Patent Literature 4 that with regard to a Cu-Ni-Co-Si-based copper alloy, bending property is excellent when the copper alloy has a crystal orientation in which the X-ray diffraction intensity obtained from {2 0 0} plane satisfies certain conditions against the X-ray diffraction intensities obtained from {111} plane, {2 0 0} plane, {2 2 0} plane, and {3 1 1} plane. It has been found in Patent Literature 5 that with 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 {4 2 0} plane and {2 2 0} plane satisfy certain conditions. It has been found in Patent Literature 6 that with regard to a Cu-Ni-Si-based copper alloy, bending property is excellent when the copper alloy has a crystal orientation which satisfies certain conditions in connection with the orientation [1 2

3] <4 1 2>. It has been found in Patent Literature 7 that with regard to a Cu-Ni-Si-based copper alloy, bending property in a Bad Way (which will be described below) is excellent when the copper alloy has a crystal orientation in which the X-ray diffraction intensities obtained from {1 1 1} plane, {3 1 1} plane, and {2 2 0} plane satisfy certain conditions. Further, it has been found in Patent Literature 8 that with 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, {3 1 1} plane, and {2 2 0} plane satisfy certain conditions.
The definitions based on the X-ray diffraction intensities in Patent Literatures 1, 2, 4, 5, 7, and 8 are directed to the definitions of the accumulation of particular crystal planes in the sheet plane direction (direction normal to the rolling direction, ND).

CITATION LIST

PATENT LITERATURES

[0005]

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-2009-007666
Patent Literature 5: JP-A-2008-223136
Patent Literature 6: JP-A-2007-092135
Patent Literature 7: JP-A-2006-016629
Patent Literature 8: JP-A-11-335756

SUMMARY OF INVENTION

TECHNICAL PROBLEM

[0006] However, the inventions described in Patent Literatures 1 and 2 are based on the analysis of crystal orientations by X-ray diffraction obtained from particular crystal planes, and are 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 (ND), and no control can be made on which crystal plane is oriented toward the rolling direction (RD) or the sheet transverse direction (TD). Thus, those techniques are still unsatisfactory for controlling the bending property completely. Further, in the invention described in Patent Literature 3, the effectiveness in the Cube orientation has been pointed out; however, the crystal orientation components other than that are not controlled, and the improvement of bending property has been insufficient in some cases. Also, in Patent Literatures 4 to 8, studies have been made only on the analysis and control of the particular crystal planes or orientations described above in each case, and similarly to Patent Literatures 1 to 3, the improvement of bending property is insufficient in some cases.
[0007] 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, and has an excellent mechanical strength, 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 method of producing the copper alloy sheet material.

SOLUTION TO PROBLEM

[0008] 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 cracks upon bending are suppressed, by reducing the region in which (1 1 1) plane is oriented toward the transverse direction (TD) of a rolled sheet; and that the bending property can be remarkably improved, when the area ratio of the region is set to a predetermined value or less. In addition to those, the inventors also found that when particular additive elements are contained in the copper alloy system, the mechanical strength and/or the stress relaxation resistance can be enhanced, without loosing electrical conductivity and/or the bending property. Thus, the inventors of the present invention have attained the present invention based on these findings.
[0009] That is, the present invention provides the following means:

(1) A copper alloy sheet material, wherein, in crystal orientation analysis by an EBSD (electron back scatter diffraction)

analysis, in connection with accumulation of atomic planes oriented toward the transverse direction (TD) of a rolled sheet, an area ratio of a region having atomic planes in which the angle formed by the normal direction of (1 1 1) plane and the TD is 20° or less, is 50% or less, a proof stress is 500 MPa or greater, and an electrical conductivity is 30 %IACS or higher.

(2) The copper alloy sheet material described in item (1), having an alloy composition containing any one or both of Ni and Co in an amount of 0.5 to 5.0 mass% in total, and Si in an amount of 0.1 to 1.5 mass%, with the balance being copper and inevitable impurities.

(3) The copper alloy sheet material described in item (1) or (2), wherein the alloy composition 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.

(4) The copper alloy sheet material described in any one of items (1) to (3), which is a material for connectors.

(5) A method of producing the copper alloy sheet material described in any one of items (1) to (4), comprising: subjecting a copper alloy having the alloy composition to give the copper alloy sheet material, to the steps of:

casting [Step 1]; a homogenization heat treatment [Step 2]; hot-working [Step 3]; cold-rolling [Step 6]; a heat treatment [Step 7]; cold-rolling [Step 8]; an intermediate recrystallization heat treatment [Step 9]; and a final solution heat treatment [Step 10], in this order, and then subjecting to an aging precipitation heat treatment [Step 11],

wherein the intermediate recrystallization heat treatment [Step 9] involves: maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours, and the final solution heat treatment [Step 10] involves: maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 10 minutes, in which P°C represents the complete solid solution temperature of solute atoms.

(6) The method of producing described in item (5), wherein cold-rolling [Step 12] and temper annealing [Step 13] are conducted in this order, after the aging precipitation heat treatment [Step 11].

ADVANTAGEOUS EFFECTS OF INVENTION

[0010] 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, the method of the present invention of producing the copper alloy sheet material is suitable as a method of producing the above-mentioned copper alloy sheet material, which 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.

BRIEF DESCRIPTION OF DRAWINGS

[0011]

{Fig. 1}

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

{Fig. 2}

Fig. 2 is a graph illustrating a typical example of the electrical conductivity change as a result of elevation in the heat treatment temperature, and the graph schematically illustrates a method of determining the temperature (P) °C at which the solute atoms are completely made into a solid solution thereby.

{Fig. 3}

Fig. 3(a) is a diagram illustrating an example of an atomic plane in which the angle formed by the normal direction of (1 1 1) plane and the TD is 20° or less, and Fig. 3(b) is a diagram illustrating an example of an atomic plane in which the angle formed by the normal direction of (1 1 1) plane and the TD is greater than 20°. The conical regions indicated by dashed lines in Figs. 3(a) and 3(b) each represent a region in which the angle formed by the normal direction of the (111) plane and the TD is 20° or less.

{Fig. 4}

Fig. 4 is a table illustrating, among the representative crystal texture orientation components in FCC (face-centered cubic) metals, examples of the crystal texture orientation component in which the atomic plane having an angle formed by the normal direction of (1 1 1) plane and the TD of 20° or less is oriented toward the transverse direction (TD) of the rolled sheet.

MODE FOR CARRYING OUT THE INVENTION

[0012] 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)

[0013] In order to clarify the cause of the occurrence of cracks upon bending of a copper alloy sheet material, the inventors of the present invention conducted a detailed investigation on the metal texture of the material after bending deformation. 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, due to the non-uniform modification, wrinkles that are several micrometers deep, or fine cracks are occurred at the surface of a substrate material upon bending, but no solution has been known for the problem. However, the inventors of the present invention, having conducted a thorough investigation, found that, when the region of atomic planes in which the (111) plane is oriented toward the transverse direction (TD) of a rolled sheet defined by an EBDS analysis (this region will be described below in detail) is decreased, non-uniform deformation is suppressed, to reduce the wrinkles occurred at the surface of the substrate material, and to suppress cracks.
As a mechanism of this phenomenon, the (111) plane is one of the orientations that are most easily work-hardened against tensile stress, and can be considered as an orientation in which dislocations are likely to increase even under the stress upon bending deformation. Highly-dense dislocations serve as the origin of the occurrence of microvoids, and cause cracks. We presume that, when the proportion of the region of atomic planes in which this (111) plane is oriented toward the TD is decreased, the bending property is improved, particularly against the BW bending in which the bending axis is in parallel to the rolling direction.

[0014] Fig. 4 shows representative examples of the orientation components of the crystal texture in which atomic planes having an angle formed by the normal direction of the (1 1 1) plane and the TD of 20° or less are oriented toward the TD. Examples include the P orientation {0 1 1} <1 1 1>, the SB orientation {1 8 6} <2 1 1>, the S orientation {1 3 2} <6 4 3>, the Z orientation {1 1 1} <1 1 0>, the Twin orientation of the Cube orientation {1 2 2} <2 2 1>, and the Brass orientation {1 1 0} <1 1 2>. The state in which the proportion of the crystal texture orientation components in which the (111) plane is oriented toward the TD, including those orientation components, is comprehensively suppressed, is the crystal texture having a predetermined area ratio as defined by the invention. Conventionally, it is not known to simultaneously control the area ratio of atomic planes having these orientations.
When the area ratio of the region having atomic planes in which the angle formed by the normal direction of the (111) plane and the TD is 20° or less, in the transverse direction (TD) of a rolled sheet, is 50% or less, the effects described above can be obtained. Preferably, the area ratio is 45% or less, more preferably from 1% to 40%, and particularly preferably from 30% to 35%. By defining this area ratio and specifying the area ratio in the range described above, improvement of the bending property can be attained, as described above.

[0015] 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 (ND) normal to the rolling direction in the Z-axis, and the proportion of a region in which the (111) plane is oriented toward the TD is defined with the area ratio. The angle formed by the two vectors of the normal direction of the (111) plane of each grain within the measured region and the TD is calculated, and the sum of the area is calculated for the region having atomic planes in which this angle is 20° or less. A value obtained by dividing this sum by the total measured area is defined as the ratio of the area (i.e. area ratio) (%) of a region having atomic

planes in which the angle formed by the normal direction of the (1 1 1) plane and the TD is 20° or less.
That is, in the present invention, in connection with the accumulation of those atomic planes oriented toward the transverse direction (TD) of a rolled sheet, the region having atomic planes in which the angle formed by the normal direction of the (111) plane and the TD is 20° or less, means the sum total of regions having planes that are oriented toward the transverse direction (TD) of the rolled sheet, that is, in connection with the accumulation of atomic planes facing to the TD, regions combining each of the (111) plane itself which adopts the transverse direction (TD) of the rolled sheet as the normal direction, which is an ideal orientation, and the atomic planes in which the angle formed by the normal direction of the (111) plane and the TD is 20° or less. Hereinafter, these regions will also be simply referred to as a region of atomic planes in which the (111) plane is oriented toward the TD.
Fig. 3 illustrates the matters described above. Fig. 3(a) is a diagram illustrating an example of the atomic plane in which the angle formed by the normal direction of the (1 1 1) plane and the TD is 20° or less. In the present specification, since the atomic plane described in this example is described in simplified description, together with the atomic plane having an orientation in which the (111) plane is oriented toward the transverse direction (TD) of the rolled sheet, even in the case where it is described as an atomic plane having an orientation in which the (1 1 1) plane is oriented toward the transverse direction (TD) of the rolled sheet, the atomic plane is regarded to represent the sum of plane orientations of the atomic planes in which the angle formed by the normal direction of the (1 1 1) plane and the TD is 20° or less.
Fig. 3(b) illustrates an example of an atomic plane in which the angle formed by the normal direction of the (111) plane and the TD is greater than 20°, and the atomic plane shown with this example is referred to as an atomic plane having an orientation in which the (111) plane is not oriented toward the transverse direction (TD) of the rolled sheet. In a copper alloy, there are eight (1 1 1) planes, but among them, only for the (1 1 1) plane in which the normal direction vector is closest to the TD, the region of vectors in which the angle formed by the normal direction of the (111) plane and the TD is 20° or less, is indicated by a cone (dashed line) in the diagram.
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.

[0016] 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, is subjected to an analysis of the orientation, by scanning in a stepwise manner at an interval of 0.5 μm.
Since EBSD measurement is used for the analysis of crystal orientation, this is largely different from the measurement of the accumulation of particular atomic plane(s) against the plane direction (ND) according to the conventional X-ray diffraction method, and three-dimensional crystal orientation data that is closer to the complete one is obtained with higher resolution power. Therefore, it is possible to obtain completely novel finding on the crystal orientation that governs bending property.

[0017] 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. Further, the measurement is conducted from the sheet surface.

(Alloy composition and the like)

• Ni, Co, Si

[0018] As the material of the present invention for connectors, copper or a copper alloy is used. As a material having electrical conductivity, mechanical strength, and heat resistance that are required of connectors, use can be preferably made of any of copper alloys, such as phosphor bronze, brass, nickel silver, beryllium copper, and Corson-based alloys (Cu-Ni-Si-based), as well as copper. Particularly, when it is desired to obtain an area ratio which satisfies the specific relation of crystal orientation accumulation according to the present invention, pure copper-based materials, or precipitate-type alloys including beryllium copper and Corson-based alloys are preferred. Further, in order to achieve a balance between high mechanical strength and high electrical conductivity, which is required of high-tech small-sized terminal materials, Cu-Ni-Si-based, Cu-Ni-Co-Si-based, and Cu-Co-Si-based precipitate-type copper alloys are preferred.
This is because, in solid solution-type alloys, such as phosphor bronze and brass, there are fewer micro-regions having the Cube orientation in cold-rolled materials, while the micro-regions serve as the nuclei of the Cube orientation grain growth in the growth of grains upon a heat treatment. This is because, in a system having low accumulation defect energy, such as phosphor bronze or brass, shear bands are likely to develop upon cold-rolling.

[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 content of any one of or two of Ni and Co is, 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 Ni is preferably 1.5 to 4.2 mass%, more preferably 1.8 to 3.9 mass%; and the content of Co is preferably 0.3 to 1.8 mass%, more preferably 0.5 to 1.5 mass%. In the case where it is particularly desired to increase the electrical conductivity, it is preferable to essentially add Co. When the total amount of addition of these elements is not made excessively large, sufficient electrical conductivity can be secured. Furthermore, when the total amount of addition is not made excessively small, sufficient mechanical strength can be secured. Further, the content of Si is preferably 0.1 to 1.5 mass%, more preferably 0.2 to 1.2 mass%.

• Other elements

[0020] Next, the effects of additive elements that enhance the characteristics (secondary characteristics), such as stress relaxation resistance, will be described. Preferable examples of the additive element include Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf. In order to sufficiently utilize the effects of addition thereof and to prevent a decrease in the electrical conductivity, the additive element(s) needs to be added, in a total amount, of preferably 0.005 to 2.0 mass%, more preferably 0.01 to 1.5 mass%, and further preferably 0.03 to 0.8 mass%. When the total amount of addition of these additive elements is not made excessively large, sufficient electrical conductivity can be secured. Furthermore, when the total amount of addition of these additive elements is not made excessively small, the effects of adding these elements can be sufficiently exhibited.

[0021] The effects of adding the additive 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 sorely added, the stress relaxation resistance is further improved by synergistic effects. Further, an effect of remarkably improving solder brittleness is obtained.

[0022] Mn, Ag, B, and P, when added, improve hot-workability, and at the same time, enhance the mechanical strength.

[0023] 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.

(Production method and the like)

[0024] Next, the method of the present invention of producing the copper alloy sheet material (method of controlling the crystal orientation of the material) will be explained. 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-working and cold-working, conducting a final solution heat treatment at a temperature in the range of 700 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 of the resultant copper alloy 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.

[0025] Examples of the method of producing the copper alloy sheet material of the present invention include a method of obtaining the copper alloy sheet material of the present invention by carrying out [Step 1] to [Step 13] in the following order: that is, melting a copper alloy raw material formed from a predetermined alloying element composition in a high-frequency melting furnace, followed by casting this molten product to obtain an ingot [Step 1]; subjecting the ingot to a homogenization heat treatment at 700 to 1,020°C for 10 minutes to 10 hours [Step 2]; hot-rolling at a working temperature of 500 to 1,020°C at a working ratio of 30 to 98% [Step 3]; water cooling [Step 4]; face milling [Step 5]; cold-rolling at a working ratio of 50 to 99% [Step 6]; a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes [Step 7]; cold-working at a working ratio of 5 to 55% [Step 8]; an intermediate recrystallization heat treatment of maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours [Step 9]; a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 10 minutes [Step 10]; then carrying out an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours [Step 11]; finish rolling at a working ratio of 2 to 45% [Step 12]; and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours [Step 13].

[0026]

Table A

	Step (1)								
	Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10
	Homogenization treatment	Hot-rolling	Water cooling	Surface milling	Cold-rolling	Intermediate heat treatment	Cold-working	Intermediate recrystallization	Final solution heat treatment
Temperature °C	700 to 1,020	500 to 1,020	-	-	-	600 to 900	-	(P-200) to (P-10)	(P+10) to (P+150)
Working ratio %	-	30 to 98	-	-	50 to 99	-	5 to 55	-	-
Time period*	10m to 10h	-	-	-	-	10s to 5m	-	1s to 20h	1s to 1h

Table A (continued)

	Step (2)		
	Step 11	Step 12	Step 13
	Aging precipitation heat treatment	Cold-rolling	Temper annealing
Temperature °C	350 to 600	-	300 to 700
Working ratio %	-	2 to 45	-
Time period *	5m to 20h	-	10s to 2h

* s: sec., m: min., and h: hour

The copper alloy sheet material of the present invention is preferably produced by the production method of the above-described embodiment, but if the abode-described specific area ratio according to the crystal orientation analysis in EBSD measurement, satisfies the defined conditions, the method is not necessarily restricted to have all of the [Step 1] to [Step 13] in the sequence described above. Although included in the method described above, a method which is terminated at, for example, [Step 11] as the final step among the above-described [Step 1] to [Step 13], is also acceptable. Alternatively, any one or two or more of the [Step 11] to [Step 13] may also be repeatedly carried out two times or more. For example, before the [Step 11] is carried out, cold-rolling at a working ratio of 2 to 45% [Step 12'] may be carried out. When the completion temperature of the hot-rolling [Step 3] is low, the speed of precipitation decreases, thus water cooling [Step 4] is not necessarily required. At what temperature or lower the hot-rolling should be finished so that water cooling would be unnecessary, would vary depending on the alloy concentration or the amount of precipitation in the hot-rolling, and it may be appropriately selected. Face milling [Step 5] may be omitted, depending on the degree of scales occurred on the material surface after the hot-rolling. Further, the scales may be removed, by dissolution with acid washing or the like.

There are occasions in which high-temperature rolling that is carried out at or above the dynamic recrystallization temperature is termed as hot-rolling, and high-temperature rolling that is carried out at a high temperature from the room temperature or higher to the dynamic recrystallization temperature or lower is termed as warm rolling. However, it is general to collectively refer to the two processes as hot-rolling. In the present invention as well, the two processes are collectively referred to as hot-rolling.

[0027] In the method of producing the copper alloy sheet material of the present invention, if it is intended to reduce the proportion of the (1 1 1) plane that is oriented toward the transverse direction in the final solution heat treatment, a production method as described below is effective.

As a usual production method of conventional precipitate-type copper alloy, since recrystallization occurs upon a solution heat treatment, the two objects of making solute atoms into a solid solution and recrystallization were achieved together. On the other hand, in the method of producing the copper alloy sheet material of the present invention, these two objects are individually achieved and combined, thereby to control the crystal orientation of the crystal structure. For this reason, the production method of the present invention is to carry out by the separated heat treatments, respectively. That is, the sample provided is, first, subjected to the intermediate recrystallization heat treatment [Step 9], and then to the final solution heat treatment [Step 10].

Furthermore, the temperatures of these intermediate recrystallization heat treatment and final solution heat treatment are defined to be in the specific temperature ranges defined by using P°C, which is a temperature at which the solute atoms are completely made into a solid solution.

The temperature of the intermediate recrystallization heat treatment is (P-200)°C or more and (P-10)°C or less. If this temperature is too low, recrystallization is insufficient, and on the contrary, if the temperature is too high, the proportion of the (1 1 1) plane oriented toward the TD is not sufficiently lowered. The temperature of the intermediate recrystallization heat treatment is preferably (P-170)°C to (P-20)°C, and more preferably (P-140)°C to (P-30)°C.

The temperature of the final solution heat treatment is (P+10)°C or more and (P+150)°C or less. If this temperature is too low, solid solution of the solute atoms is insufficiently made, and on the contrary, if the temperature is too high, the grains become coarse. The temperature of the final solution heat treatment is preferably (P+20)°C to (P+130)°C, and more preferably (P+30)°C to (P+100)°C.

[0028] The temperature P°C at which solute atoms are completely made into a solid solution is determined according to a usual method as described below. That is, an ingot is homogenized for 1 hour at 1,000°C, followed by subjecting to hot-rolling and cold-rolling to give a sheet material. Then, the sheet material is subjected to a heat treatment of maintaining in a salt bath for 30 seconds in each increment of 10°C up to 700 to 1,000°C, followed by water quenching, to thereby freeze the solid solution state and the precipitation state at each temperature, to measure the electrical conductivity. The thus-measured electrical conductivity is used as an alternative characteristic of the amount of elements made into a solid solution, and the temperature at which the decrease of the electrical conductivity that is accompanied by elevation in the heat treatment temperature is saturated, is defined as the complete solid solution temperature, P°C. Typical electrical conductivity changes, and the method of determining the temperature P (°C) in accordance therewith are schematically shown in Fig. 2. The complete solid solution temperature P (°C) for a particular composition may vary depending on the type of alloy, the conditions of workings and/or treatments, and the like. However, in a typical example, the temperature P is generally about 720 to 980°C.

[0029] The treatment time period of the intermediate recrystallization heat treatment is 1 second to 20 hours, and more preferably 5 seconds to 10 hours. If the treatment time period of the intermediate recrystallization heat treatment is too short, recrystallization does not proceed. Furthermore, if this time is too long, grains become coarse, to result in poor formability.

The treatment time period of the final solution heat treatment is 1 second to 10 minutes, and more preferably 5 seconds to 5 minutes. If the treatment time period of the final solution heat treatment is too short, solid solution of the solute atoms is insufficiently made, and if this time is too long, grains become coarse, to result in poor formability.

[0030] In the present invention, the intermediate heat treatment (Step 7) also has a special technical significance, and therefore, the heat treatment will be explained herein. A texture in which all faces are not recrystallized is obtained at a temperature slightly lower than the complete solid solution temperature P°C, and by a heat treatment under the conditions of a relatively low temperature. That is, even among the crystal orientations of a rolled material, since crystal orientations that exhibit fast restoration and crystal orientations that exhibit slow restoration exist, a non-uniformly recrystallized texture is formed due to the difference between the crystal orientations. This non-uniformity that is intentionally induced accelerates preferential development of the recrystallized crystal texture in the intermediate recrystallization heat treatment [Step 9]. A portion of the orientation which exhibits slow restoration forms a recrystallized texture, but the texture crystal orientation that exhibits fast restoration does not undergo recrystallization.

[0031] The copper alloy sheet material of the present invention can satisfy the characteristics required, for example, of a copper alloy sheet material for use in connectors. In particular, the copper alloy sheet material can realize such favorable characteristics that the 0.2% proof stress is 500 MPa or greater (preferably 600 MPa or greater, and particularly preferably 700 MPa or greater); the bending property, in terms of the value (r/t) obtained by dividing the minimum bending radius (r: mm) capable of bending without cracks in the 90° W bending test, by the sheet thickness (t: mm), is 1 or less; and the electrical conductivity is 30%IACS or greater (preferably 35%IACS or greater, and particularly preferably 40%IACS or greater); and further, the stress relaxation resistance, in terms of a stress relaxation ratio (SR), can be 30% or less (preferably, 25% or less), as determined by the measurement method of maintaining at 150°C for 1,000 hours as will be described below.

EXAMPLES

[0032] 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

[0033] As shown with the respective composition in the column of alloying elements in Table 1-1, an alloy containing at least one or both of Ni and Co in an amount of 0.5 to 5.0 mass% in total, and Si in an amount of 0.1 to 1.5 mass%, with the balance being Cu and unavoidable impurities, was melted in a high-frequency melting furnace, followed by casting, to obtain an ingot. Then, the resultant ingots were subjected to a homogenization heat treatment at 700 to 1,020°C for 10 minutes to 10 hours, hot-rolling at a working temperature of 500 to 1,020°C at a working ratio of 30% to 98%, water quenching, and cold-rolling at a working ratio of 50 to 99%, in this order, and the resultant sheets in this state were used as test materials, respectively; and test specimens of copper alloy sheet materials of Examples 1-1 to 1-19 according to the present invention and Comparative Examples 1-1 to 1-9 were produced, in any of the following Steps A to F.

(Step A)

[0034] Each of the test specimens was produced in the following manner. The respective test material was subjected to a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes; cold-working at a working ratio of 5 to 55%; an intermediate recrystallization heat treatment of maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours; and a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 1 minute. Then, the resultant sheet was subjected to an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours; finish rolling at a working ratio of 2 to 45%; and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours.

(Step B)

[0035] Each of the test specimens was produced in the following manner. The respective test material was subjected to a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes; cold-working at a working ratio of 5 to 55%; an intermediate recrystallization heat treatment of maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours; and a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 1 minute. Then, the resultant sheet was subjected to rolling at a working ratio of 2 to 40%; an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours; finish rolling at a working ratio of 2 to 45%; and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours.

(Step C)

[0036] Each of the test specimens was produced in the following manner. The respective test material was subjected to a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes; cold-working at a working ratio of 5 to 55%; an intermediate recrystallization heat treatment of maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours; and a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 1 minute. Then, the resultant sheet was subjected to an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours.

(Step D)

[0037] Each of the test specimens was produced in the following manner. The respective test material was subjected to a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes; cold-working at a working ratio of 5 to 55%; an intermediate recrystallization heat treatment of maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours; and a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 1 minute. Then, the resultant sheet was subjected to rolling at a working ratio of 2 to 40%; and an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours.

(Step E)

[0038] Each of the test specimens was produced in the following manner. The respective test material was subjected to an intermediate recrystallization heat treatment of maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours; and a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 1 minute. Then, the resultant sheet was subjected to an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours; finish rolling at a working ratio of 2 to 45%; and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours.

(Step F)

[0039] Each of the test specimens was produced in the following manner. The respective test material was subjected to a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes; cold-working at a working ratio of 5 to 55%; and a final solution heat treatment of maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 1 minute. Then, the resultant sheet was subjected to an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours; finish rolling at a working ratio of 2 to 45%; and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours.

[0040] 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.

[0041]

Table B

		Step (1)-1					Step (1)-2			
		Step 2	Step 3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9	Step 10
		Homogenization treatment	Hot-rolling	Water cooling	Surface milling	Cold-rolling	Intermediate heat treatment	Cold-working	Intermediate recrystallization	Final solution
Step A	Ex	o	o	o	o	o	o	o	o	o
Step B	Ex	o	o	o	o	o	o	o	o	o
Step C	Ex	o	o	o	o	o	o	o	o	o
Step D	Ex	o	o	o	o	o	o	o	o	o
Step E	C Ex	o	o	o	o	o	-	-	o	o
Step F	C Ex	o	o	o	o	o	o	o	-	o

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

Table B (continued)

		Step (2)			
		Step 12'	Step 11	Step 12	Step 13
		Cold-rolling	Aging precipitation	Cold-rolling	Temper annealing
Step A	Ex	-	o	o	o
Step B	Ex	o	o	o	o
Step C	Ex	-	o	-	-
Step D	Ex	o	o	-	-
Step E	C Ex	-	o	o	o
Step F	C Ex	-	o	o	o

[0042] The thus-obtained test specimens were subjected to examination of the properties as described below. Herein, the thickness of the respective test specimen was set at 0.15 mm. The results of Examples according to the present invention are shown in Table 1-1, and those of Comparative Examples are shown in Table 1-2.

[0043] a. Area ratio of region of atomic planes in which (111) plane was oriented toward TD:

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, with respect to the regions combining the (111) plane whose the normal line was the TD, which is the ideal orientation, and the atomic planes in which the angle formed by the normal direction of the (111) plane and the TD was 20° or less, (these planes together constituted the region of atomic planes in which the (1 1 1) plane was oriented toward the TD as described above), the total area ratio of these regions was calculated by the following equation:

$$\text{Area ratio (\%)} = \{(\text{Sum of area of the atomic planes in which the angle formed by the normal direction of the (1 1 1) plane and the TD was } 20^\circ \text{ or less})/\text{total measured area}\} \times 100$$

In the following respective tables, this is simply indicated as "area ratio (%)".

As an EBSD analyzer, OIM 5.0 HIKARI manufactured by TSL Solutions, Ltd. was used.

[0044] b. Bending property:

A sample was taken, by cutting out from the respective test specimen perpendicularly to the rolling direction, into a size with width 10 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 occurrence (i.e. presence or absence) of cracks at the thus-bent portion was examined, by observing the bent portion under an optical microscope with a magnification of 50.

A sample which had no crack at the bent portion and had minor wrinkles is rated as "good" (◉), a sample which had no crack but had large wrinkles, although they cause no practical problems, is rated as "fair" (o), and a sample which had cracks is rated as "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.

[0045] c. 0.2% proof stress [YS]:

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.

[0046] d: Electrical conductivity [EC]:

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.

[0047] e. Stress relaxation ratio [SR]:

The stress relaxation ratio was measured, according to JCBA T309:2001 of the Japan Copper and Brass Association (which is a provisional standard; the former standard was the "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.

[0048] Figs. 1(a) and 1(b) each are a drawing explaining the method of testing the stress relaxation resistance, in which Fig. 1(a) shows the state before heat treatment, and Fig. 1(b) shows the state after the heat treatment. As shown in Fig. 1(a), the position of a test 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. 1(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: $\{(H_t - Hi)/(\delta_0 - H_1)\} \times 100$. 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.

[0049]

Table 1-1

ID number	Allowing elements			Step	Area ratio (%)	Bending property		YS	EC	SR
	Ni	Co	Si			GW	BW			
	mass%	mass%	mass%					MPa	%IACS	%
Ex 1-1	0.49	1.02	0.37	D	25	o	o	639	53.9	25.4
Ex 1-2	0.98	0.51	0.39	D	30	o	o	696	51.0	24.7
Ex 1-3	-	0.82	0.46	A	34	o	o	668	52.8	24.8
Ex 1-4	0.49	1.53	0.36	B	42	o	o	701	51.7	25.5
Ex 1-5	0.78	1.22	0.43	C	15	⊙	⊙	694	50.7	23.6
Ex 1-6	0.98	1.02	0.49	D	10	o	o	714	49.7	24.8
Ex 1-7	2.27	-	0.66	B	24	o	o	690	40.3	26.5
Ex 1-8	0.88	1.73	0.62	D	15	o	o	813	46.3	25.3
Ex 1-9	1.08	1.53	0.56	C	30	o	o	809	45.6	25.7
Ex 1-10	-	1.41	0.39	B	34	o	o	774	44.5	25.3
Ex 1-11	1.32	1.17	0.62	C	42	o	o	715	52.7	25.6
Ex 1-12	1.32	1.17	0.62	A	15	o	⊙	762	42.8	25.6
Ex 1-13	1.47	1.122	0.60	D	10	⊙	⊙	764	43.8	24.2
Ex 1-14	-	1.86	0.56	C	24	o	o	742	43.2	24.5
Ex 1-15	2.45	0.51	0.72	B	15	o	⊙	807	42.8	23.2
Ex 1-16	3.05	-	0.70	B	15	o	o	799	42.7	22.8
Ex 1-17	1.47	1.53	0.84	C	10	⊙	⊙	833	42.5	22.2
Ex 1-18	3.68	-	0.93	A	24	o	o	735	42.7	22.4
Ex 1-19	3.14	1.84	1.22	C	15	o	o	832	40.8	20.2
"Ex" means Example according to this invention.										

[0050]

Table 1-2

ID number	Alloying elements			Step	Area ratio (%)	Bending property		YS	EC	SR
	Ni	Co	Si							
	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
C Ex 1-1	0.22	0.15	0.65	B	65	o	o	482	28.5	22.6
C Ex 1-2	4.12	1.44	0.95	D	57	o	o	734	23.8	26.5
C Ex 1-3	-	1.12	0.08	D	67	o	o	488	37.8	35.8
C Ex 1-4	2.82	-	1.72	C	62	o	o	737	18.1	24.5
C Ex 1-5	1.50	2.50	0.9	E	68	×	×	746	46.0	23.5
C Ex 1-6	1.50	1.20	1.6	F	72	×	×	847	44.1	29.6
C Ex 1-7	-	1.02	0.35	E	59	×	×	643	55.1	25.8
C Ex 1-8	2.50	-	0.59	F	57	×	×	822	44.7	25.8
C Ex 1-9	2.72	-	0.62	E	55	×	×	842	38.2	35.2
"C Ex" means Comparative Example.										

[0051] As shown in Table 1-1, Examples 1-1 to 1-19 according to the present invention were excellent in the bending property, the proof stress, the electrical conductivity, and the stress relaxation resistance.
On the contrary, as shown in Table 1-2, when the requirements of the present invention were not satisfied, results were poor in any of the properties.
That is, since Comparative Example 1-1 had a too small total amount of Ni and Co, the density of the compounds (precipitates) that contribute 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. 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 Examples 1-5 to 1-9 each had a too high proportion in which the (111) plane was oriented toward the TD, and were poor in the bending property. Particularly, for the BW bending, conspicuous cracks were observed.

Example 2

[0052] 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 2-17 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 examination of the properties in the same manner as in Example 1. The results are shown in Table 2.
[0053]

Table 2

ID number	Alloying elements			Other elements	Step	Area ratio (%)	Bending property		YS	EC	SR
	Ni	Co	Si								
	mass%	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
Ex 2-1	0.50	1.00	0.36	0.15Sn, 0.2Ag	D	25	o	o	655	53.9	23.1
Ex 2-2	1.00	0.50	0.38	0.03Zr, 0.05Mn	D	30	o	o	716	50.7	20 5
Ex 2-3	-	0.80	0.45	0.32Ti, 0.21Fe	C	34	o	o	691	52.2	21.6

(continued)

ID number	Alloying elements			Other elements	Step	Area ratio (%)	Bending property		YS	EC	SR
	Ni	Co	Si								
	mass%	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
Ex 2-4	0.50	1.50	0.35	0.2Ag, 0.05B, 0.1Mg	B	42	o	o	718	51.7	23.2
Ex 2-5	0.80	1.20	0.42	0.14Mg, 0.15Sn, 0.3Zn	C	15	o	o	714	50.4	19.4
Ex 2-6	1.00	1.00	0.48	0.23Cr, 0.14Mg, 0.10P	D	10	o	o	738	49.0	21.6
Ex 2-7	2.32	-	0.65	0.2Hf, 0.2Zn	A	24	o	o	707	40.2	24.2
Ex 2-8	0.90	1.70	0.61	0.04Zr, 0.42Ti, 0.11Mg	D	15	o	o	836	45.9	21.0
Ex 2-9	1.10	1.50	0.55	0.15Sn, 0.2Ag	C	30	o	o	834	44.9	22 4
Ex 2-10	-	1.38	0.38	0.11Mg, 0.32Zn	B	34	o	o	793	44.4	23 0
Ex 2-1	1.35	1.15	0.61	0.14Mg, 0.15Sn, 0.3Zn	C	42	o	o	736	52.4	21.3
Ex 2-12	1.35	1.15	0.61	0.22Cr, 0.05Mn	C	15	o	o	871	42.1	22.3
Ex 2-13	1.5	1.1	0.59	0.11Mg, 0.32Zn, 0.5Ti	A	10	o	o	783	43.7	22.0
Ex 2-14	-	1.82	0 55	0 14Mg. 0.15Sn, 0 3Zn	C	24	o	o	763	42.8	20.3
Ex 2-15	2.50	0.50	0.71	0.23Cr, 0.11Mg, 0.32Zn	B	15	o	o	832	42.1	20.0
Ex 2-16	3.11	-	0.69	0.20Cr, 0.2Sn, 0.2Ag	B	15	o	o	821	42.6	18 6
Ex 2-17	1.50	1.50	0.82	0.04Mn, 0.2Fe, 0 1Hf	C	10	o	o	859	42.1	19 0
C Ex 2-1	2.32	-	0.65	0.62Hf, 1.55Zn	B	22	o	o	707	28.2	24 2
C Ex 2-2	1.35	1.15	0.61	0.42Mg, 0 82Sn, 1.53Zn	C	25	o	o	736	27.2	21 3

(continued)

ID number	Alloying elements			Other elements	Step	Area ratio (%)	Bending property		YS	EC	SR
	Ni	Co	Si								
	mass%	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
C Ex 2-3	-	1.82	0.55	0.61Mn, 0.32Cr, 1.42Ag	D	35	o	o	763	25.2	20.3
"Ex" means Example according to this invention, and "C Ex" means Comparative Example.											

[0054] As shown in Table 2, Examples 2-1 to 2-17 according to the present invention were excellent in the bending property, the proof stress, the electrical conductivity, and the stress relaxation resistance.
On the contrary, when the requirements of the present invention were not satisfied, results were poor in any of the properties. That is, since Comparative examples 2-1, 2-2, and 2-3 (each of which was a comparative example against the invention according to the item (3) above) each had a too large content of elements other than Ni, Co, and Si, they were poor in the electrical conductivity.

Example 3

[0055] By using the copper alloy having the composition shown in Table 3, with the balance being Cu and inevitable impurities, the ingot was subjected to a homogenization heat treatment at 700 to 1,020°C for 10 minutes to 10 hours, followed by hot-rolling, water cooling, cold-rolling at a working ratio of 50 to 99%, a heat treatment of maintaining at 600 to 900°C for 10 seconds to 5 minutes, and cold-working at a working ratio of 5% to 55%, in this order, in the same manner as in Example 1.
Then, the intermediate recrystallization heat treatment and final solution heat treatment, as shown in Table 4, were carried out. Then, the resultant sheet was subjected to an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours, finish rolling at a working ratio of 2 to 45%, and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours, to produce a test specimen. The properties were examined in the same manner as in Example 1. The results are shown in Table 4.
[0056]

Table 3

Additive elements	Ni	Co	Si	Sn	Zn	Mg	Cr
mass%	2.71	0.32	0.76	0.17	0.31	0.07	0.17

[0057]

Table 4

ID number	Intermediate recrystallization heat treatment		Final solution heat treatment		Area ratio (%)	Bending property		YS	EC	SR
	Retention temperature	Retention time period	Retention temperature	Retention time period		GW	BW	MPa	%IACS	%
Ex 3-1	(P-20)°C	15 min.	(P+50)°C	15 sec.	25	o	o	634	44.2	25.4
Ex 3-2	(P-170)°C	4 hr.	(P+60)°C	30 sec.	30	o	o	745	41.4	24.7
Ex 3-3	(P-100)°C	30 min.	(P+40)°C	15 sec.	34	o	o	682	38.2	24.8
Ex 3-4	(P-110)°C	1 hr	(P+130)°C	5 sec.	42	o	o	725	38.7	25.5
Ex 3-5	(P-80)°C	1 hr.	(P+20)°C	15 min.	15	⊙	⊙	768	40.8	23.6
Ex 3-6	(P-70)°C	10 min.	(P+30)°C	8 min.	10	o	o	714	42.2	24.8

(continued)

ID number	Intermediate recrystallization heat treatment		Final solution heat treatment		Area ratio (%)	Bending property		YS	EC	SR
	Retention temperature	Retention time period	Retention temperature	Retention time period		GW	BW	MPa	%IACS	%
C Ex 3-1	(P-250)°C	1 hr.	(P+30)°C	30 sec.	62	×	×	782	40.3	26.5
C Ex 3-2	(P+30)°C	4 hr.	(P+60)°C	1 min.	57	×	×	776	41.2	25.3
C Ex 3-3	(P-140)°C	30 hr.	(P+20)°C	15 sec.	30	o	o	482	45.6	25.7
C Ex 3-4	(P-70)°C	4 hr.	(P-60)°C	15 sec.	34	o	o	488	42.3	25.3
C Ex 3-5	(P-70)°C	5 hr.	(P+180)°C	15 sec.	42	o	o	475	43.5	25.6
C Ex 3-6	(P-70)°C	6 hr.	(P+50)°C	1 hr.	45	o	o	488	42.8	25.6
"Ex" means Example according to this invention, and "C Ex" means Comparative Example.										

[0058] As shown in Table 4, Examples 3-1 to 3-6 according to the present invention were excellent in the bending property, the proof stress, the electrical conductivity, and the stress relaxation resistance.
On the contrary, when the requirements of the present invention were not satisfied, results were poor in any of the properties. That is, in Comparative Example 3-1, since the temperature of the intermediate recrystallization heat treatment was too low, the region in which the (1 1 1) plane was oriented toward the TD was increased too much, resulted in poor bending property. In Comparative Example 3-2, since the temperature of the intermediate recrystallization heat treatment was too high, the region in which the (111) plane was oriented toward the TD was increased too much, resulted in poor bending property. In Comparative Example 3-3, since the treatment time period of the intermediate recrystallization heat treatment was too long, the solute atoms formed coarse precipitates, solid solution was not sufficiently formed upon the final solution heat treatment, resulted in poor proof stress. In Comparative Example 3-4, since the treatment temperature of the final solution heat treatment was too low, solid solution of the solute atoms insufficiently occurred, resulted in poor proof stress. In Comparative Example 3-5, since the treatment temperature of the final solution heat treatment was too high, grains became coarse, resulted in poor proof stress. In Comparative Example 3-6, since the treatment time period of the final solution heat treatment was too long, grains became coarse, resulted in poor proof stress. Furthermore, in Comparative Examples 3-5 and 3-6, since the grain size was too large, bending wrinkles were conspicuously large, which were not satisfactory.
[0059] As described in the above, according to the present invention, quite favorable characteristics can be realized, which are required of, for example, materials for vehicle-mounted parts, such as connector materials, and materials for electrical/electronic equipments (particularly, substrate material for the parts).
[0060] 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

[0061] An alloy formed by blending the same metal elements as those in Example 1-1 according to the present invention, 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.
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.

[0062] 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.

[0063] The test specimen c01 thus obtained was different from those in the examples according to this invention, in terms of the intermediate recrystallization heat treatment [Step 9 in the present application], whether conducted or not conducted, in connection with the production conditions, and resulted in a conspicuously high area ratio of the (111) plane oriented toward the TD, and not satisfying the required level on the bending property.

(Comparative Example 102) ••• Conditions described in JP-A-2006-283059

[0064] A copper alloy having the same composition as in Example 1-1 according to this invention was melted in the air under 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-rollings and heat treatments (cold-rolling 1 → solution continuous annealing → cold-rolling 2 → aging → cold-rolling 3 → short-time annealing), to produce a copper alloy sheet (c04) with a predetermined thickness.

[0065] The test specimen c02 thus obtained was different from that in Example 1 according to this invention, in terms of the heat treatment [Step 7 in the present application] and the intermediate recrystallization heat treatment [Step 9 in the present application], whether conducted or not conducted, in connection with the production conditions, and resulted in a conspicuously high area ratio of the (1 1 1) plane oriented toward the TD, and not satisfying the bending property.

(Comparative Example 103) ••• Conditions described in JP-A-2006-152392

[0066] An alloy having the same composition as in Example 1-1 according to this invention 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.

[0067] Then, the resultant sheet was subjected to a solution treatment by heating at the 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 (c03) 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.

[0068]

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

[0069] The test specimen c03 thus obtained was different from that in Example 1 according to this invention, in terms of the heat treatment [Step 7 in the present application] and the intermediate recrystallization heat treatment [Step 9 in the present application], whether conducted or not conducted, in connection with the production conditions, and resulted in a conspicuously high area ratio of the (1 1 1) plane oriented toward the TD, and not satisfying the bending property.

(Comparative Example 104) ••• Conditions described in JP-A-2008-223136

[0070] 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 pass schedule was set to the rolling ratio in the temperature range of 950 to 700°C to be 60% or higher, and to conduct rolling even in the temperature range of lower than 700°C. The final pass temperature of hot-rolling was between 600°C 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).

[0071] 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 regarded 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 period 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 c04 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 Example 1 of JP-A-2008-223136]

[0072]

Hot-rolling ratio at below 700°C to 400°C: 56% (one pass)
Cold-rolling ratio before solution treatment: 92%
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

[0073] The test specimen c04 thus obtained was different from that in the Example 1, in terms of the heat treatment [Step 7 in the present application] and the intermediate recrystallization heat treatment [Step 9 in the present application], whether conducted or not conducted, in connection with the production conditions, and resulted in a conspicuously high area ratio of the (1 1 1) plane oriented toward the TD, and not satisfying the bending property.

REFERENCE SIGNS LIST

[0074]

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, wherein, in crystal orientation analysis by an EBSD (electron back scatter diffraction) analysis, in connection with accumulation of atomic planes oriented toward the transverse direction (TD) of a rolled sheet, an area ratio of a region having atomic planes in which the angle formed by the normal direction of (1 1 1) plane and the TD is 20° or less, is 50% or less, a proof stress is 500 MPa or greater, and an electrical conductivity is 30 %IACS or higher.

2. A copper alloy sheet material, having an alloy composition containing any one or both of Ni and Co in an amount of 0.5 to 5.0 mass% in total, and Si in an amount of 0.1 to 1.5 mass%, with the balance being copper and inevitable impurities,
wherein, in crystal orientation analysis by an EBSD (electron back scatter diffraction) analysis, in connection with accumulation of atomic planes oriented toward the transverse direction (TD) of a rolled sheet, an area ratio of a region having atomic planes in which the angle formed by the normal direction of (1 1 1) plane and the TD is 20° or

less, is 50% or less, a proof stress is 500 MPa or greater, and an electrical conductivity is 30 %IACS or higher.

3. A copper alloy sheet material, having an alloy composition containing any one or both of Ni and Co in an amount of 0.5 to 5.0 mass% in total, Si in an amount of 0.1 to 1.5 mass%, and 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, with the balance being copper and inevitable impurities,
wherein, in crystal orientation analysis by an EBSD (electron back scatter diffraction) analysis, in connection with accumulation of atomic planes oriented toward the transverse direction (TD) of a rolled sheet, an area ratio of a region having atomic planes in which the angle formed by the normal direction of (1 1 1) plane and the TD is 20° or less, is 50% or less, a proof stress is 500 MPa or greater, and an electrical conductivity is 30 %IACS or higher.

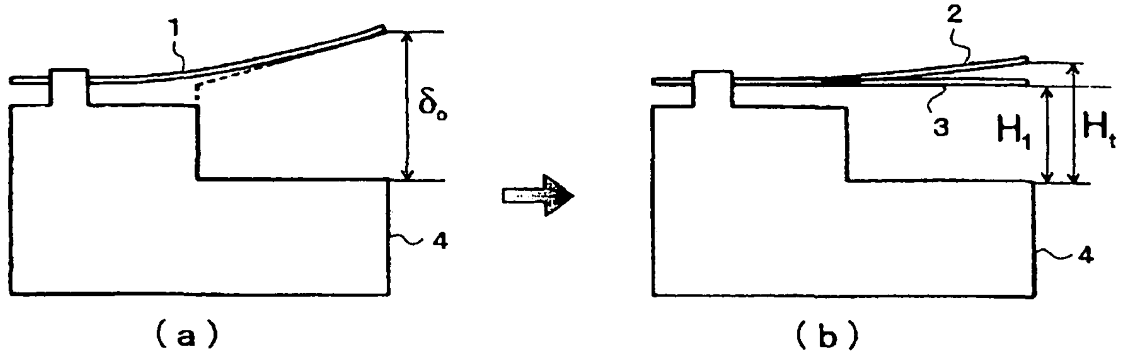
4. The copper alloy sheet material according to any one of claims 1 to 3, which is a material for connectors.

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

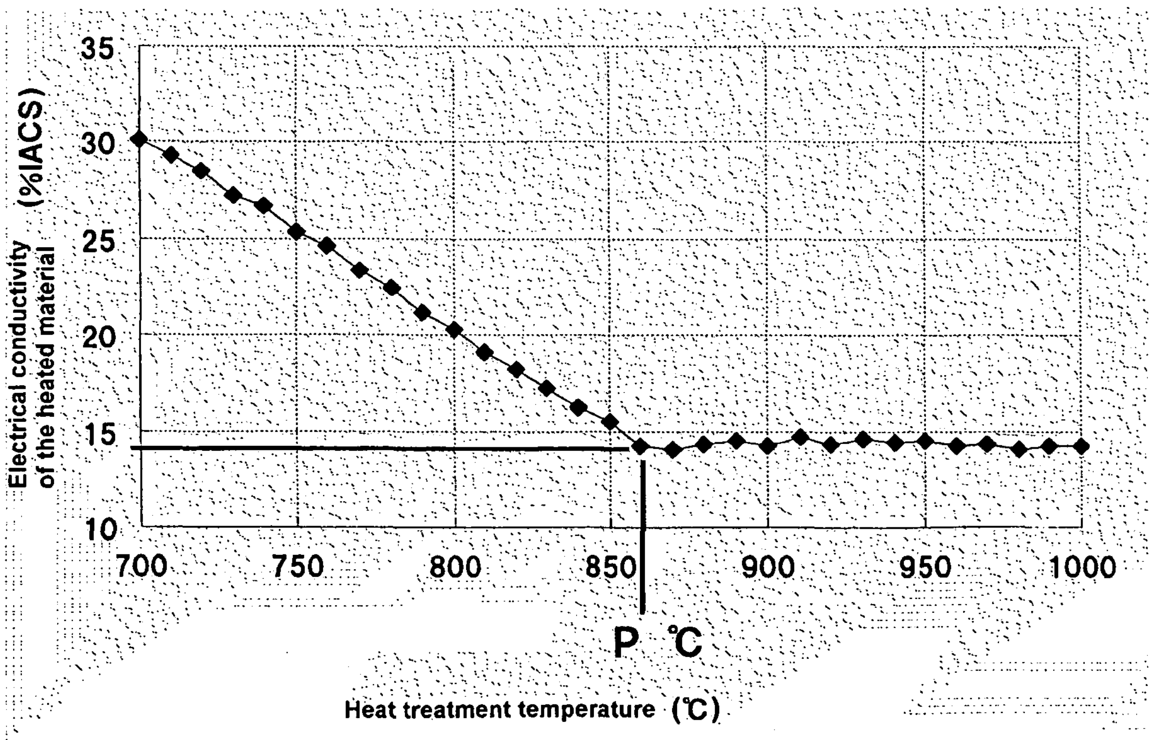
casting [Step 1]; a homogenization heat treatment [Step 2]; hot-working [Step 3]; cold-rolling [Step 6]; a heat treatment [Step 7]; cold-rolling [Step 8]; an intermediate recrystallization heat treatment [Step 9]; and a final solution heat treatment [Step 10], in this order, and then subjecting to an aging precipitation heat treatment [Step 11],
wherein the intermediate recrystallization heat treatment [Step 9] involves: maintaining at a temperature from (P-200)°C to (P-10)°C for 1 second to 20 hours, and the final solution heat treatment [Step 10] involves: maintaining at a temperature from (P+10)°C to (P+150)°C for 1 second to 10 minutes, in which P°C represents the complete solid solution temperature of solute atoms.

6. The method of producing according to claim 5, wherein cold-rolling [Step 12] and temper annealing [Step 13] are conducted in this order, after the aging precipitation heat treatment [Step 11].

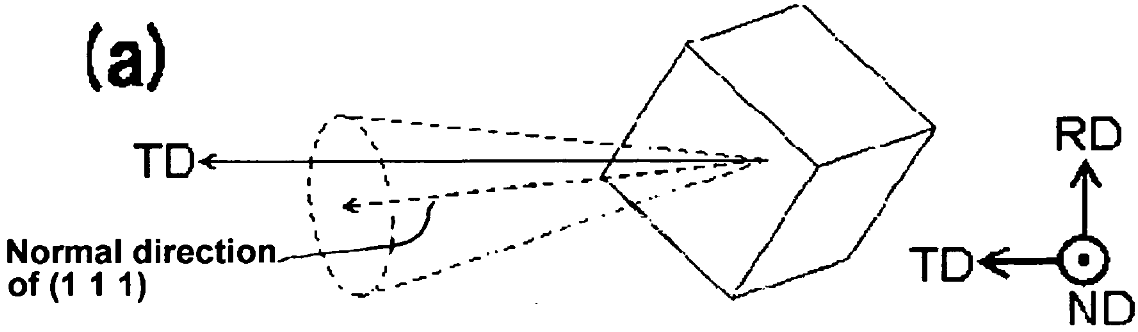
{FIG. 1}


1
δo
4
(a)
2
3
H1
Ht
4
(b)

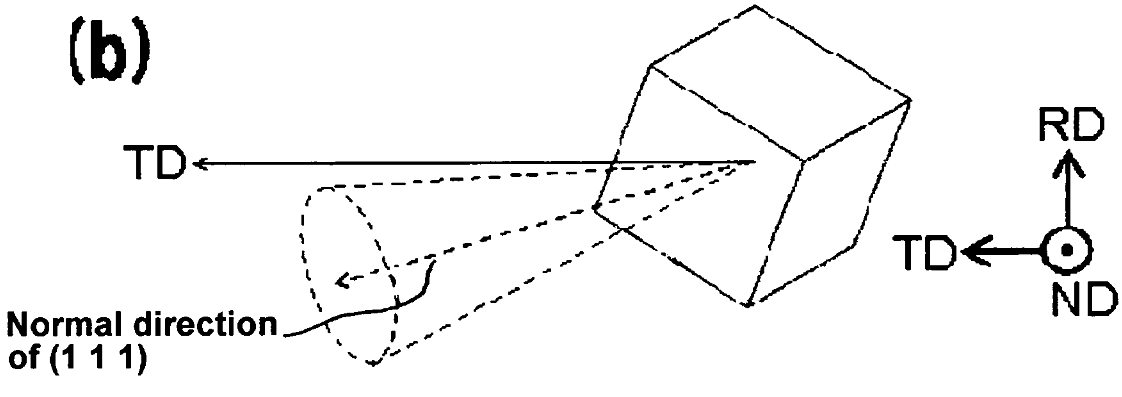
{FIG. 2}


Electrical conductivity of the heated material (%IACS)
35
30
25
20
15
10
700
750
800
850
900
950
1000
P ℃
Heat treatment temperature (℃)

{FIG. 3}

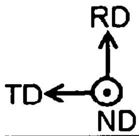
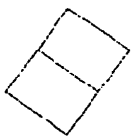
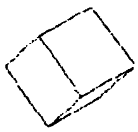
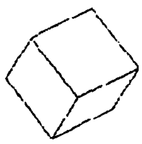
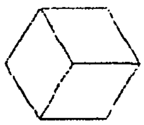
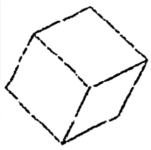
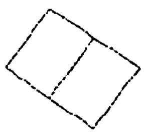


Angle formed by the normal direction of (1 1 1) plane and the TD is 20° or less



Angle formed by the normal direction of (1 1 1) plane and the TD is greater than 20°

{FIG. 4}

Name	P	SB	S	Z	Twin of Cube	Brass
Orientation of unit cell 						
HKL	011	186	132	111	122	110
UVW	1-11	2-11	6-43	1-10	2-21	1-12
Angle *	19.5°	9.9°	18.5 °	19.5 °	15.8°	0°

Note: * Angle formed by normal direction of (111) plane and TD

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2010/071499

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.
X A	JP 2006-283059 A (Kobe Steel, Ltd.), 19 October 2006 (19.10.2006), claims; paragraphs [0001], [0011] to [0049] (Family: none)	1-4 5,6
A	JP 2006-152392 A (Kobe Steel, Ltd.), 15 June 2006 (15.06.2006), entire text; all drawings (Family: none)	1-6
A	JP 2000-80428 A (Kobe Steel, Ltd.), 21 March 2000 (21.03.2000), entire text (Family: none)	1-6

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

* Special categories of cited documents:
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 18 February, 2011 (18.02.11)	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/JP2010/071499

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 2007-270171 A (Dowa Holdings Co., Ltd., Kiyohito ISHIDA), 18 October 2007 (18.10.2007), entire text; all drawings (Family: none)	1-6
A	JP 2006-219733 A (Kobe Steel, Ltd.), 24 August 2006 (24.08.2006), entire text (Family: none)	1-6

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

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2006009137 A **[0005]**
- JP 2008013836 A **[0005]**
- JP 2006283059 A **[0005]**
- JP 2009007666 A **[0005]**
- JP 2008223136 A **[0005]**
- JP 2007092135 A **[0005]**
- JP 2006016629 A **[0005]**
- JP 11335756 A **[0005]**