(19) Europäisches
Patentamt
European
Patent Office
Office européen
des brevets

(11) **EP 2 508 635 A1**

(12) **EUROPEAN PATENT APPLICATION**
published in accordance with Art. 153(4) EPC

(43) Date of publication:
10.10.2012 Bulletin 2012/41

(21) Application number: **10834585.1**

(22) Date of filing: **01.12.2010**

(51) Int Cl.:
C22C 9/06 $^{(2006.01)}$
C22C 9/02 $^{(2006.01)}$
C22C 9/05 $^{(2006.01)}$
C22F 1/08 $^{(2006.01)}$
H01B 5/02 $^{(2006.01)}$
C22C 9/00 $^{(2006.01)}$
C22C 9/04 $^{(2006.01)}$
C22C 9/10 $^{(2006.01)}$
H01B 1/02 $^{(2006.01)}$
C22F 1/00 $^{(2006.01)}$

(86) International application number:
PCT/JP2010/071518

(87) International publication number:
WO 2011/068135 (09.06.2011 Gazette 2011/23)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **02.12.2009 JP 2009274994**

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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, having an R value of 1 or greater, which is defined by:

$$R = ([BR] + [RDW] + [W])/([C] + [S] + [B])$$

wherein [BR], [RDW], [W], [C], [S], and [B] represent an area ratio of crystal texture orientation component of BR orientation {3 6 2} <8 5 3>, RD-rotated-cube orientation {0 1 2} <1 0 0>, cube orientation {1 0 0} <0 0 1>, copper orientation {1 2 1} <1 1 1>, S-orientation {2 3 1} <3 4 6>, and brass orientation {1 1 0} <1 1 2>, respectively, in crystal orientation analysis in an EBSD (electron back scatter diffraction) analysis, and having a proof stress of 500 MPa or greater, and an electrical conductivity of 30%IACS or higher; and a production method of the same.

Printed by Jouve, 75001 PARIS (FR)

Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy sheet material and a method of producing the same, and specially 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 in recent years 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 sheet 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 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 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>. 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 {1 1 1} 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 of [1

2 3] <4 1 2> plane. 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 increasing the BR orientation, the RD-rotated-cube orientation (hereinafter, also referred to as RDW orientation), and the cube orientation, each of which can be characterized by the EBSD method, and reducing the copper orientation, the S-orientation, and the brass orientation; and that the bending property can be remarkably improved, when the area ratio of the crystal texture orientation components of each of those orientations is set to a predetermined ratio. In addition to those, the inventors also found that when particular additive elements are contained in the copper alloy system, the mechanical strength or the stress relaxation resistance 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.

[0009] That is, the present invention provides the following means:

(1) A copper alloy sheet material, having an R value of 1 or greater, which is defined by:

$$R = ([BR] + [RDW] + [W])/([C] + [S] + [B])$$

wherein [BR], [RDW], [W], [C], [S], and [B] represent an area ratio of crystal texture orientation component of BR orientation {3 6 2} <8 5 3>, RD-rotated-cube orientation {0 1 2} <1 0 0>, cube orientation {1 0 0} <0 0 1>, copper orientation {1 2 1} <1 1 1>, S-orientation {2 3 1} <3 4 6>, and brass orientation {1 1 0} <1 1 2>, respectively, in crystal orientation analysis in an EBSD (electron back scatter diffraction) analysis, and
having a proof stress of 500 MPa or greater, and an electrical conductivity of 30%IACS or higher.
(2) The copper alloy sheet material described in (1), having an alloy composition comprising any one or two of Ni and Co 0.5 to 5.0 mass% in total, and Si 0.1 to 1.5 mass%, with the balance being copper and unavoidable impurities.
(3) The copper alloy sheet material described in (2), further containing at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf 0.005 to 2.0 mass% in total.
(4) The copper alloy sheet material described in any one of (1) to (3), which is a material for connectors.
(5) A connector, which is composed of the copper alloy sheet material described in (1) to (4).
(6) A method of producing the copper alloy sheet material described in any one of (1) to (5), comprising the steps of: subjecting a copper alloy having the alloy composition to give the copper alloy, to 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], and a final solution heat treatment [Step 9], in this order, and then subjecting the resultant copper alloy to an aging precipitation heat treatment [Step 10],
wherein the hot-working [Step 3] is carried out, by first conducting two or more passes of hot-rolling at a temperature from (P+30)°C to 1,020°C (in which P (°C) represents the complete solid solution temperature of solute atoms) at a working ratio per pass of 25% or higher, cooling to a temperature (P-30)°C or lower, and then conducting two or more passes of hot-rolling at a temperature from 400°C to (P-30)°C at a working ratio per pass of 25% or lower.
(7) The method of producing the copper alloy sheet material described in (6), wherein cold-rolling [Step 11] and temper annealing [Step 12] are conducted in this order, after the aging precipitation heat treatment [Step 10].

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 the examples, 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.

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.

[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, we found that, due to that non-uniform deformation, wrinkles of a depth of several micrometers or micro-cracks occur, at the surface of the substrate material after bending.

Further, we found that when there are many of the BR orientation, the RDW orientation, and the cube orientation, and there are fewer of the copper orientation, the S-orientation, and the brass orientation, non-uniform deformation is suppressed, and the wrinkles that occur at the surface of the substrate material are reduced, so that cracks are suppressed. In the observation of the texture of a bent cross-section, we also confirmed that there are fewer local deformation bands observed in the grains of the BR orientation, the RDW orientation, and the cube orientation, and there are more local deformation bands observed in the grains of the copper orientation, the S-orientation, and the brass orientation.

(Definition by EBSD analysis)

[0014] When the area ratios of the respective crystal texture orientation components of the BR orientation {3 6 2} <8 5 3>, the RD-rotated-cube orientation {0 1 2} <1 0 0>, the cube orientation {1 0 0} <0 0 1>, the copper orientation {1 2 1} <1 1 1>, the S-orientation {2 3 1} <3 4 6>, and the brass orientation {1 1 0} <1 1 2>, as defined by the EBSD method, are designated as [BR], [RDW], [W], [C], [S], and [B], respectively, when R that is defined by: R = ([BR] + [RDW] + [W]) /([C] + [S] + [B]) is 1 or greater, the effects described above can be obtained. The value of R is preferably 1.1 or greater, more preferably from 1.2 to 6. Any techniques have not been hitherto known to simultaneously control the area ratios of the atomic planes having these orientations.

[0015] 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 six kinds of orientations according to the present invention are respectively expressed by the indices such as described above.

[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, was subjected to an analysis of the orientation, by scanning in a stepwise manner at an interval of 0.5 μm.

In the present invention, the grains having orientation components of the texture of each of the above BR orientation, RD-rotated-cube (RDW) orientation, cube (W) orientation, copper (C) orientation, S orientation, and brass (B) orientation and the area of the planes of atoms thereof are defined in connection with whether the grains and the area are within the range of the predetermined deviation angle that will be described below.

In regard to the deviation angle from the ideal orientation represented by the above-mentioned index, for (i) the crystal orientation at each measurement point and (ii) any one of the BR-orientation, RDW-orientation, cube-orientation, copper-orientation, S-orientation, and brass-orientation as an ideal orientation as an object measurement, an angle of rotation around the axis of rotation that is common to (i) and (ii) is calculated, and the angle of rotation is designated as the deviation angle. For example, with regard to the S-orientation (2 3 1) [6 -4 3], the orientation (1 2 1) [1 -1 1] is in a relationship of being rotated by 19.4° around the (20 10 17) direction as the axis of rotation, and this angle is designated as the deviation angle. The common axis of rotation consists of three integers of 40 or less, but the integer that can be expressed with the smallest deviation angle among the integers of 40 or less 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 respective deviation angle of the BR-orientation, RDW-orientation, cube-orientation, copper-orientation, S-orientation, and brass-orientation is divided by the total measured area, and the resultant value is designated as the ratio of the area (area ratio) of atomic planes having the respective orientation.

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.

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 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 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 desired to increase the electrical conductivity, it is preferable to essentially add Co. If the amounts of addition of those elements of Ni, Co and Si in total are too large, the electrical conductivity is apt to be decreased, and if the amounts of addition are too small, the mechanical strength is apt to be insufficient. Further, the content of Si is preferably 0.1 to 1.5 mass%, more preferably 0.2 to 1.2 mass%. Further, since Co is a rare element, and since Co raises the solution temperature when added in a given amount, if it is not necessary to significantly increase electrical conductivity depending on the use, it is preferable not to add Co.

- 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%. If the total amount of these additive elements is too large, it becomes the cause of an adverse affection of decreasing the electrical conductivity. If the total amount of these additive elements is too small, the effects of adding these elements are hardly exhibited.

[0021] The effects of adding various 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.

[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-rolling and cold-rolling, 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 12] 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 1,020 to 700°C for 10 minutes to 10 hours [Step 2]; conducting two or more passes of hot-rolling at a temperature in the range of 1,020°C to (P + 30)°C at a working ratio of 25% or higher per pass [Step 3-1]; cooling the resultant hot-rolled sheet to a temperature (P - 30)°C or lower by air cooling or water cooling [Step 3-2]; conducting two or more passes of hot-rolling at a temperature in the range of (P - 30)°C to 400°C at a working ratio of 25% or less per pass [Step 3-3]; 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]; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour [Step 9]; then carrying out an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours [Step 10]; finish rolling at a working ratio of 2 to 45% [Step 11]; and temper annealing of maintaining at 300 to 700°C for 10 seconds to 2 hours [Step 12].

[0026]

Table A

	Step (1)									
	Step 2	Step 3-1	Step 3-2	Step 3-3	Step 4	Step 5	Step 6	Step 7	Step 8	Step 9
	Homogenization treatment	Hot-rolling (1)	Cooling	Hot-rolling (2)	Water cooling	Surface milling	Cold-rolling	Intermediate heat treatment	Cold-rolling	Final solution heat treatment
Temperature °C	700 to 1,020	(P+30) to 1,020	(P-30)	400 to (P-30)	-	-	-	600 to 900	-	750 to 1,000
Working ratio %	-	>25% 2 or more passes	-	<25% 2 or more passes	-	-	50 to 99	-	5 to 55	-
Time period*	10m to 10h	-	-	-	-	-	-	10s to 5m	-	1s to 1h

Table A (continued)

	Step (2)		
	Step 10	Step 11	Step 12
	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

[0027] 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 R according to a 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 12] in the sequence described above. Although included in the method described above, a method which is terminated at, for example, [Step 10] as the final step among the above-described [Step 1] to [Step 12], is also acceptable. Alternatively, any one or two or more of the [Step 10] to [Step 12] may also be repeatedly carried out two or more times. For example, before the [Step 10] is carried out, cold-rolling at a working ratio of 2 to 45% [Step 11'] may be carried out.

When the completion temperature of the hot-rolling [Step 3-3] 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.

[0028] In the production method of the copper alloy sheet material of the present invention, in the final solution heat treatment, in order to decrease the area ratios of the brass orientation, the S-orientation, and the copper orientation, and to increase the area ratios of the BR orientation, the RDW orientation, and the cube orientation, it is preferable to select the conditions described above in the hot-working that is carried out after homogenizing the ingot ([Step 3] composed of [Step 3-1] to [Step 3-3]). In usual production methods for conventional copper alloys, a high-temperature working to be carried out after homogenization is conducted at a temperature as high as possible, for the purpose of lowering deformation resistance, or in the case of precipitate-type alloys, for the purpose of suppressing precipitation in a large quantity. On the other hand, the method of producing the copper alloy sheet material of the present invention is characterized in that hot-rolling ([Step 3-1]) is carried out as a first hot-rolling step, and then cooling ([Step 3-2]) is conducted, and re-hot-rolling ([Step 3-3]) is carried out as a second hot-rolling step, at a temperature lower than that of the first step. Further, the temperature of these first step and second step are defined to be in a specific temperature range that is defined by using P°C, which is the temperature at which solute atoms are completely made into a solid solution. The temperature in the first hot-rolling step is 1,020°C to (P + 30)°C. Due to high-temperature brittleness when this temperature is too high, and on the other hand, due to not occurring destruction of the cast texture by recrystallization when the temperature is too low, cracks may occur in each case. Preferably, the temperature is 1,000°C to (P + 50)°C, more preferably 980°C to (P + 70)°C.

The temperature in the second hot-rolling step is (P - 30)°C to 400°C. Due to that the resultant texture is equivalent to that obtained via conventional and usual rolling when this temperature is too high, and on the other hand, due to intermediate-temperature brittleness when the temperature is too low, cracks may occur in each case. Preferably, the temperature is (P - 50)°C to 450°C, more preferably (P - 70)°C to 500°C.

It is preferable that the temperature of the first hot-rolling step (T1) be higher than the temperature of the second hot-rolling step (T2) (T1 > T2), and to take a typical example, the difference between the two temperatures (T1 - T2) is preferably 60 to 100°C, more preferably 100 to 140°C.

[0029] Further, in the production method of the present invention, it is important to provide the cooling step in the mid course of the first hot-rolling step and the second hot-rolling step. The cooling end-point temperature is (P - 30)°C or lower, and although the lower limit temperature is not particularly limited, the lower limit is practically 450°C or higher. The technical significance of this cooling step will be described herein. The temperature range between T1 and T2 that are defined by using P°C is a temperature range in which precipitation of solute elements occurs most rapidly. On the other hand, at a temperature higher than this intermediate temperature range, since the solute elements are made into a solid solution, the diffusion of atoms is slow at a temperature lower than this intermediate temperature range, and coarsening of the precipitate occurs only slightly. When the alloy material is subjected to rolling at a temperature in this intermediate temperature range, the progress of precipitation is further accelerated by an increase in the lattice defects, and thus coarse precipitates having a size of around submicron scale are formed. In the subsequent cold-rolling, since strain is concentrated in the surrounding of these coarse precipitate particles having a size of around several micrometers, in the intermediate solution heat treatment, recrystallized grains of random orientations are formed from the high strain region around the particles, and the desired area ratio of orientations may not be obtained. That is, in order to achieve the area ratio of orientations as defined in the present invention, it is important to control coarse precipitate particles that cause randomization of orientations, and in order to do so, it is preferable not to conduct rolling at a temperature in the intermediate temperature range described above.

[0030] Further, in the production method of the present invention, the intermediate heat treatment that is carried out after the hot-rolling has a significant meaning. It is preferable to conduct the intermediate heat treatment at a temperature of 600 to 900°C in the mid course of cold-rolling as explained above. As such, by employing the intermediate heat treatment step, a texture in which the entire plane has not been recrystallized can be obtained. That is, even among the crystal orientations in the rolled material, there are crystal orientations which are restored fast, and crystal orientations which are restored slowly. Therefore, due to such a difference, a non-uniformly recrystallized texture is formed. This non-uniformity that is intentionally introduced accelerates the preferential development of a recrystallized crystal texture in the intermediate recrystallization heat treatment [Step 9].

[0031] 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 presented in Fig. 2. To take a typical example, the temperature P is practically 750 to 950°C.

[0032] The one-pass working ratio (i.e. working ratio per pass) in the first hot-rolling step is preferably 25% or higher. If this is too low, destruction of the cast texture may not occur. The upper limit may vary depending on the specifications of the rolling machine to be utilized, and there are no particular limitations on the upper limit; however, the upper limit is generally 50% or lower.

The one-pass working ratio in the second hot-rolling step is preferably 25% or lower. If this is too high, since the working is conducted at a relatively low temperature, working cracks may occur. The lower limit is not particularly limited, but in view of operation efficiency, the lower limit is generally 3% or higher.

[0033] 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 the material at 150°C for 1,000 hours as will be described below.

EXAMPLES

[0034] 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

[0035] 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. The resultant ingots in this state were used as test materials, and test specimens of copper alloy sheet materials of Examples 1-1 to 1-19 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)

[0036] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at 1,020 to 700°C for 10 minutes to 10 hours; three passes of hot-rolling at a working ratio of 25% or higher at a temperature in the range of 1,020°C to (P + 30)°C; air cooling; three passes of hot-rolling at a working ratio of 25% or lower at a temperature in the range of (P - 30)°C to 400°C; 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; cold-working at a working ratio of 5 to 55%; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. 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)

[0037] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at 1,020 to 700°C for 10 minutes to 10 hours; three passes of hot-rolling at a working ratio of 25% or higher at a temperature in the range of 1,020°C to (P + 30)°C; air cooling; three passes of hot-rolling at a working ratio of 25% or lower at a temperature in the range of (P - 30)°C to 400°C; 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; cold-working at a working ratio of 5 to 55%; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. Then, the resultant sheet was subjected to rolling at a working ratio of 2 to 45%; 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)

[0038] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at 1,020 to 700°C for 10 minutes to 10 hours; three passes of hot-rolling at a working ratio of 25% or higher at a temperature in the range of 1,020°C to (P + 30)°C; air cooling; three passes of hot-rolling at a working ratio of 25% or lower at a temperature in the range of (P - 30)°C to 400°C; 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; cold-working at a working ratio of 5 to 55%; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. 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)

[0039] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at 1,020 to 700°C for 10 minutes to 10 hours; three passes of hot-rolling at a working ratio of 25% or higher at a temperature in the range of 1,020°C to (P + 30)°C; air cooling; three passes of hot-rolling at a working ratio of 25% or lower at a temperature in the range of (P - 30)°C to 400°C; 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; cold-working at a working ratio of 5 to 55%; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. Then, the resultant sheet was subjected to rolling at a working ratio of 2 to 45%; and an aging precipitation heat treatment at 350 to 600°C for 5 minutes to 20 hours.

(Step E)

[0040] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at 1,020 to 700°C for 10 minutes to 10 hours; three passes of hot-rolling at a working ratio of 25% or higher at a temperature in the range of 1,020°C to (P + 30)°C; air cooling; three passes of hot-rolling at a working ratio of 25% or lower at a temperature in the range of (P - 30)°C to 400°C; water cooling; cold-rolling at a working ratio of 50% to 99%; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. 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)

[0041] Each of the test specimens was produced in the following manner. The respective test material was subjected to a homogenization heat treatment at 1,020 to 700°C for 10 minutes to 10 hours; three passes of hot-rolling at a working ratio of 25% or higher at a temperature in the range of 1,020°C to (P + 30)°C; 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; cold-working at a working ratio of 5 to 55%; and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. 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.

[0042]

Table B

		Step (1)							
		Homogenization treatment	Hot-working (1) *1	Air cooling	Hot-working (2) *1	Water cooling	Intermediate heat treatment	Cold-rolling	Solution treatment
Step A	Ex	o	o	o	o	o	o	o	o
Step B	Ex	o	o	o	o	o	o	o	o
Step C	Ex	o	o	o	o	o	o	o	o
Step D	Ex	o	o	o	o	o	o	o	o
Step E	C Ex	o	o	o	o	o	-	-	o
Step F	C Ex	o	o	-	-	o	o	o	o

Table B (continued)

		Step (2)			
		Cold-rolling	Aging treatment	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

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

*1 The case where the conditions fall within the ranges defined in Table A, is indicated as "o"; the case where the conditions fall outside the ranges defined in Table A, is indicated as "x"; and other items, if carried out, are indicated as "o".

[0043] 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.

[0044] 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.

a. Area ratios of the regions of BR orientation, RDW orientation, cube orientation, copper orientation, S orientation, and brass orientation:

[0045] 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 atomic planes of grains having a deviation angle of 10° or less in each of the ideal orientations, the area of an atomic plane having each orientation was determined, and the area ratio (R) was calculated by the following equation:

$$R = ([BR] + [RDW] + [W])/([C] + [S] + [B]).$$

b. Bending property:

[0046] 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), 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.

c. 0.2% proof stress [YS]:

[0047] 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.

d: Electrical conductivity [EC]:

[0048] 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.

e. Stress relaxation ratio [SR]:

[0049] 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.

[0050] 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: $\{(H_t - H_1)/(\delta_0 - H_1)\} \times 100$. 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.

[0051]

Table 1-1

ID number	Alloying elements			Step	R	Bending property		YS	EC	SR
	Ni	Co	Si							
	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
Ex 1-1	0.49	1.02	0.37	B	1.3	○	○	626	55.0	24.6
Ex 1-2	0.98	0.51	0.39	D	1.5	○	○	682	52.1	24.0
Ex 1-3	-	0.82	0.46	C	1.8	○	⊙	655	53.9	24.1
Ex 1-4	0.49	1.53	0.36	A	1.4	○	○	687	52.8	24.7
Ex 1-5	0.78	1.22	0.43	B	1.3	○	○	680	51.8	22.9
Ex 1-6	0.98	1.02	0.49	D	1.6	○	○	700	50.6	24.1
Ex 1-7	2.27	-	0.66	C	2.1	○	⊙	732	41.1	25.7
Ex 1-8	0.88	1.73	0.62	A	1.7	⊙	○	797	47.2	24.5
Ex 1-9	1.08	1.53	0.56	A	1.4	○	○	792	46.5	24.9
Ex 1-10	-	1.41	0.39	D	1.8	○	⊙	759	45.4	24.5
Ex 1-11	1.32	1.17	0.62	C	1.6	○	⊙	701	53.8	24.8
Ex 1-12	1.32	1.17	0.62	B	1.9	○	⊙	828	43.6	24.8
Ex 1-13	1.47	1.122	0.60	C	2.2	⊙	⊙	749	44.7	23.5
Ex 1-14	-	1.86	0.56	A	1.7	○	○	727	44.0	23.8
Ex 1-15	2.45	0.51	0.72	A	1.9	○	○	790	43.6	22.5
Ex 1-16	3.05	-	0.70	B	2.6	⊙	⊙	783	43.5	22.1
Ex 1-17	1.47	1.53	0.84	C	1.8	○	○	816	43.3	21.6
Ex 1-18	3.68	-	0.93	D	2.1	○	⊙	712	43.5	21.7
Ex 1-19	3.14	1.84	1.22	A	2.2	⊙	⊙	815	41.6	19.6
"Ex" means Example according to the present invention.										

[0052]

Table 1-2

ID number	Allying elements			Step	R	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	C	1.1	○	○	492	29.1	23.1
C Ex 1-2	4.12	1.44	0.95	C	1.2	○	○	749	24.3	27.1
C Ex 1-3	-	1.12	0.08	D	1.3	○	○	498	38.6	36.5
C Ex 1-4	2.82	-	1.72	C	1.2	○	○	752	18.5	25.0
C Ex 1-5	1.50	2.50	0.9	E	0.5	×	×	812	47.0	23.9
C Ex 1-6	1.50	1.20	1.6	F	0.6	×	×	786	44.9	30.2
C Ex 1-7	-	1.02	0.35	E	0.7	×	×	640	56.2	26.3
C Ex 1-8	2.50	-	0.59	F	0.5	×	×	795	45.6	26.3

(continued)

ID number	Allying elements			Step	R	Bending property		YS	EC	SR
	Ni	Co	Si							
	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
C Ex 1-9	2.72	-	0.62	E	0.3	×	×	835	39.0	35.9
"C Ex" means Comparative Example.										

[0053] 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 low R value, and were poor in the bending property.

Example 2

[0054] 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.

[0055]

Table 2

ID number	Alloying elements			Other elements	Step	R	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	1.6	○	○	675	53.4	23.3
Ex 2-2	1.00	0.50	0.38	0.03Zr, 0.05 Mn	A	2.1	○	○	737	50.2	20.7
Ex 2-3	-	0.80	0.45	0.32Ti, 0.21Fe	C	1.7	○	○	712	51.7	21.8
Ex 2-4	0.50	1.50	0.35	0.2Ag, 0.05B, 0.1Mg	B	1.4	○	○	740	51.2	23.4
Ex 2-5	0.80	1.20	0.42	0.14Mg, 0.155n, 0.3Zn	C	1.8	○	○	735	49.9	19.6
Ex 2-6	1.00	1.00	0.48	0.23Cr, 0.14Mg, 0.10P	D	1.6	○	○	760	48.5	21.8
Ex 2-7	2.32	-	0.65	0.2Hf, 0.2Zn	B	1.9	○	○	785	39.8	24.4

(continued)

ID number	Alloying elements			Other elements	Step	R	Bending property		YS	EC	SR
	Ni	Co	Si								
	mass%	mass%	mass%	mass%			GW	BW	MPa	%IACS	%
Ex 2-8	0.90	1.70	0.61	0.04Zr, 0.42Ti, 0.11 Mg	D	2.2	○	○	811	45.4	21.2
Ex 2-9	1.10	1.50	0.55	0.15Sn, 0.2Ag	C	1.7	○	○	795	44.5	22.6
Ex 2-10	-	1.38	0.38	0,11mg, 0.32Zn	B	1.6	○	○	817	44.0	23.2
Ex 2-11	1.35	1.15	0.61	0.14Mg, 0.15Sn, 0.3Zn	C	1.9	○	○	758	51.9	21.5
Ex 2-12	1.35	1.15	0.61	0.22Cr, 0.05Mn	A	2.2	○	○	789	41.7	22.5
Ex 2-13	1.5	1.1	0.59	0.11Mg, 0.32Zn, 0.5Ti	A	2.1	○	○	806	43.3	22.2
Ex 2-14	-	1.82	0.55	0.14Mg, 0.15Sn, 0.3Zn	C	1.7	○	○	786	42.4	20.5
Ex 2-15	2.50	0.50	0.71	0.23Cr, 0.11 Mg, 0.32Zn	B	1.4	○	○	788	41.7	20.2
Ex 2-16	3.11	-	0.69	0.20Cr, 0.2Sn, 0.2Ag	B	1.8	○	○	814	42.2	18.8
Ex 2-17	1.50	1.50	0.82	0.04Mn, 0.2Fe, 0.1Hf	C	2	○	○	803	41.7	19.2
C Ex 2-1	2.32	-	0.65	0.62Hf, 1 .55Zn	B	1.2	○	○	728	27.9	24.4
C Ex 2-2	1.35	1.15	0.61	0.42Mg, 0.82Sn, 1.53Zn	C	1.3	○	○	758	26.9	21.5
C Ex 2-3	-	1.82	0.55	0.61Mn, 0.32Cr, 1.42Ag	D	1.2	○	○	786	24.9	20.5
"Ex" means Example according to the present invention, and "C Ex" means Comparative Example.											

[0056] 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

[0057] 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 1,020 to 700°C for 10 minutes to 10 hours, followed by hot-rolling as shown in Table 4, water cooling, face milling, 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, cold-working at a working ratio of 5% to 55%, and a final solution heat treatment of maintaining at 750 to 1,000°C for 5 seconds to 1 hour. 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.

[0058]

Table 3

Additive elements	Ni	Co	Si	Sn	Zn	Mg	Cr
mass%	12.71	0.32	0.76	0.17	0.31	0.07	0.17

[0059]

Table 4

	Hot-working Working temperature/working ratio per pass			
	1st pass	2nd pass	3rd pass	4th pass
Ex 3-1	(P+100)°C/33%	(P+80)°C/33%	(P+50)°Cs/33% → Air cooling	(P-50)°C/15%
Ex 3-2	(P+130)°C/28%	(P+120)°C/28% → Air cooling	(P-50)°C/20%	(P-70)°C/20%
Ex 3-3	(P+130)°C/30%	(P+120)°C/30%	(P+110)°C/30%	(P+100)°C/30% → Water cooling
Ex 3-4	(P+130)°C/27%	(P+110)°C/30%	(P+90)°C/30% → Water cooling	(P-150)°C/20%
C Ex 3-1	(P+100)°C/30%	(P+80)°C/31%	(P+60)°C/32%	(P+40)°C/33%
C Ex 3-2	(P+80)°C/15%	(P+70)°C/15%	(P+50)°C/15% → Air cooling	(P-50)°C/15%
C Ex 3-3	(P+130)°C/27%	(P+110)°C/30%	(P+90)°C/30% → Water cooling	(P-50)°C/35%
C Ex 3-4	(P-50)°C/15%	(P-70)°C/15%	(P-80)°C/15%	(P-100)°C/15%

Table 4 (continued)

	Hot-working Working temperature /working ratio per pass				R	Bending property		YS	EC	SR
	5th pass	6th pass	7th pass	8th pass		GW	BW	MPa	%IACS	%
Ex 3-1	(P-80)°C/15%	(P-110)°C/15%	-	-	1.6	o	o	738	49.0	21.6
Ex 3-2	-	-	-	-	1.9	o	o	707	40.2	24.2
Ex 3-3	(P-80)°C/20%	(P-100)°C/20%	(P-110)°C/20%	(P-130)°C/20%	2.2	o	o	780	45.9	21.0
Ex 3-4	(P-170)°C/20%	(P-190)°C/20%	(P-210)°C/20%	-	1.7	o	o	785	44.9	22.4
C Ex 3-1	-	-	-	-	0.8	×	×	796	46.0	23.5
C Ex 3-2	(P-80)°C/15%	(P-110)°C/15%	-	-	0.6	×	×	821	39.3	29.6
C Ex 3-3	(P-70)°C/35%	(P-80)°C/35%	-	-	0.7	×	×	788	39.2	25.8
C Ex 3-4	(P-110)°C/15%	(P-130)°C/15%	-	-	0.5	×	×	779	37.8	25.8

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

[0060] As shown in Table 4, Examples 3-1 to 3-4 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 3-1 to 3-4 were conducted under the conditions on the hot-working outside the ranges defined in the present invention, the respective value of R as defined in the present invention did not satisfy the predetermined value, and they were poor in the electrical conductivity.

[0061] 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).

[0062] 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

[0063] 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.
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. With regard to the working ratio and the number of passes in the hot-working, 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 to 1,020°C, one-pass working ratio 35 to 40%, and the number of passes 2 to 5 times.

[0064] 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.

[0065] Test specimen c01 thus obtained was different from the examples according to the present invention in terms of the second hot-rolling step, whether conducted or not, among the hot-rolling conditions in the production conditions, and resulted in not satisfying the required characteristics for the bending property due to the too low R value.

(Comparative Example 102) ··· Conditions described in JP-A-11-335756

[0066] 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). With regard to the working ratio and the number of passes in the hot-rolling, the hot rolling was conducted by employing the conditions that were usually used at the time of filing of the present application, that is, the conditions of a working ratio 35 to 40%, and the number of passes 2 to 5 times.

[0067] Test specimen c02 thus obtained was different from the examples according to the present invention in terms of the heat treatment [Step 7] and the cold-working [Step 8], whether conducted or not, and the second hot-rolling step, whether conducted or not, among the hot-rolling conditions in the production conditions, and resulted in not satisfying the bending property due to the too low R value.

(Comparative Example 103) ··· Conditions described in JP-A-2008-223136

[0068] 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).

[0069] 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 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 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 specimen c03 was obtained. Surface milling was conducted in the mid course, as necessary, and thus the sheet thickness of the test specimen was set to 0.2 mm. The principal production conditions are as described below.

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

[0070]

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

[0071] Test specimen c03 thus obtained was different from Example 1 in terms of the cooling process, whether conducted or not, between the first step and the second step in the hot-rolling, the working ratio of the second step, and the heat treatment [Step 7] and the cold-working [Step 8], whether conducted or not, in the production conditions, and resulted in not satisfying the bending property due to the too low R value.

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

[0072] Test specimen c04 was produced in the same manner as in Comparative Example 103, except that the working conditions of the following items were changed as described below.

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

[0073]

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

Test specimen c04 thus obtained was different from Example 1 in terms of the cooling process, whether conducted or not, between the first step and the second step in the hot-rolling, and the heat treatment [Step 7] and the cold-working [Step 8], whether conducted or not, in the production conditions, and resulted in not satisfying the bending property due to the too low R value.

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, having an R value of 1 or greater, which is defined by:

$$R = ([BR] + [RDW] + [W])/([C] + [S] + [B])$$

wherein [BR], [RDW], [W], [C], [S], and [B] represent an area ratio of crystal texture orientation component of BR orientation {3 6 2} <8 5 3>, RD-rotated-cube orientation {0 1 2} <1 0 0>, cube orientation {1 0 0} <0 0 1>, copper orientation {1 2 1} <1 1 1>, S-orientation {2 3 1} <3 4 6>, and brass orientation {1 1 0} <1 1 2>, respectively, in crystal orientation analysis in an EBSD (electron back scatter diffraction) analysis, and
having a proof stress of 500 MPa or greater, and an electrical conductivity of 30%IACS or higher.

2. The copper alloy sheet material according to claim 1, having an alloy composition comprising any one or two of Ni and Co 0.5 to 5.0 mass% in total, and Si 0.1 to 1.5 mass%, with the balance being copper and unavoidable impurities.

3. The copper alloy sheet material according to claim 2, further containing at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf 0.005 to 2.0 mass% in total.

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

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

6. A method of producing the copper alloy sheet material according to any one of claims 1 to 5, comprising the steps of: subjecting a copper alloy having the alloy composition to give the copper alloy, to 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], and a final solution heat treatment [Step 9], in this order, and then subjecting the resultant copper alloy to an aging precipitation heat treatment [Step 10],
wherein the hot-working [Step 3] is carried out, by first conducting two or more passes of hot-rolling at a temperature from (P+30)°C to 1,020°C (in which P (°C) represents the complete solid solution temperature of solute atoms) at a working ratio per pass of 25% or higher, cooling to a temperature (P-30)°C or lower, and then conducting two or more passes of hot-rolling at a temperature from 400°C to (P-30)°C at a working ratio per pass of 25% or lower.

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

Amended claims under Art. 19.1 PCT

1. A copper alloy sheet material, having an R value of 1 or greater, which is defined by:

$$R = ([BR] + [RDW] + [W])/([C] + [S] + [B])$$

wherein [BR], [RDW], [W], [C], [S], and [B] represent an area ratio of crystal texture orientation component of BR orientation {3 6 2} <8 5 3>, RD-rotated-cube orientation {0 1 2} <1 0 0>, cube orientation {1 0 0} <0 0 1>, copper orientation {1 2 1} <1 1 1>, S-orientation {2 3 1} <3 4 6>, and brass orientation {1 1 0} <1 1 2>, respectively, in crystal orientation analysis in an EBSD (electron back scatter diffraction) analysis, and
having a proof stress of 500 MPa or greater, and an electrical conductivity of 30%IACS or higher.

2. The copper alloy sheet material according to claim 1, having an alloy composition comprising any one or two of Ni and Co 0.5 to 5.0 mass% in total, and Si 0.1 to 1.5 mass%, with the balance being copper and unavoidable impurities.

3. The copper alloy sheet material according to claim 2, further containing at least one selected from the group consisting of Sn, Zn, Ag, Mn, B, P, Mg, Cr, Fe, Ti, Zr, and Hf 0.005 to 2.0 mass% in total.

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

5. Amended) A connector, which is composed of the copper alloy sheet material according to any one of claims 1 to 4.

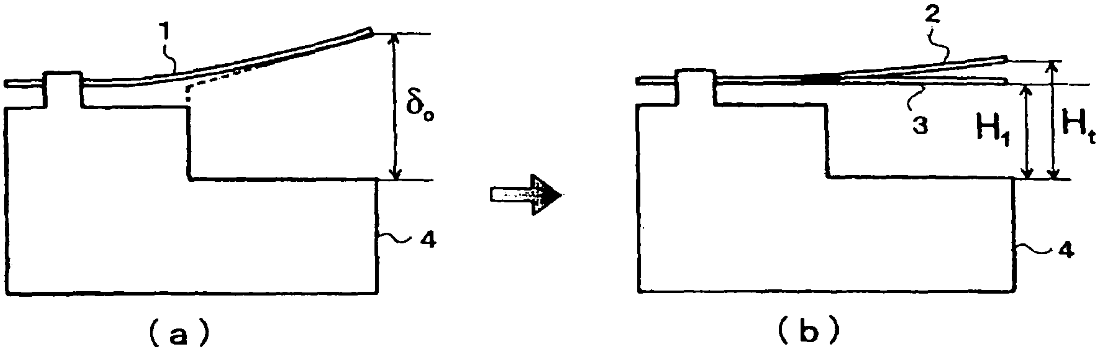
6. Amended) A method of producing the copper alloy sheet material according to any one of claims 1 to 4, comprising the steps of: subjecting a copper alloy having the alloy composition to give the copper alloy, to casting [Step 1], a homogenization heat treatment [Step 2], hot-working [Step 3], cold-rolling [Step 6], a heat treatment [Step 7], cold-rolling [Step 8], and a final solution heat treatment [Step 9], in this order, and then subjecting the resultant copper alloy to an aging precipitation heat treatment [Step 10],
wherein the hot-working [Step 3] is carried out, by first conducting two or more passes of hot-rolling at a temperature from (P+30)°C to 1,020°C (in which P (°C) represents the complete solid solution temperature of solute atoms) at a working ratio per pass of 25% or higher, cooling to a temperature (P-30)°C or lower, and then conducting two or more passes of hot-rolling at a temperature from 400°C to (P-30)°C at a working ratio per pass of 25% or lower.

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

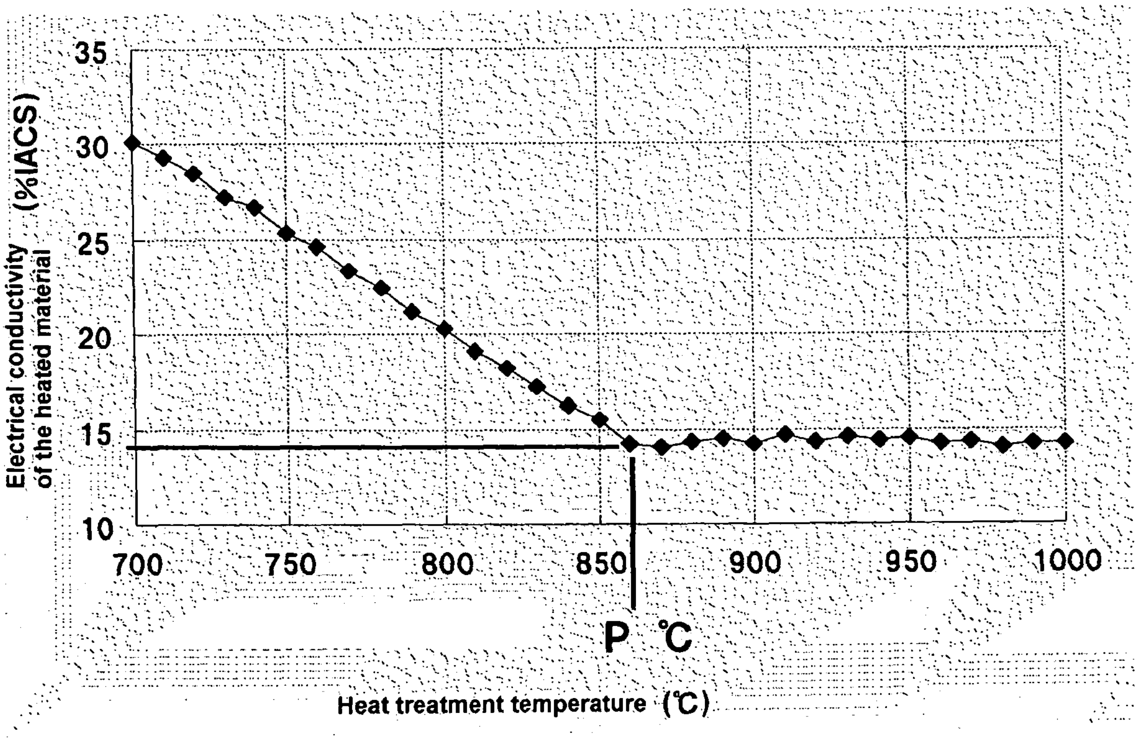
Statement under Art. 19.1 PCT

Claims 5 to 7
Claims 5 to 7 were amended to correct the typographic errors as indicated in the Written Opinion of the International Searching Authority.

{FIG. 1}


1
δ_o
4
(a)
2
3
H_1
H_t
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 (℃)

INTERNATIONAL SEARCH REPORT	International application No. PCT/JP2010/071518

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-C22C9/10, 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 2006-152392 A (Kobe Steel, Ltd.), 15 June 2006 (15.06.2006), entire text; all drawings (Family: none)	1-7
A	JP 2006-283059 A (Kobe Steel, Ltd.), 19 October 2006 (19.10.2006), entire text; all drawings (Family: none)	1-7
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	1-7

☒ 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 15 February, 2011 (15.02.11)	Date of mailing of the international search report 01 March, 2011 (01.03.11)
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/JP2010/071518

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 2008-223136 A (Dowa Metaltech Co., Ltd.), 25 September 2008 (25.09.2008), claims & US 2008/0190523 A1 & EP 1967596 A1 & EP 1964937 A1 & CN 101503770 A & CN 101245422 A	1-7
A	JP 2009-74125 A (Hitachi Cable, Ltd.), 09 April 2009 (09.04.2009), claims (Family: none)	1-7
A	JP 61-87838 A (Kobe Steel, Ltd.), 06 May 1986 (06.05.1986), claims; page 3, upper left column (Family: none)	1-7
A	JP 2009-132965 A (Hitachi Cable, Ltd.), 18 June 2009 (18.06.2009), entire text; all drawings (Family: none)	1,4-7

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- 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]**