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(54) COPPER ALLOY MATERIAL FOR ELECTRICAL AND ELECTRONIC COMPONENTS, AND MANUFACTURING METHOD THEREFOR

(57) A copper alloy material for an electric/electronic part, having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities, in which a copper alloy of a matrix has a grain size of 3 to 35 μ m, a precipitate composed of Co and Si has a particle size of 5 to 50 nm, the

precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and the copper alloy material has a tensile strength of 550 MPa and an electrical conductivity of 50 %IACS or more.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a part for an electric/electronic equipment, for example, a connector, a terminal material, and the like. Especially, the present invention relates to a copper alloy material applicable to electric/electronic parts, such as a high-frequency relay and a switch, which are desired to be high in electrical conductivity, or to a connector, a terminal material, which are, for example, mounted in vehicles, and a lead frame.

10 BACKGROUND ART

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[0002] Hitherto, copper alloys, such as brass (C26000), phosphor bronze (C51910, C52120, C52100), beryllium copper (C17200, C17530), and Corson-series copper alloy (hereinafter, also simply referred to as Corson copper, for example, C70250), and the like, have been used for parts for electric/electronic equipments, such as connectors, terminals, relays, switches, and the like. Herein, the term "Cxxxxx" denotes types of copper alloys specified in CDA (Copper Development Association).

[0003] In recent years, since electric current applied to electric/electronic equipments becomes large, the copper alloy materials to be used for parts for the electric/electronic equipments have been required to have a high electrical conductivity. For example, although brass and phosphor bronze each have a low electrical conductivity and the Corson copper shows a medium electrical conductivity (electrical conductivity is about 40 %IACS) as a connecter material, a higher electrical conductivity has been required. Further, it is also well known that beryllium copper is expensive. On the other hand, pure copper (C11000), tin bearing copper (C14410), and the like, which have a high electrical conductivity, have a drawback that their mechanical strength is low. Thus, a copper alloy has been desired which has an electrical conductivity higher than that of a conventional Corson copper, and a tensile strength and a bending property at the same level of those of the conventional Corson copper. As a copper alloy fulfilling this requirement, a Cu-Co (cobalt)-Si (silicon) series alloy is attracting attention. This Cu-Co-Si series alloy is a precipitation strengthening type copper alloy utilizing an intermetallic compound between Co and Si.

[0004] Particularly, among the parts for electronic equipments of recent years, there are many connectors or terminals that have been subjected to complicated and severe bending, concomitantly with the size reduction of electronic equipments. This is because although the size of connectors is also reduced along with the size reduction, it is desired to take a contact length as long as possible in order to maintain the reliability of contact. A connector or terminal having such a design concept is, in many cases, referred to as bellows (corrugated) bent connector or bellows bent terminal. That is, there is a strong demand for the mounting and installation of terminals or connectors that are bent in a complicated manner in small parts. On the other hand, the material of connectors and terminals to be used is becoming thinner concomitantly with the size reduction. This trend is furthered from the viewpoint of weight reduction and resource saving. Thin materials are demanded to have higher mechanical strength as compared with thick materials, in order to maintain the same contact pressure.

[0005] As a method of increasing the mechanical strength of a copper alloy material, there are various strengthening methods, such as solid solution strengthening, work strengthening and precipitation strengthening. In a copper alloy material, the electrical conductivity and mechanical strength are generally in a contrasting relationship, but it is known that precipitation strengthening is promising as a method of enhancing the mechanical strength without decreasing the electrical conductivity of the copper alloy material. This precipitation strengthening is a technique of subjecting an alloy to which elements causing precipitation have been added, to a heat treatment at high temperature to thereby solid-dissolve these elements into the copper matrix, and then heat treating the alloy at a temperature lower than the temperature used for the solid solution, thereby precipitating the solid-dissolved elements. For example, beryllium copper, Corson copper and the like employ that strengthening method.

[0006] However, in a copper alloy material, the relationship between bending property and mechanical strength is also a contrasting relationship, in addition to the relationship between electrical conductivity and mechanical strength. In order to enhance the mechanical strength, it is considered effective to increase the final cold rolling ratio; however, if the cold rolling ratio is increased, there is a tendency that the bending property is noticeably deteriorated. It has hitherto been considered that beryllium copper, Corson copper, titanium copper and the like as precipitation type copper alloys have a good balance between bending property and mechanical strength. However, beryllium copper is such that beryllium, which is an additive element, is regarded as an environmental burden material, and there is a demand for a substitute material. Furthermore, Corson copper or titanium copper generally does not have an electrical conductivity of 50 %IACS or higher. Examples of the applications where a high electrical conductivity of 50 %IACS or higher is required, include battery terminals and relay contacts to which high current is applied. Furthermore, since materials having high electrical conductivity are generally excellent in the thermal conduction property as well, materials for the sockets or heat sinks of central processing units (CPU; integrated logic elements), which require heat emission properties,

are also required to have high electrical conductivity. Particularly, recent hybrid cars or CPUs handling high speed processing are required to use materials having high electrical conductivity and high mechanical strength.

[0007] Under such circumstances, copper alloys which have mechanical strength, bending property and electrical conductivity (thermal conductivity) and use an intermetallic compound containing Co and Si, are increasingly attracting attention. Copper alloys essentially containing Co and Si are known as shown below.

[8000]

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Patent Literature 1 discloses a copper alloy essentially containing, for improving a hot workability, Zn (zinc), Mg (magnesium), and S (sulfur), in addition to Co and Si.

Patent Literature 2 discloses an alloy containing Mg, Zn, and Sn (tin), in addition to Co and Si.

Patent Literature 3 discloses an alloy essentially containing Sn and Zn, in addition to Co and Si.

Patent Literature 4 discloses a precipitation strengthening Cu-Co-Si-series alloy for the use of a lead frame.

Patent Literature 5 discloses a Cu-Co-Si series alloy, in which the size of inclusions precipitated is 2 µm or less.

Patent Literature 6 discloses a Cu-Co-Si-series alloy, in which a Co₂Si compound is precipitated.

[0009]

Patent Literature 1: JP-A-61-87838 ("JP-A" means unexamined published Japanese patent application)

Patent Literature 2: JP-A-63-307232 Patent Literature 3: JP-A-02-129326 Patent Literature 4: JP-A-02-277735 Patent Literature 5: JP-A-2008-88512 Patent Literature 6: JP-A-2008-56977

25 DISCLOSURE OF INVENTION

TECHNICAL PROBLEM

[0010] However, in the techniques disclosed in the patent literatures 1 to 6, there are problems as mentioned below. [0011] For example, all of these are not intended to satisfy, simultaneously, mechanical strength, electrical conductivity, solder wettability, solder adhesive strength, and bending property as in the case of the use in electric/electronic parts, and those are silent on the details of their alloy state.

Furthermore, all of the techniques described in the patent literatures do not satisfy all of the mechanical strength, bending property, and electrical conductivity (thermal conductivity) at a high level.

The technique disclosed in Patent Literature 1 is a copper alloy containing sulfur (S) as an essential constituent element, unlike the present invention, and the purpose of the technique is to enhance hot workability, unlike the present invention. Therefore, for example, Patent Literature 1 does not have any description on precipitates (particularly, a precipitate of Co and Si), does not clarify what the precipitate is like, and does not clearly describe a method of controlling these. Furthermore, the results of evaluating various properties such as mechanical strength and electrical conductivity required of electric/electronic parts are not described.

Patent Literature 2 has a description that the precipitate of Co and Si is a Co_2Si compound, but the details of the precipitate (such as particle size) or the controlling method is not clearly described. In addition, regarding the production method, it is described that annealing is carried out at a temperature of 500°C for one hour or at a temperature of 450°C for one hour; however, there is no description on the recrystallization treatment, and even if such a description were present, the grain size of the matrix would not be clearly known. That is, it is thought that the properties of the copper alloy based on the technique disclosed in Patent Literature 2 are not satisfactory as the properties of a copper alloy for use in electric/ electronic parts where high electrical conductivity and high mechanical strength are required.

Patent Literature 3 also has a description that the precipitate of Co and Si is a $\rm Co_2Si$ compound; however, the details of the precipitate (particle size and the like) or the controlling method is not clearly described, and the electrical conductivity is relatively low, such as 30 %IACS or less. Furthermore, in regard to the production method, there is a description that a solution heat treatment at 950°C and cold rolling are carried out before annealing at a temperature of 400°C to 500°C for one hour, but the electrical conductivity is relatively low, such as 30 %IACS or less, and it can be said that the properties of the copper alloy based on the technique disclosed in Patent Literature 3 are not satisfactory as the properties of a copper alloy for use in electric/electronic parts where high electrical conductivity and high mechanical strength are

The Cu-Co-Si-based alloy described in Patent Literature 4 is described to have a use in lead frames and is a precipitation strengthened type alloy, but the specific compound forming the precipitate and the details of the alloy (particle size and the like) are not clearly described. Furthermore, in regard to the production method, there is a description that a heat

treatment for one hour at a temperature of 500°C, subsequent cold rolling, and strain-relieving annealing for one hour at 300°C are carried out. However, there is no description that a recrystallization treatment is carried out, and even if there were a description on this, the grain size of the matrix would not be clearly known. That is, it is thought that the properties of the copper alloy obtained based on the technique disclosed in Patent Literature 4 are not satisfactory as the properties of a copper alloy for use in electrical/electronic parts where high electrical conductivity and high mechanical strength are required.

In regard to the Cu-Co-Si alloy described in Patent Literature 5, there is a description that the size of the inclusion that precipitates within the alloy is 2 μ m or less; however, the details such as the method of defining the inclusion are not clearly described. Furthermore, an example has been reported, in which the production is carried out by a step of rolling an ingot directly at room temperature. Herein, when it is considered that strict particle size control is generally required in order to obtain desired alloy properties, it is thought that the properties of the copper alloy obtained based on the technique disclosed in Patent Literature 5 are not satisfactory as the properties of a copper alloy for use in electrical/ electronic parts where high electrical conductivity and high mechanical strength are required.

Patent Literature 6 also has a description that the precipitate of Co and Si is a Co_2Si compound, but the details of the precipitate (particle size and the like), the controlling method or the density is not clearly described. Furthermore, in regard to the production method, it is described that a heat treatment at 700°C to 1,050°C is carried out before the final rolling, but it is also described that the compound precipitated at this temperature is re-solid-dissolved (solution treatment temperature). Thus, it is not clearly described whether a precipitate of Co and Si is present after all. As a result, it is thought that the properties of the copper alloy are not satisfactory as the properties of a copper alloy for use in electrical/electronic parts where high electrical conductivity and high mechanical strength are required.

Furthermore, Patent Literature 5 and Patent Literature 6 disclose examples in which bending property is evaluated under the conditions of R/t = 1 for a particular mechanical strength level, where an inner bending radius of the material is designated as R, and a sheet thickness as t. However, it is thought that with the mechanical strength level of this extent, definitely there will be instances where the resulting alloys are not capable of coping with the bending property demanded in the future.

[0012] As described above, the techniques disclosed in Patent Literatures 1 to 6 have matters that are not clearly discussed or that are described in a contradictory manner. Therefore, materials having high electrical conductivity and high mechanical strength cannot be obtained only based on the techniques disclosed in the patent literatures described above, and furthermore, materials that have satisfactory properties, including the stress relaxation resistance (creep resistance), cannot be obtained.

[0013] Furthermore, in order to obtain alloy properties that are satisfactory as the properties of a copper alloy for the use in electric/electronic parts where high electrical conductivity and high mechanical strength are required, it is necessary to strictly control the grain size of the matrix and the particle size of the precipitate, but the patent literatures do not have description in connection therewith. That is, it is thought that the properties of the copper alloys based on the inventions illustrated in the patent literatures are not satisfactory as the properties of a copper alloy for use in electrical/electronic parts where high electrical conductivity and high mechanical strength are required.

[0014] For solving the above-mentioned problems in the conventional techniques, the present invention is, first, contemplated for providing a copper alloy material suitable for connectors, terminal materials, relays, and the like, which is excellent in electrical conductivity and mechanical strength, and is also excellent in stress relaxation resistance.

[0015] The present invention is, second, contemplated for providing a copper alloy material which is excellent in electrical conductivity, mechanical strength, solder wettability, solder adhesive strength, and bending property, and is suitable for the use in connectors, terminal materials, relays, and the like.

[0016] Furthermore, the present invention is, third, contemplated for providing a copper alloy material which has the value of the grain size of a Cu-Co-Si series copper alloy controlled to a predetermined range, so as to satisfy all of high electrical conductivity, high mechanical strength, and satisfactory bending property.

SOLUTION TO PROBLEM

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[0017] The inventors of the present invention found a particular suitable relationship that controls the size and density of the precipitate in connection with an attempt to obtain a copper alloy material having excellent electrical conductivity and mechanical strength as well as excellent stress relaxation resistance, and further conducted an investigation to finally complete the present invention.

Furthermore, the inventors of the present invention conducted further investigations on the relationship between electrical conductivity, mechanical strength, bending property, solder wettability, and solder adhesive strength in a copper alloy material, in order to obtain a copper alloy material suitable for the use in electric/electronic parts where particularly high electrical conductivity and high mechanical strength are required, and thus completed the present invention.

[0018] According to the present invention, there is provided the following means:

- (1) A copper alloy material for an electric/electronic part, having a composition comprising Co (cobalt) 0.5 to 2.0 mass% and Si (silicon) 0.1 to 0.5 mass%, with the balance of Cu (copper) and inevitable impurities,
- wherein a copper alloy of a matrix has a grain size of 3 to 35 μ m, wherein a precipitate composed of Co and Si has a particle size of 5 to 50 nm, and the precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and
- wherein the copper alloy material has a tensile strength of 550 MPa and an electrical conductivity of 50 %IACS or more;

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- (2) The copper alloy material for an electric/electronic part as described in the above item (1), comprising at least one of Sn (tin) and Mg (magnesium) 0.1 to 0.5 mass% in total;
- (3) The copper alloy material for an electric/electronic part as described in the above item (1) or (2), comprising at least one of Zn (zinc) and Mn (manganese) 0.1 to 0.5 mass% in total;
- (4) The copper alloy material for an electric/electronic part as described in any one of the above items (1) to (3), comprising at least one selected from the group consisting of Fe (iron), Cr (chronium) and Ni (nickel) 0.1 to 1.0 mass% in total;
- (5) The copper alloy material for an electric/electronic part as described in any one of the above items (1) to (4), wherein a stress relaxation ratio after a lapse of 1,000 hours in an air atmosphere at a temperature of 150°C is less than 40%:
- (6) A method of producing a copper alloy material for an electric/electronic part, comprising the steps a and b of:
 - step a: subjecting a copper alloy material having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities, to an aging heat treatment at 500 to 600°C for 1 to 4 hours; and
 - step b: after the step a, setting a cooling speed from the temperature at the time of the aging heat treatment to a temperature of the copper alloy material of 300°C to be in a range of 20 to 100 K/hour (K representing the absolute temperature),
 - whereby a copper alloy material is obtained, in which a copper alloy of a matrix has a grain size of 3 to 35 μ m, a precipitate containing Co and Si has a particle size of 5 to 50 nm, the precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and the copper alloy material has a tensile strength of 550 MPa or more and an electrical conductivity of 50 %IACS or more;
- (7) The copper alloy material for an electric/electronic part as described in the above item (1), wherein the surface roughness as the copper alloy material is such that Ra is 0.2 μm or less and Rt is 2 μm or less;
 - (8) The copper alloy material for an electric/electronic part as described in the above item (7), comprising at least one selected from the group consisting of Zn, Sn and Mg 0.1 to 1.0 mass% in total;
 - (9) The copper alloy material for an electric/electronic part as described in the above item (7) or (8), comprising at least one selected from the group consisting of Fe, Cr and Ni 0.1 to 1.0 mass% in total;
 - (10) A method of producing a copper alloy material for an electric/electronic part, comprising the steps of:
 - subjecting a copper alloy material having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities, to an aging heat treatment;
 - acid-dissolving the surface of the aged material; and grinding the acid-dissolved surface,
 - whereby a copper alloy material is obtained, in which a copper alloy of a matrix has a grain size of 3 to 35 μ m, a precipitate containing Co and Si has a particle size of 5 to 50 nm, the precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and the copper alloy material has a surface roughness of 0.2 μ m or less in Ra and 2 μ m or less in Rt, and a tensile strength of 550 MPa or more, and an electrical conductivity of 50 %IACS or more;
 - (11) The copper alloy material for an electric/electronic part as described in the above item (1), wherein the Co content is 0.7 to 2.0 mass%, the mass ratio of Co to Si (Co/Si) is from 3 to 5, the arithmetic mean of the grain size of the copper alloy of a matrix is 3 to 20 μm, the standard deviation is 8 μm or less, and the standard deviation is smaller than the arithmetic mean.
 - (12) The copper alloy material for an electric/electronic part as described in the above item (11), further comprising at least one selected from the group consisting of Cr, Ni and Fe 0.01 to 1.0 mass% in total, with the balance of Cu and inevitable impurities;
 - (13) The copper alloy material for an electric/electronic part as described in the above item (11) or (12), further comprising at least one selected from the group consisting of Sn, Mg, Zn and Mn 0.01 to 1.0 mass% in total, with the balance of Cu and inevitable impurities; and
- (14) The copper alloy material for an electric/electronic part as described in any one of the above items (11) to (13), further comprising at least one selected from the group consisting of Zr (zirconium) and Ti (titanium) 0.01 to 1.0 mass% in total, with the balance of Cu and inevitable impurities.

Hereinafter, a first embodiment of the present invention means to include the copper alloy materials for electric/electronic parts described in the above items (1) to (5) and the method of producing a copper alloy material for electric/electronic parts described in the above item (6).

[0019] A second embodiment of the present invention means to include the copper alloy materials for electric/electronic parts described in the above items (7) to (9) and the method of producing a copper alloy material for electric/electronic parts described in the above item (10).

[0020] A third embodiment of the present invention means to include the copper alloy materials described in the above items (11) to (14).

[0021] Herein, the present invention means to include all of the above first, second, and third embodiments, unless otherwise specified.

[0022] Herein, the stress relaxation ratio is measured by a cantilever method according to the Japan Copper and Brass Association Technical Standards "JCBA T309:2001 (provisional)". In this evaluation, as the stress relaxation ratio is lower, the material may be said to be a satisfactory material without a decrease in the contact pressure occurring when the copper alloy material is used in a connector.

[0023] Furthermore, the term "particle diameter (size) of the precipitate" refers to an average particle size of the precipitate determined by a method that will be described below, and the "grain size" refers to a value measured based on JIS-H0501 (cutting method) that will be described below.

ADVANTAGEOUS EFFECTS OF INVENTION

[0024] The first embodiment of the present invention can provide a copper alloy material favorable for the use in electric/electronic equipments, which is excellent in mechanical strength, conductivity, and stress relaxation resistance.

[0025] The second embodiment of the present invention can provide a copper alloy material favorable for the use in electric/electronic equipments, which is high in mechanical strength and electrical conductivity, and is excellent in solder

wettability, solder adhesive strength and bending property.

The third embodiment of the present invention can provide a copper alloy material favorable for the use in electric/ electronic equipments, which is excellent in mechanical strength, electrical conductivity, and bending property.

[0026] Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawings.

BRIEF DESCRIPTION OF THE DRAWINGS

[0027]

{Fig. 1}

Fig. 1 is a schematic diagram explaining a testing method for solder adhesive strength.

DESCRIPTION OF REFERENCE NUMERALS

40 [0028]

- 1 EF line (steel line coated with copper)
- 2 Solder
- 3 Test material (copper alloy material)

BEST MODE FOR CARRYING OUT THE INVENTION

[0029] Preferable embodiments of the copper alloy 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 (herein, the copper alloy base material means a mixture of component elements of a copper alloy not having the concept of shape) is processed into a predetermined shape (for example, sheet, strip, foil, rod, or wire). Furthermore, the term "copper alloy of matrix" means a copper alloy not having the concept of shape.

In addition, explanation will be given on a sheet material and a strip material as a preferable specific examples of the copper alloy material, but the shape of the copper alloy material is not limited to the sheet material or the strip material.

[0030] Hereinafter, the first embodiment of the present invention is explained in detail.

First, the composition and constituent elements of the copper alloy base material that constitutes the copper alloy material are described. In the composition of a copper alloy base material in the first embodiment of the present invention, the essential additive elements are Co (cobalt) and Si (silicon). In regard to the addition amount of these elements, the

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addition amount of Co is set at 0.5 to 2.0 mass% and the addition amount of Si at 0.1 to 0.5 mass%, because these elements form an intermetallic compound of Co_2Si and contribute to precipitation strengthening, as mentioned above. If the content of Co is less than 0.5 mass%, since the precipitation strengthening degree is small, the target mechanical strength of 550 MPa cannot obtained. If the content of Co is more than 2.0 mass%, the solution heat temperature becomes high, and the effect due to Co is saturated. Furthermore, from a stoichiometric proportion, the optimum addition ratio of the compound is Co/Si nearly equals to 4.2, and the addition amount of Si is set not to be much deviated from this value (specifically, to fall in the range of $3.5 \le Co/Si \le 4.8$).

[0031] A preferable addition amount of Co varies with the temperature, at which the recrystallization heat treatment is carried out. For example, when the temperature, at which the recrystallization heat treatment is carried out, is 800 to 900°C, the addition amount of Co is preferably in the range from 0.5 to 1.2 mass%, and when the temperature is 900 to less than 950°C, the addition amount of Co is preferably in the range of 1.0 to 2.0 mass%. This is determined from the grain size of the copper alloy that is the matrix of the copper alloy material that will be defined below. In addition, the temperature, at which the recrystallization heat treatment is carried out, may be 800 to 1,025°C, and in the case where the addition amount of Co is 1.0 to 2.0 mass%, the temperature, at which the recrystallization heat treatment is carried out, can be set at 900 to 1,025°C.

[0032] In the first embodiment of the present invention, the grain size of the copper alloy that serves as the matrix of the copper alloy material is set in the range of 3 to 35 μ m. This is because when the grain size is 3 μ m or more, there is no risk that there would be mixed grains including unrecrystallization where insufficient recrystallized portions are observed, and bending property is enhanced. Furthermore, when the grain size is 35 μ m or less, the grain boundary density is high, and the bending stress (loaded strain) can be sufficiently absorbed, thereby the bending property being enhanced. The grain size is preferably 3 to 20 μ m, and more preferably 10 to 20 μ m.

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[0033] Furthermore, in the first embodiment of the present invention, the electrical conductivity of the copper alloy material is 50 %IACS or more. Herein, "%IACS" is a unit which indicates an electrical conductivity of a material and the term "IACS" is an abbreviation of "International Annealed Copper Standard". This property is a property obtained preferably, for example, by setting the addition amount of Co or Si in the range described above, and precipitating the intermetallic compound of Co₂Si, or the like. The electrical conductivity is more preferably 55 %IACS or more, and even more preferably 60 %IACS or more, and it is preferable that the electrical conductivity is as high as possible, but the upper limit is generally approximately 75 %IACS. In order to enhance the electrical conductivity, it is preferable to cool the copper alloy material while keeping the cooling speed from the temperature of the aging heat treatment that precipitates the precipitate in the range of 20 to 100 K/hour (herein, the term "K" indicates "Kelvin" which represents an absolute temperature; hereinafter, the same applies), and to keep the cooling speed until the temperature reaches 300°C. Herein, it was found that in the case where the copper alloy, after the aging heat treatment, is cooled to room temperature, 100°C, or 200°C by keeping the cooling speed mentioned above, the electrical conductivity undergoes almost no change as compared with the case where the temperature is kept to 300°C. Furthermore, when cooling the copper alloy, which has been cooled from the temperature after the aging heat treatment to 300°C, further to room temperature, it does not matter even if the cooling speed exceeds 100 K/hour, for example, as in the case of air cooling (spontaneous cooling). In addition, in the first embodiment of the present invention, the tensile strength of the copper alloy material is defined to be 550 MPa or more. This tensile strength is more preferably 600 MPa or more, and even more preferably 750 MPa or more, and it is preferable that the tensile strength is as high as possible, but the upper limit is generally approximately 900 MPa.

[0034] In the copper alloy material of the first embodiment of the present invention, the particle size (average particle size) of the precipitate composed of Co and Si is defined to be 5 to 50 nm. When the particle size of the precipitate is 5 nm or more, a sufficient precipitate strengthening degree can be obtained. Furthermore, since this precipitate precipitates out coherently to the copper matrix and strengthens the material, when the particle size of the precipitate is 50 nm or less, the mechanical strength of the material is secured. Preferably, the size of the precipitate is 10 to 30 nm, and more preferably 20 to 30 nm.

[0035] With regard to the precipitation density, the distribution density of the precipitate composed of Co and Si is defined to be 1×10^8 to 10^{10} number/mm². By setting the distribution density of the precipitate to be in this range, sufficient mechanical strength and sufficient stress relaxation resistance are obtained. In the first embodiment of the present invention, the stress relaxation ratio after a lapse of 1,000 hours in an air atmosphere at a temperature of 150°C is preferably less than 40%. In addition, the precipitation density is correlated with the addition amount of Co. When the addition amount of Co is adjusted to 0.5 mass% or more, even if the particle size of the precipitate is as fine (approximately 5 nm) as to an acceptable extent, the distribution density falls in the range described above. Furthermore, when the addition amount of Co is 2.0 mass% or less, even if the particle size of the precipitate is as coarse (approximately 50 nm) as to an acceptable extent, the distribution density falls in the range mentioned above.

Preferably, the precipitation density is 1×10^8 to 8×10^8 number/mm² in the case where the addition amount of Co is 0.5 to 1.0 mass%, 5×10^8 to 7×10^9 number/mm² in the case where the addition amount of Co is 1.0 to 1.5 mass%, and 1 $\times10^9$ to 10^{10} number/mm² in the case where the addition amount of Co is 1.5 to 2.0 mass%.

[0036] Hereinafter, preferable additive elements will be described. The addition of Sn and Mg is effective in improving the stress relaxation resistance. Although the effect may be shown by individual addition of Sn and Mg, these elements exhibit the effect synergistically by adding them simultaneously. When the addition amount of Sn and Mg is such that the addition amount of at least one kind of these elements is 0.1 mass% or more in total, the effect is markedly exhibited, and when the addition amount is 0.5 mass% or less in total, there is no adverse effect such as a decrease in electrical conductivity. Furthermore, in the case where the addition ratio is such that $Sn/Mg \ge 1$, the stress relaxation resistance tends to be further enhanced.

[0037] Next, other preferable additive elements other than Sn and Mg are described. Zn and Mn improve the property by solid solution strengthening. Thus, the addition amount of at least one kind thereof is adjusted to 0.1 to 0.5 mass% in total. When the amount is 0.1 mass% or more in total, the effect is noticeably exhibited, and when the amount is 0.5 mass% or less in total, there is no adverse effect such as a decrease in electrical conductivity. The addition amount of Zn and Mn is preferably such that the addition amount of at least one of these elements is 0.2 to 0.4 mass% in total.

[0038] Furthermore, Fe, Cr and Ni are elements that contribute to enhance the mechanical strength by being replaced with Co and forming a compound with Si. Fe, Ni and Cr have a function of forming a (Co, χ)₂Si compound (χ = Fe, Ni, Cr) to enhance the mechanical strength, by being replaced with a part of Co. These elements also have an effect of making the grain size fine. Therefore, the addition amount of at least one kind of these elements (which may be any of the cases of individual elements, a combination of any two kinds of the elements, and a combination of all three kinds of the elements) is adjusted to the range from 0.1 to 1.0 mass% in total. When the addition amount is 0.1 mass% or more, the effect due to the elements is noticeably exhibited, and when the addition amount is 1.0 mass% or less in total, there is no chance of causing crystallization during casting or forming an intermetallic compound that does not contribute to mechanical strength, and there is no adverse effect such as a decrease in electrical conductivity. Furthermore, these elements provide almost the same effect even if the elements are added in combination or added individually; however, when Ni is added, a remarkable effect of enhancing the mechanical strength is exhibited. The addition amount of Fe, Ni and Cr is preferably such that the addition amount of at least one kind of the elements is 0.5 to 0.8 mass% in total. Examples of inevitable impurities in the copper alloy material according to the first embodiment of the present invention include H, C, O, S and the like.

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[0039] The producing method of the copper alloy material of the first embodiment of the present invention is explained below. The recrystallization heat treatment temperature prior to the final rolling is preferably set at 800 to 1,000°C in consideration of the effects of partial melting or deformation of the material. More preferably, the upper limit is lower than 950°C. This is because it is preferable to set the recrystallization heat treatment temperature at 800°C or higher in order to achieve sufficient solution and recrystallization of the above-mentioned elements such as Co, and when the recrystallization heat treatment temperature is 1,000°C or lower, the risk of generation of partial melting or shape deformation of the material is decreased. Preferably, when the addition amount of Co is 0.5 to 1.2 mass%, the recrystallization heat treatment is set at 800 to 900°C, and when the addition amount of Co is 1.0 to 1.5 mass%, the recrystallization heat treatment is set at 900 to 950°C (not including 950°C). In the case where the addition amount of Co is 1.5 mass% or more (2.0 mass% or less), it is preferable to carry out the recrystallization heat treatment at a temperature of 950°C or higher (when the affection of partial melting or deformation of the material are taken into consideration, 1,025°C or lower, and preferably 1,000°C or lower).

Subsequently, when the copper alloy material is cooled at a cooling speed of 50 K/sec or more from the temperature at which the recrystallization heat treatment is carried out, the precipitate containing Co precipitates out coherently and enhances the mechanical strength of the material. This cooling speed means an average cooling speed from the temperature of high temperature heat treatment to 300°C.

[0040] After the recrystallization heat treatment, an aging heat treatment for forming a compound of Co and Si is carried out. The aging heat treatment may be carried out after the recrystallization heat treatment, or after a predetermined cold rolling is carried out. In the first embodiment of the present invention, the condition for this aging heat treatment is such that in the case of conducting the aging heat treatment after the recrystallization heat treatment and before the final cold rolling, a condition of a temperature from 500 to 600°C and a time period from 1 to 4 hours is preferable, on the other hand, in the case of conducting the aging heat treatment after the final cold rolling and before the recrystallization heat treatment, a condition of a temperature from 450 to 550°C and a time period of 1 to 4 hours is preferable. Furthermore, the cooling speed after this aging heat treatment is set at 20 to 100 K/hour, in order that the cooling speed contributes to an enhancement of electrical conductivity. The temperature range, in which cooling is carried out at the cooling speed mentioned above, is preferably adjusted to the cooling range from the recrystallization heat treatment temperature to 300°C. In addition, after the material temperature is lowered to below 300°C, the material may be rapidly cooled without any problem.

The cooling speed after the aging heat treatment can be adjusted by controlling the temperature at a heating furnace. Furthermore, in the case where it is required to conduct a rapid cooling, the rapid cooling can be conducted by taking out the subject from a heating zone of the heating furnace and subjecting the subject to forced air cooling or water quenching.

[0041] Hereinafter, an example of the process of producing the copper alloy material of the first embodiment of the present invention is described in detail.

<Melt-casting>

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[0042] A copper alloy ingot having a predetermined size is obtained by melting copper, cobalt, silicon, and the like, which are the raw materials of the target copper alloy, pouring the resultant melt alloy into a mold, followed by casting under cooling at a cooling speed from 10 to 30 K/sec. The ingot has, for example, a size of 30 mm in thickness, 100 mm in width, and 150 mm in length.

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<Hot rolling, face-milling, and cold rolling>

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[0043] Then, this ingot is kept at a temperature from 930 to 1,050°C (preferably 950 to 1,050°C) for 30 minutes to 60 minutes, followed by working by hot rolling, and quenching by water cooling (rapid cooling) immediately, further followed by milling the rolled surface to remove an oxide layer on the surface, and cold rolling.

<Recrystallization heat treatment>

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[0044] Then, for the purpose of conducting solution and recrystallization, a recrystallization heat treatment is carried out for a certain time period in a salt bath (salt bath furnace) kept at a temperature of 800 to 1,025°C, followed by quenching by water cooling. During the recrystallization heat treatment, the heat treatment is carried out by adjusting the temperature raising speed by interposing the subject between stainless steel plates having different plate thicknesses. A preferable temperature raising speed in this occasion is 10 to 300 K/sec at a temperature of 300°C or higher. A preferable cooling speed is 50 to 200 K/sec.

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<Aging heat treatment>

[0045] Then, for the purpose of performing aging precipitation, an aging heat treatment is carried out at a temperature from 500 to 600°C for 1 to 4 hours.

30 The temperature raising speed from room temperature to the highest temperature in that occasion is in the range from 5 to 50 K/min. With regard to temperature lowering, cooling is carried out inside the furnace at a speed in the range from 20 to 100 K/minute until the temperature reaches 300°C, which is a temperature sufficiently lower than the temperature zone considered to affect the precipitation.

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<Finish rolling (according to the necessity)>

cold rolling (finish rolling) at a working ratio from 0 to 40%, and thus a finish rolled material is obtained. It is not necessarily required to carry out the finish rolling. Herein, the term "a working ratio of 0%" means that the finish rolling is not carried out.

<Strain-relieving annealing>

[0047] After completion of the aging heat treatment (in the case of conducting the finish rolling, after completion of the finish rolling), the copper alloy material is subjected to strain-relieving annealing, according to the necessity.

[0046] The copper alloy material that has been subjected to the aging heat treatment is further subjected to a final

<With respect to repeating steps>

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[0048] Each of the recrystallization heat treatment, the aging heat treatment and the cold rolling may be repeated two or more times under the conditions described above, respectively, and the sequence of conducting these steps may be changed.

[0049] Next, a preferable embodiment of the copper alloy material according the second embodiment of the present invention is explained in detail.

[0050] First, the composition and constituent elements of the copper alloy base material that constitutes the copper alloy material are described. In the composition of the copper alloy base material in the second embodiment of the present invention, the essential additive elements are Co (cobalt) and Si (silicon). The addition amounts of these elements are set at 0.5 to 2.0 mass% for Co and 0.1 to 0.5 mass% for Si, because when these elements form an intermetallic compound of Co₂Si and contribute to precipitation strengthening, if the addition Co is set at 0.5 mass% or more, the precipitation strengthening degree becomes large, and therefore, the mechanical strength of the copper alloy material

can be adjusted to 550 MPa or more and when the addition amount of Co is 2.0 mass% or less, the solution heat treatment temperature can be set in a proper range. Furthermore, from a stoichiometric proportion, the optimum addition ratio of the compound is Co/Si nearly equals to 4.2, and the addition amount of Si is set not to be much deviated from this value (specifically, to fall in the range of $3.5 \le \text{Co/Si} \le 4.8$).

[0051] A preferable addition amount of Co varies with the temperature, at which the recrystallization heat treatment is carried out. For example, when the temperature, at which the recrystallization heat treatment is carried out, is 800 to 900°C, the addition amount of Co is preferably in the range from 0.5 to 1.2 mass%, and when the temperature, at which the recrystallization heat treatment is carried out, is 900 to less than 980°C, the addition amount of Co is preferably in the range from 1.0 to 2.0 mass%. This is determined from the grain size of the copper alloy that will be defined below.

[0052] The reason for setting the grain size of the copper alloy of the matrix at 3 to 35 μ m and the preferable range of the grain size in the second embodiment of the present invention, are the same as those mentioned in the first embodiment of the present invention.

[0053] Further, in the second embodiment of the present invention, the electrical conductivity of the copper alloy material is $50\,\%$ IACS or more. In order to obtain this property, the addition amount of Co or Si is set in the range described above and the intermetallic compound of Co_2Si is precipitated. As a result, this property can be obtained. Additionally, in order to extract the highest electrical conductivity in this alloy system, it is preferable to conduct the aging heat treatment, which precipitates the precipitate, at a temperature from $500\,\text{to}\,600\,^\circ\text{C}$ for $1\,\text{to}\,4$ hours. The electrical conductivity is more preferably $55\,\%$ IACS or more, and even more preferably $60\,\%$ IACS or more, and it is preferable the electrical conductivity is as high as possible, but the upper limit is generally approximately $75\,\%$ IACS. In addition, in the second embodiment of the present invention, the tensile strength of the copper alloy material is defined to be $550\,\text{MPa}$ or more. The tensile strength is more preferably $600\,\text{MPa}$ or more, and even more preferably approximately $900\,\text{MPa}$.

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[0054] It is also possible to increase the electrical conductivity by controlling the cooling speed from the aging heat treatment temperature described above. A preferable condition is such that cooling is performed at a speed of 10 to 80 K/hour (herein, the term "K" indicates "Kelvin" which represents an absolute temperature; hereinafter, the same applies) until the temperature of the copper alloy material reaches 300°C after the aging heat treatment. When cooling is performed under the condition, the electrical conductivity is enhanced. In addition, after the cooling, the speed of cooling from 300°C to room temperature may be carried out by that of air cooling (spontaneous cooling).

[0055] In the copper alloy material of the second embodiment of the present invention, the particle size (average particle size) of the precipitate composed of Co and Si is adjusted to 5 to 50 nm for the same reasons as those mentioned for the first embodiment of the present invention. If the particle size of the precipitate is large, there is a risk that the solder adhesiveness may be deteriorated, but when the particle size is in the range from 5 to 50 nm, the solder adhesiveness is excellent. Preferably, the size of precipitate is 10 to 35 nm, more preferably 15 to 30 nm.

[0056] Hereinafter, preferable addition elements are mentioned. In the second embodiment of the present invention, when Sn, Mg and Zn are added, the properties can be enhanced due to solid solution strengthening. Therefore, in the second embodiment of the present invention, at least one kind of Sn, Mg and Zn (which may be any of the cases of individual elements, a combination of any two kinds of elements, and a combination of all three kinds of the elements) is added in an amount from 0.1 to 1.0 mass% in total. The reason is because when the total addition amount of at least one kind of these elements is 0.1 mass% or more, the effect due to the elements is noticeably exhibited, and when the total addition amount is 1.0 mass% or less, there is no adverse effect such as a decrease in electrical conductivity. Furthermore, the total addition amount of at least one kind of these elements is preferably 0.2 to 0.4 mass%. Sn and Mg have an effect of improving the stress relaxation resistance (creep resistance), and when both of them are added, the effect of improvement is high. In addition, Mg has an effect of improving hot workability, and Zn has a marked effect of suppressing a change over time in the solder adhesiveness (deterioration property).

Examples of the inevitable impurities in the copper alloy material of the second embodiment of the present invention include H, C, O, S, and the like which are the same as the inevitable impurities for the copper alloy material of the first embodiment.

[0057] In the second embodiment of the present invention, Fe, Cr and Ni are elements that contribute to enhance the mechanical strength by being replaced with Co to form a compound with Si, as in the first embodiment of the present invention. Preferable contents of these elements are also the same as those of the first embodiment of the present invention.

[0058] Furthermore, in the copper alloy material of the second embodiment of the present invention, the surface roughness (unevenness) is defined such that Ra is 0.2 μ m or less and Rt is 2 μ m or less. Thereby, the copper alloy material according to the second embodiment of the present invention is excellent in solder wettability, and as a result, the solder adhesive strength becomes good.

It is good that Ra and Rb are as small as possible, and preferably, Ra is 0.15 μm or less, while Rt is 1.5 or less, and more preferably Ra is 0.1 μm or less, while Rt is 1.0 or less. Ra and Rt are respectively measured based on JIS B 0601-2001.

[0059] Hereinafter, an example of the process of producing the copper alloy material of the second embodiment of the present invention is described.

<Melt-casting>

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[0060] A copper alloy ingot is obtained by melting copper, cobalt, silicon, and the like, which are the raw materials of the target copper alloy, pouring the resultant melt alloy into a mold, followed by casting under cooling at a cooling speed from 10 to 30 K/sec. The ingot has, for example, a size of 30 mm in thickness, 100 mm in width, and 150 mm in length.

10 <Hot rolling, face-milling, and cold rolling>

[0061] Then, this ingot is kept at a temperature from 930 to 1,050°C (preferably 950 to 1,050°C) for 30 minutes to 60 minutes, followed by working by hot rolling, and quenching by water cooling (rapid cooling) immediately, further followed by milling the rolled surface to remove an oxide layer on the surface, and cold rolling.

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<Recrystallization heat treatment>

[0062] Then, for the purpose of conducting solution and recrystallization, a recrystallization heat treatment is carried out for a certain time period in the salt bath (salt bath furnace) kept at a temperature of 800 to 1,025°C, followed by quenching by water cooling. During the recrystallization heat treatment, the heat treatment is carried out by adjusting the temperature raising speed by interposing the subject between stainless steel plates having different plate thicknesses. A preferable temperature raising speed in this occasion is 10 to 300 K/sec at a temperature of 300°C or higher. A preferable cooling speed is 30 to 200 K/sec.

25 <Aging heat treatment>

[0063] Then, for the purpose of performing aging precipitation, an aging heat treatment is carried out. The temperature raising speed from room temperature to the highest temperature in that occasion is in the range from 5 to 50 K/min. With regard to temperature lowering, cooling is carried out inside the furnace at a speed in the range from 1 to 10 K/minute until the temperature reaches 300°C, which is a temperature sufficiently lower than the temperature zone considered to affect the precipitation.

<Acid dissolving and grinding>

[0064] In the method for producing the copper alloy material according to the second embodiment of the present invention, the material surface is washed with acid before the final cold rolling to thereby dissolve and remove copper oxide and the like that are present on the material surface, and then the material surface after the acid washing is grinded. Preferable examples of the acid used in the acid dissolving include mixed dilutions of hydrochloric acid, nitric acid, phosphoric acid and hydrofluoric acid. There are no particular limitations to the method of surface grinding after the acid washing, and the surface grinding can be carried out according to a conventional method. For example, it is preferable to grind 0.2 to 2 mm of both surfaces of the material by means of mechanical means or the like.

<Finish rolling (according to the necessity)>

[0065] The copper alloy material that has been subjected to the acid dissolving and the following grinding is further subjected to a final cold rolling at a working ratio from 0 to 40%, and thus a finish rolled material is obtained. It is not necessarily required to carry out the finish rolling. Herein, the term "a working ratio of 0%" means that the finish rolling is not carried out.

50 <Strain-relieving annealing>

[0066] After completion of the aging heat treatment (in the case of conducting the finish rolling, after completion of the finish rolling), the copper alloy material is subjected to strain-relieving annealing, according to the necessity.

55 <With respect to repeating steps>

[0067] Each of the recrystallization heat treatment, the aging heat treatment and the cold rolling may be repeated two or more times under the conditions described above, respectively, and the sequence of conducting these steps may be

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[0068] Hereinafter, the preferable embodiment of the copper alloy material of the third embodiment of the present invention is explained in detail.

[0069] In the third embodiment of the present invention, the copper alloy material contains, as an essential additive element, Co (cobalt) in an amount of 0.7 to 2.0 mass%, and Si (silicon) in an amount in the range such that the mass ratio of Co to Si (Co/Si) is from 3 to 5 (preferably in the range from 0.1 to 0.5 mass%). Thereby, the copper alloy material has an electrical conductivity of 60 %IACS or more and a tensile strength of 570 MPa or more, and the requirements of high electrical conductivity and high mechanical strength can be satisfied at a particularly high level. In the third embodiment of the present invention, the electrical conductivity of the copper alloy material is set at 50 %IACS or higher. The electrical conductivity is more preferably 55 %IACS or more, and even more preferably 60 %IACS or more, and it is preferable that the electrical conductivity is as high as possible, but the upper limit is generally approximately 75 %IACS. In addition, in the third embodiment of the present invention, the tensile strength of the copper alloy material is defined to be 550 MPa or more. The tensile strength is more preferably 600 MPa or more, and even more preferably 750 MPa or more, and it is preferable the tensile strength is as high as possible, but the upper limit is generally approximately 900 MPa.

[0070] When the arithmetic mean of the grain size of the copper alloy of the matrix is 3 to 20 μ m and the standard deviation is 8 μ m or less, it is useful for further enhancement of bending property. Here, it is preferable that the standard deviation is as small as possible, and it is more preferable that the standard deviation of the grain size have a smaller value than that of the arithmetic mean of the grain size. When the arithmetic mean and standard deviation of the grain size of the copper alloy of the matrix are in the ranges mentioned above, the bending stress (loaded strain) can be sufficiently dispersed. In the case of further enhancing bending property, it is preferable that the value, obtained by subtracting the standard deviation from the arithmetic mean of the grain size of the copper alloy of the matrix, is more than 0 μ m, and it is more preferable that the value, obtained by dividing the standard deviation by the arithmetic mean, is 0.65 or less, and furthermore preferably 0.4 or less. In addition, it is practical that the lower limit of the value, obtained by dividing the standard deviation by the arithmetic mean, is 0.2 or more, and if the value is smaller than this value, the properties are enhanced, but there is a tendency that the actual production become difficult. Herein, it is preferable to set the measurement parameter, used for determining the arithmetic mean and standard deviation of the grain size of the copper alloy of the matrix, at 100 or more, and it is more preferable to set the measurement parameters of the arithmetic mean and standard deviation to be of the same value.

[0071] In regard to the bending property, when the tensile strength is 570 MPa to 650 MPa, the value of R/t is preferably 0.5 or less; when the tensile strength is more than 650 MPa to 700 MPa, the value of R/t is preferably 1.0 or less; and when the tensile strength is more than 700 MPa, the value of R/t is preferably 1.5 or less. Herein, the term "R/t" means a result obtained by conducting a W bending test at a bending angle of 90° according to the "Standard test method of bend formability for sheets and strips of copper and copper alloys (JBMA T307)" of the Japan Copper and Brass Association Technical Standards and means a value obtained by subjecting a sheet material cut out in a direction perpendicular to rolling, to a bending test under the condition of a predetermined bending radius (R), determining the R value of the limit at which any crack (breakage) does not occur at the top, and normalizing the value by the sheet thickness (t). In general, a smaller value of R/t gives more satisfactory bending property. In the copper alloy material for electric/ electronic parts of the present invention, it is preferable that the tensile strength and bending property (R/t) have the relationship described above. Furthermore, the lower limit of the bending property (R/t) is 0.

[0072] Hereinafter, additive elements other than Co and Si are described.

Fe, Cr and Ni are elements that contribute to enhance the mechanical strength by being replaced with Co and forming a compound with Si. Fe, Ni and Cr have a function of forming a $(Co, \chi)_2Si$ compound $(\chi = Fe, Ni, Cr)$ to enhance the mechanical strength, by being replaced with a part of Co. The addition amount of at least one kind of these elements (which may be any of the cases of individual elements, a combination of any two kinds of the elements, and a combination of all three kinds of the elements) is adjusted to the range from 0.01 to 1.0 mass% in total. When the addition amount is 0.01 mass% or more, the effect due to the elements is noticeably exhibited, and when the addition amount is 1.0 mass% or less in total, there is no chance of causing crystallization during casting or forming an intermetallic compound that does not contribute to mechanical strength, and there is no adverse effect such as a decrease in electrical conductivity. Furthermore, these elements provide almost the same effect even if the elements are added in combination or added individually; however, when Ni is added, a remarkable effect of enhancing the mechanical strength is exhibited. The addition amount of Fe, Ni and Cr is preferably such that the addition amount of at least one kind of the elements is 0.05

[0073] Furthermore, Zr or Ti also provides almost the same effects as Fe, Ni and Cr, but Zr or Ti is prone to be oxidized, and when added in a large amount, crack may occur in a material during the production. Thus, in regard to the addition amount of Zr and Ti, it is preferable to set the addition amount of at least one kind of these elements in the range from 0.01 to 0.1 mass% in total.

[0074] Sn, Zn, Mg and Mn have a feature of being solid-dissolved in the copper matrix and strengthening the copper

alloy material. When the addition amount of at least one kind of these elements is 0.01 mass% or more in total, the effect due to these elements is exhibited, and when the addition amount is 1.0 mass% or less, the electrical conductivity is not decreased. A preferred addition amount is 0.05 to 0.2 mass% for at least one kind of these elements.

Examples of the inevitable impurities in the copper alloy material of the third embodiment of the present invention include H, C, O, S, and the like which are the same as the inevitable impurities for the copper alloy material of the first or second embodiment.

[0075] Zn also has an effect of enhancing solder adhesiveness, and Mn also has an effect of improving hot workability. Furthermore, the addition of Sn and Mg is effective in an improvement of the stress relaxation resistance. The same effect can also be obtained by adding Sn and Mg individually, but when the elements are added simultaneously, these elements exhibit the effect synergistically. When the addition amount of at least one kind of these elements is 0.1 mass% or more in total, the effect due to the element is exhibited. When the addition amount is 1.0 mass% or less, the electrical conductivity of the copper alloy material is not decreased, and an electrical conductivity of 50 %IACS or more is secured. On the other hand, in regard to the addition ratio of Sn and Mg, where Sn/Mg \geq 1, the stress relaxation resistance is further enhanced.

[0076] Hereinafter, an example of the process of producing the copper alloy material of the third embodiment of the present invention is described.

<Melt-casting>

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20 [0077] A copper alloy ingot is obtained by melting copper, cobalt, silicon, and the like, which are the raw materials of the target copper alloy, pouring the resultant melt alloy into a mold, followed working by casting under cooling at a cooling speed from 10 to 30 K/sec (herein, the term "K" indicates "Kelvin" which represents an absolute temperature; hereinafter, the same applies), to obtain the ingot having a size of 160 mm in width, 30 mm in thickness, and 180 mm in length.

25 <Hot rolling, face-milling, and cold rolling>

[0078] Then, the thus-obtained ingot is kept at a temperature of 900 to 1,000°C for 30 minutes to 60 minutes, followed by working by hot rolling to be a thickness 12 mm, and quenching by water cooling (rapid cooling) immediately, further, in order to remove an oxide layer on the surface, followed by face-milling to reduce approximately 1 mm of the rolled surfaces to be a thickness approximately 10 mm and cold rolling to be a thickness approximately 0.1 to 0.3 mm.

<Recrystallization heat treatment>

[0079] Then, for the purpose of conducting solution and recrystallization, a recrystallization heat treatment is carried out for a certain time period (30 seconds, in this case) in the salt bath (salt bath furnace) kept at a temperature of 800 to 1,025°C, followed by quenching by water cooling. During the recrystallization heat treatment, the heat treatment is carried out by adjusting the temperature raising speed by interposing the subject between stainless steel plates having different plate thicknesses. A preferable temperature raising speed in this occasion is 10 to 300 K/sec at a temperature of 300°C or higher. A preferable cooling speed is 30 to 200 K/sec.

<Aging heat treatment>

[0080] Then, for the purpose of performing aging precipitation, an aging heat treatment is carried out at a temperature of 525°C for 120 minutes. The temperature raising speed from room temperature to the highest temperature in that occasion is in the range from 3 to 25 K/min. With regard to temperature lowering, cooling is carried out inside the furnace at a speed in the range from 1 to 2 K/minute until the temperature reaches 300°C, which is a temperature sufficiently lower than the temperature zone considered to affect the precipitation.

<Finish rolling (according to the necessity)>

[0081] The copper alloy material that has been subjected to the aging heat treatment is further subjected to a final cold rolling at a working ratio from 0 to 40% (the upper limit is preferably 20%), and thus a finish rolled material is obtained. It is not necessarily required to carry out the finish rolling. Herein, the term "a working ratio of 0%" means that the finish rolling is not carried out.

<Strain-relieving annealing>

[0082] After completion of the aging heat treatment (in the case of conducting the finish rolling, after completion of the

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finish rolling), the copper alloy material is subjected to strain-relieving annealing, according to the necessity.

<With respect to repeating steps>

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5 **[0083]** Each of the recrystallization heat treatment and the aging heat treatment may be repeated two or more times under the conditions described above.

[0084] Basically, the grain size of grains and the distribution thereof (standard deviation) are determined based on the recrystallization heat treatment and aging heat treatment. In order to change the grain size of grains and the distribution thereof, it is effective to control the temperature raising speed, the temperature at which the subject is kept during heat treatment, and cooling speed, in the recrystallization heat treatment and aging heat treatment.

[0085] Furthermore, since the temperature raising speed, the temperature at which the subject is kept during heat treatment, and the cooling speed are also related to the addition amount of Co and Si, which are essential additive elements in the copper alloy material of the third embodiment of the present invention, the grain size of the grains and the distribution thereof can also be changed by adjusting the addition amount of Co and Si. Furthermore, when elements other than Cu, Co and Si are added, the precipitate other than the grains can be dispersed within the copper alloy, and thereby the grain size of the grains and the distribution thereof can be changed.

[0086] In order to satisfy all of high electrical conductivity, high mechanical strength and good bending property, it is required of the copper alloy material of the third embodiment of the present invention to have an arithmetic mean of the grain size from 3 μ m to 20 μ m, and to have a standard deviation of 8 μ m or less. It is preferable that the standard deviation is as small as possible, and it is more preferable that the standard deviation of the grain size have a smaller value than that of the arithmetic mean of the grain size. When the arithmetic mean and standard deviation of the grain size of the copper alloy of the matrix fall in the range mentioned above, the bending stress (loaded strain) can be sufficiently dispersed.

Thus, the additive elements or production conditions (particularly, the conditions for recrystallization heat treatment and aging heat treatment) are appropriately adjusted so as to satisfy the conditions of the arithmetic mean and standard deviation of the grain size. Particularly, when the arithmetic mean of the grain size is less than 3 μ m, unrecrystallized regions remain, which are directly related to the deterioration of bending property. Thus, it is preferable that the standard deviation of the grain size has a smaller value than that of the arithmetic mean of the grain size, and it is more preferable that the standard deviation is 3 μ m or more.

In the case of further enhancing bending property, it is preferable that the value, obtained by subtracting the standard deviation from the arithmetic mean of the grain size of the copper alloy of the matrix, is more than 0 μm, and it is more preferable that the value, obtained by dividing the standard deviation by the arithmetic mean, is 0.65 or less, and furthermore preferably 0.4 or less. In addition, it is realistic in practical production that the lower limit of the value, obtained by dividing the standard deviation by the arithmetic mean, is 0.2 or more.

[0087] Herein, the temperature raising speed in the recrystallization heat treatment will be explained.

If the temperature raising speed is too slow, the heating treatment is overdone, and coarsening of the precipitate or crystallized product occurs, and there is a risk of causing a decrease in mechanical strength. Furthermore, there is a risk that coarsening of grains due to overheating may occur. On the other hand, if the temperature raising speed is too fast, the production yield of the precipitate that prevents the coarsening of grains is decreased, and thus there is a risk that the coarsening of grains may occur. For this reason, a preferable temperature raising speed is as described above. [0088] Furthermore, in regard to the recrystallization heat treatment temperature, it is also effective to adjust the temperature by the addition amount of Co. When the addition amount of Co is less than 1 mass%, it is preferable to set the temperature at which the subject is kept during the recrystallization heat treatment at a temperature from 850°C to lower than 900°C, and when the addition amount of Co is 1 mass% or more, it is preferable to set the temperature at which the subject is kept during the recrystallization heat treatment at a temperature from 900°C to lower than 1,000°C. It is because when the temperature at which the subject is kept during the recrystallization heat treatment is lower than this range, a risk, that mechanical strength may be insufficient, becomes high, and when the temperature at which the subject is kept during the recrystallization of bending property may be occur due to the coarsening of grains, but also deformation of the copper alloy material may occur.

50 [0089] Other preferable embodiments of the present invention are described below.

(B1) A copper alloy material for an electric/electronic part, having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities,

wherein a copper alloy of a matrix has a grain size of 3 to 35 μm,

wherein a precipitate composed of Co and Si has a particle size of 5 to 50 nm,

wherein a surface roughness as the copper alloy material is such that Ra is 0.2 μm or less and Rt is 2 μm or less, and wherein the copper alloy material has a tensile strength of 550 MPa or more and an electrical conductivity of 50 %IACS or more. (B2) A method of producing a copper alloy material for an electric/electronic part, comprising the steps of:

subjecting a copper alloy material having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities, to acid-dissolving the surface of the material; grinding the acid-dissolved surface; and

a final cold rolling,

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whereby a copper alloy material is obtained, in which a copper alloy of a matrix has a grain size of 3 to 35 μ m, a precipitate composed of Co and Si has a particle size of 5 to 50 nm, and the copper alloy material has a surface roughness of 0.2 μ m or less in Ra and 2 μ m or less in Rt, and a tensile strength of 550 MPa or more, and an electrical conductivity of 50 %IACS or more

 10 (C3) A copper alloy material, wherein the Co content is 0.7 to 2.5 mass% (the upper limit is preferably 2.0 mass%), the mass ratio of Co to Si (Co/Si) is 3 to 5, an arithmetic mean of a grain size of the copper alloy of a matrix is 3 to 20 μm, a standard deviation is 8 μm or less, and a standard deviation is smaller than the arithmetic mean.

Embodiments of (B1) and (B2) are all the same as the second embodiment of the present invention in terms of, for example, the alloy composition, additive elements, states of grains and precipitate, surface roughness, and production method of the copper alloy material (production steps, production conditions, and the like), as well as their specific examples or preferred ranges, except for the constituent elements that are different from the constituent elements of the second embodiment. Furthermore, the embodiments of (B1) and (B2) provide the same effects as the second embodiment of the present invention.

Embodiment of (C3) is all the same as the third embodiment of the present invention in terms of, for example, the alloy composition, additive elements, states of grains and precipitate, and production method of the copper alloy material (various production steps, production conditions, and the like), as well as their specific examples or preferred ranges, except for the constituent elements that are different from the constituent elements of the third embodiment. Furthermore, the embodiment of (C3) provides the same effects as the third embodiment of the present invention.

25 EXAMPLES

[0090] 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.

30 (Example 1)

[0091] Alloys (1a to 36a and 1b to 24b) containing the components shown in Tables 1 and 2, with the balance composed of Cu and inevitable impurities, were melted with a high-frequency melting furnace, followed by casting at a cooling speed from 10 to 30 K/sec, to obtain ingots with thickness 30 mm, width 100 mm, and length 150 mm, respectively.

The thus-obtained ingots were kept at a temperature from 930 to 970°C for 0.5 to 1.0 hour, followed by hot rolling to produce hot rolled sheets with a sheet thickness t = 12 mm. After the hot rolling, both surfaces of the sheets were face-milled to reduce a thickness of 1 mm, respectively, to be a sheet thickness t = 10 mm, and then the sheets were finished to have a sheet thickness t = 0.3 mm by cold rolling. After the cold rolling, the sheets were subjected to a recrystallization heat treatment at a temperature from 700°C to 1,025°C. The thus-prepared materials were subjected to any one of the following two processes, to produce final products.

Process A: recrystallization heat treatment - aging heat treatment (at a temperature from 500 to 600°C for 1 to 4 hours) - cold working (5 to 25%)

*Then, according to the necessity, strain-relieving annealing was conducted at a temperature from 300 to 400°C for 1 to 2 hours.

Process B: recrystallization heat treatment - cold rolling (working ratio: 5 to 25%) - aging heat treatment (at a temperature from 450 to 550°C for 1 to 4 hours)

[0092] In the following Tables, the working ratios mentioned in the processes A and B are shown.

[0093] With respect to the test materials, investigations of the following properties were conducted.

a. Tensile strength

[0094] Tensile strengths of 3 test pieces prepared according to JIS Z 2201-13B cut out from the test material in a direction parallel to the rolling direction, were measured according to JIS Z 2241, and an average value thereof is shown.

b. Measurement of electrical conductivity

[0095] The electrical conductivity of two of each test pieces, respectively, was measured in a thermostatic tank controlled at 20° C ($\pm 1^{\circ}$ C) by using a four-terminal method, and its average value (%IACS) is shown in Tables 1 to 2. The

distance between the terminals was set to 100 mm.

c. Bending property

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[0096] A test piece was cut out from the test material in a direction perpendicular to the rolling direction into a size of width 10 mm and length 35 mm. The resultant test piece was W-bent (Bad-way bent) at 90° at six levels of a bending radius R which was 0 to 0.5 (mm), with a bending axis being parallel to the rolling direction. Whether cracks were occurred or not at the bent portion, was observed with the naked eye through observation with an optical microscope of 50 times magnification, and the bent sites were observed with a scanning electron microscope to examine whether cracks were observed or not. In R/t in Table 1, R represents the bending radius, and t represents the sheet thickness. A smaller value of this ratio represents a better bending property. Herein, a copper alloy material having a value of R/t of 2.5 or less is regarded as a copper alloy material having a good bending property. Preferably, the value of R/t is 2 or less.

d. Grain size

[0097] A cross-section perpendicular to the rolling direction of the test material (test piece) was finished into a mirror surface by wet polishing and buff polishing; the thus-polished surface was corroded with a liquid of chromic acid: water = 1:1 for several seconds; and then, a photograph of the resultant polished surface was taken with an optical microscope of 200 to 400 times magnification or using a secondary electronic image of the scanning electron microscope (SEM) at a magnification ratio of 500 to 2,000 times; to measure a grain size on the cross-section, according to the cutting method of JIS-H-0501 (methods for estimating average grain size of wrought copper and copper alloys). The magnification of the photographs was varied with the size of the grains observed. In addition, the term "mixed grain" means a texture, in which both recrystallized portion and unrecrystallized portion (rolling work residue) are present in mixture, and in the case of mixed grain, the particle size was not measured. It is said that if the unrecrystallized portion is present, bending property is deteriorated. Thus, the mixed grain is an undesirable texture.

e. Cooling speed after aging heat treatment

[0098] The cooling speed, during the period of cooling from the temperature at the time of aging heat treatment to 300°C, was adjusted by controlling the temperature at the heating furnace. In the case of conducting rapid cooling, the subject was taken out from the heating zone of the heating furnace and was subjected to forced air cooling or water quenching.

f. Size and density of precipitate

[0099] The size of the precipitate was evaluated by using a transmission electron microscope (TEM). Since it is difficult to observe the precipitate in the final product under the influence of strain due to work, an observation of the texture of the material after the aging heat treatment was carried out. A test piece for TEM was cut out from any site of the heat treated material, and electro-polishing (by a twin jet electro-polishing apparatus) was carried out at a temperature in the range of -20 to -25°C by using a methanol solution of nitric acid (20%), to obtain a test piece for observation.

[0100] Then, an observation was conducted at an accelerating voltage of 300 kV, the incidence direction of an electron beam was adjusted in the vicinity of (001), and 3 sheets of photographs were arbitrarily taken at a magnification of 100,000 times. An average size of the precipitates (the number of precipitates is approximately 100) and the number were determined using the photographs.

g. Stress relaxation resistance (stress relaxation ratio)

[0101] In regard to the stress relaxation ratio (SRR), each test material was subjected to a stress of 80% with 0.2% proof strength for 1,000 hours at a temperature of 150°C according to JIS Z2241 by the cantilever method based on the Japan Copper and Brass Association Technical Standards "JCBA T309:2001 (provisional)", the permanent deflection displacement after a lapse of time with respect to the initial deflection displacement was measured in three test materials, and the proportion (%) of the permanent deflection displacement after a lapse of time with respect to the initial deflection displacement of each of the test materials was determined and the average value of the proportions was calculated as the stress relaxation ratio.

{Table 1}

[0102]

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Table 1

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No.	Со	Si	Other element	Temp.*1	Speed *2	Process	Temp.*3	Time*4	GS*5	Size*6	Density*7	Ratio*9	TS*10	EC*11	SRR*13	BP*14
		(mas	s%)	(°C)	(°C/h)		(°C)	(h)	(µm)	(nm)	(num.)*8	(%)	(MPa)	(%)*12	(%)	R/t
1a	0.5	0.14		800	25	Α	525	2	20	22	3×10 ⁸	15	652	68	38	0.5
2a	0.9	0.25		825	30	Α	550	3	18	29	7×10 ⁸	10	726	69	35	1.25
3a	1.2	0.30		925	25	В	525	2	20	28	2×10 ⁹	15	715	58	33	1.25
4a	1.8	0.45		945	40	Α	550	2	12	19	6×10 ⁹	15	735	53	29	2
5a	0.7	0.17	Sn=0.13, Mg=0.1	825	80	А	550	3	10	31	4×10 ⁸	20	655	73	16	0.75
6a	0.9	0.22	Sn=0.15	830	95	А	575	2	22	33	2×10 ⁹	20	665	64	30	1
7a	0.9	0.22	511-0.15	030	95	В	525	2	22	22	1×10 ⁹	10	645	61	28	1
8a	1.1	0.28	Mg=0.08	940	25	Α	550	3	19	25	9×10 ⁸	15	671	60	20	1
9a	1	0.20	ivig=0.06	940	25	В	500	2	19	28	3×10 ⁹	5	671	60	17	1
10a	1.5	0.38	Mn=0.05	1000	40	Α	575	2	28	32	7×10 ⁹	20	720	62	25	2
11a	1.9	0.48	Zn=0.2 Sn = 0.1	1000	35	В	525	2	14	27	9×10 ⁹	25	752	52	22	2
12a	0.9	0.22	Fe=0.2	850	50	А	575	3	13	25	2×10 ⁹	20	655	73	28	1
13a	0.9	0.23	Cr=0.15	880	70	Α	575	2	15	30	3×10 ⁹	10	664	62	29	0.5
14a	0.8	0.23	01-0.10	000	70	В	525	2	13	32	5×10 ⁹	5	685	60	28	0.5
15a	1.1	0.28	Ni=0.3	920	60	Α	575	3	11	19	8×10 ⁸	10	721	63	32	2
16a	1.1	0.20	INI-U.3	320	00	В	525	3		24	1×10 ⁹	5	726	58	33	2
17a	1.4	0.35	Sn=0.15,	940	30	Α	575	2	8	25	7×10 ⁹	10	707	62	15	2

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No.	Со	Si	Other element	Temp.*1	Speed *2	Process	Temp.*3	Time*4	GS*5	Size*6	Density*7	Ratio*9	TS*10	EC*11	SRR*13	BP*14
		(mas	s%)	(°C)	(°C/h)		(°C)	(h)	(µm)	(nm)	(num.)*8	(%)	(MPa)	(%)*12	(%)	R/t
18a	1.7	0.43	Cr=0.2, Ni=0.2	945	60	Α	550	4	10	33	7×10 ⁹	25	747	52	28	2
19a	0.6	0.15	Zn=0.3,	800	50	Α	550	2	9	38	3×10 ⁸	15	603	72	37	0.5
20a	0.6	0.15	Cr=0.1	000	50	В	500	2	9	28	1×10 ⁸	10	601	74	39	0.5
21	0.9	0.23	Sn=0.15, Fe=0.2	825	70	В	475	3	12	23	5×10 ⁸	10	611	62	22	1
22a						Α	550	1		33	8×10 ⁸	15	620	62	24	0.5
23a	0.8	0.20	Mg = 0.1, Ni=0.25	800	80	Α	550	3	13	26	7×10 ⁸	15	627	72	24	0.5
24a						В	500	1		21	3×10 ⁹	10	627	61	22	0.5
25a			000			Α	525	2		26	4×10 ⁸	20	616	65	26	0.5
26a	0.7	0.18	Sn=0.2, Fe=0.3	800	90	Α	323	4	20	24	3×10 ⁸	15	614	67	28	0.25
27a						В	475	2		35	1×10 ⁹	10	615	70	25	0.5
28a		0.00	Sn=0.1,	000	50	Α	550	2	4.4	35	2×10 ⁸	20	628	71	32	0.5
29a	0.8	0.20	Zn=0.5, Cr=0.1	820	50	В	500	2	14	29	2×10 ⁹	15	621	65	28	0.5
30a	0.7	0.18	Mg=0.1, Ni=0.25, Cr=0.3	810	30	Α	550	2	10	17	8×10 ⁸	25	612	62	35	0.75
31a	1.6	0.42	Zn=0.05	940	50	Α	575	2	22	28	2×10 ⁹	20	698	55	34	1
32a	1.9	0.50	Zn=0.02,	1000	40	В	525	2	29	22	6×10 ⁹	25	745	53	38	1
33a	1.5	0.37	Cr=0.04	940	30	Α	575	2	19	23	9×10 ⁸	10	684	52	23	1
34a	1.3	0.30	Cr=0.02 Ni=0.03	945	30	Α	550	3	19	19	4×10 ⁹	25	654	61	32	1

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No.	Со	Si	Other element	Temp.*1	Speed *2	Process	Temp.*3	Time*4	GS*5	Size*6	Density*7	Ratio*9	TS*10	EC*11	SRR*13	BP*14
		(mas	s%)	(°C)	(°C/h)		(°C)	(h)	(µm)	(nm)	(num.)*8	(%)	(MPa)	(%)*12	(%)	R/t
35a	0.7	0.15	Zn=0.03,	800	40	Α	550	2	12	17	8×10 ⁸	15	671	65	29	1
36a	0.7	0.13	Cr=0.03	800	40	В	500	2	12	19	2×10 ⁸	10	609	68	33	0.5

*1: Temperature of recrystalization heat treatment

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*2: Cooling speed

- *3: Temperature of aging heat treatment
- *4: Time of aging heat treatment
- *5: Grain size
- *6: Size of precipitate
- *7: Density of precipitate
- *8: Number/mm²
- *9: Working ratio
- *10: Tensile strength
- *11: Electrical conductivity
- *12: (%IACS)
- *13: Stress relaxation ratio
- *14: Bending property

{Table 2}

[0103]

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Table 2

No.	Со	Si	Other Element	Temp.*1	Speed*2	Process	Temp.*3	Time*4	GS*5	Size*6	Density*7	Ratio*9	TS*10	EC*11	SRR*13	BP*14
		(mass	s%)	(°C)	(°C/h)		(°C)	(h)	(μm)	(nm)	(num.)*8	(%)	(MPa)	(%)*12	(%)	R/t
1b	0.35	0.08		750	80	Α	525	2	22	28	2×10 ⁸	15	485	77	45	0.5
2b	2.2	0.50		825	40	Α	550	2	25	29	6×10 ⁸	10	715	43	38	3
3b	2.5	0.80		1040	80	Α	550	2	18	32	2×10 ¹⁰	10	723	55	39	3
4b	1	0.20		720	60	В	525	3	mixed grain	28	2×10 ⁹	10	723	64	34	3
5b	0.9	0.25		880	10	Α	575	3	34	55	3×10 ⁸	15	622	62	36	3
6b	1	0.22		900	15	В	500	2	36	65	3×10 ⁹	10	625	66	34	3
7b	0.8	0.23		890	80	Α	400	2	22	2	2×10 ⁹	5	459	43	32	1.5
8b	0.9	0.20		900	30	Α	610	3	29	75	4×10 ⁸	10	488	75	34	1.5
9b	1.1	0.28		900	40	В	500	0.5	22	3	5×10 ⁹	15	481	41	34	1.5
10b	0.85	0.21		890	60	А	575	0.5	29	2	7×10 ⁹	15	481	49	38	1.5
11b	0.9	0.20		900	50	В	525	6	27	50	9×10 ⁹	10	482	49	32	1.5
12b	0.85	0.21		900	40	А	575	5	28	50	1×10 ⁹	5	478	42	34	1
13b	0.5	0.13	Zn=2	760	70	Α	550	3	22	22	2×10 ⁹	20	622	47	32	0.5
14b	0.85	0.22	Cn=1 F	830	20	Α	575	3	- 29	18	6×10 ⁹	20	714	38	32	1
15b	0.65	0.22	Sn=1.5	630	30	В	525	2	29	23	5×10 ⁸	10	612	42	21	1
16b	0.5	0.15	Fe=2.2	730	60	А	575	3	mixed grain	24	8×10 ⁹	20	647	68	32	3
17b	0.9	0.23	Cr=1.7	880	75	А	575	2	mixed 32		2×10 ⁸	10	706	51	29	3
18b						В	525	1	grain	32	2×10 ⁸	5	622	62	31	3

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No.	Со	Si	Other Element	Temp.*1	Speed*2	Process	Temp.*3	Time*4	GS*5	Size*6	Density*7	Ratio*9	TS*10	EC*11	SRR*13	BP*14
		(mas	s%)	(°C)	(°C/h)		(°C)	(h)	(µm)	(nm)	(num.)*8	(%)	(MPa)	(%)*12	(%)	R/t
19b	1.2	0.28	Ni=2.5	900	25	Α	575	3	27	32	6×10 ⁸	15	714	43	29	2
20b	1.2	0.20	141-2.5	900	23	В	525	3	21	29	9×10 ⁸	10	614	42	27	2
21b			Sn = 0.2	850	>100	Α	550	2	17	32	7×10 ⁸	10	601	55	28	0.5
22b	0.9	0.2	Sn=0.15, Mg=0.1	875	>100	В	500	2	19	31	8×10 ⁸	10	603	53	30	0.5
23b	1.3	0.3	Sn=0.1	925	>100	Α	550	2	19	30	2×10 ⁹	5	701	51	26	3
24b	1.3	0.3	Mg = 0.2	950	>100	В	500	2	25	28	3×10 ⁹	10	703	52	29	3

^{*1:} Temperature of recrystalization heat treatment

^{*2:} Cooling speed

^{*3:} Temperature of aging heat treatment

^{*4:} Time of aging heat treatment

^{*5:} Grain size

^{*6:} Size of precipitate

^{*7:} Density of precipitate

^{*8:} Number/mm²

^{*9:} Working ratio

^{*10:} Tensile strength

^{*11:} Electrical conductivity

^{*12: (%}IACS)

^{*13:} Stress relaxation ratio

^{*14:} Bending property

[0104] Examples are shown in Table 1 and Table 2, respectively. In Table 2, italic letters represent the number or the like outside the range defined in the first embodiment of the present invention. Examples 21 to 24 in Table 2 are reference examples related to the cooling speed, and the test materials were subjected to forced air cooling immediately after the completion of aging heat treatment. The examples in Table 1 satisfied all of mechanical strength, electrical conductivity, solder wettability, solder adhesive strength and bending property with a proper balance. On the contrary, in the examples shown in Table 2, at least one of the properties among mechanical strength, electrical conductivity, solder wettability, solder adhesive strength and bending property was not practical. In Examples 21 to 24 for the production method in Table 2, a tendency of having decreased electrical conductivity was observed, as compared with those examples in which the addition amount of Co or tensile strength is almost the same as that of each of the examples shown in Table 1.

(Example 2)

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[0105] Copper alloy base material containing the components shown in Tables 3 and 4, with the balance composed of Cu and inevitable impurities, were melted with the high-frequency melting furnace, followed by cooling at a cooling speed from 10 to 30 K/sec, to obtain ingots with thickness 30 mm, width 100 mm, and length 150 mm, respectively. In Cu alloy to which Si is added, there are many known literatures, in which O (oxygen) content in a raw material or a material is restricted. However, when an element having higher oxidation property than Cu is added, if O is present, such the element oxidizes earlier than Cu, and therefore, the yield ratio of Si, which is an additive element, is not stabilized. Therefore, restricting the O concentration in the raw material or the material is a technique well-known to the person ordinary skilled in the art, in the case of adding an element having stronger oxidation property than Cu. Similarly, there are many known literatures, in which H (hydrogen) in addition O are defined. However, H and O are, in many cases, attached to the surface layer of the raw material in the form of moisture, and if a pretreatment to remove O is carried out, H can also be removed. In addition, if the H concentration is high, a lot of gas bubbles are generated inside of ingot during the production of the ingot, and satisfactory sheet materials cannot be obtained. Therefore, reducing the H concentration is one of the techniques well known to the person ordinary skilled in the art in connection with the production of copper alloys.

The thus-obtained ingots were kept at a temperature from 930 to $1,050^{\circ}$ C for 0.5 to 1.0 hour, followed by hot rolling to produce hot rolled sheets having a sheet thickness t = 12 mm. After the hot rolling, both surfaces of the sheets were face-milled to reduce a thickness of 1 mm, respectively to be a sheet thickness t = 10 mm, and then the sheets were finished to have a sheet thickness t = 0.3 mm by cold rolling. After the cold rolling, the sheets were subjected to a recrystallization heat treatment at a temperature from 700° C to $1,025^{\circ}$ C. The materials after the recrystallization heat treatment were subjected to the following process, and thus test materials which were in the form of final products were produced.

Process: recrystallization heat treatment - aging heat treatment (at a temperature from 500 to 600°C for 1 to 4 hours) - acid-washing of surface/grinding - cold working (working ratio: 5 to 25%)

*Then, according to the necessity, strain-relieving annealing was conducted at a temperature from 300 to 400°C for 1 to 2 hours.

In the following Table, the working ratio mentioned in the process is shown.

Further, between the recrystallization heat treatment and aging heat treatment, a process, including an additional cold rolling having a working ratio from 5 to 25%, was conducted.

The step of acid-washing of surface was carried out by a conventional method.

[0106] With respect to the test materials, investigations of the following properties were conducted.

a. tensile strength, b. measurement of electrical conductivity, c. bending property, and d. grain size were measured in the same manner as Example 1.

In regard to bending property in the Example 2, a copper alloy material having a value of R/t of 2.5 or less is defined as a copper alloy material having good bending property. Preferably, a value of R/t is 2 or less.

e2. Particle size of precipitate

[0107] The particle size of the precipitate was evaluated by using the transmission electron microscope (TEM). Since the final product is affected by strain due to work, an observation of the texture of the material after the aging heat treatment was carried out. A test piece for TEM was cut out from any site of the heat treated material, and electropolishing (by a twin jet electro-polishing apparatus) was carried out at a temperature in the range of -20 to -25°C by using a methanol solution of nitric acid (20%), to obtain a test piece for observation.

Then, an observation was conducted at an accelerating voltage of 300 kV, the incidence direction of an electron beam was adjusted in the vicinity of (001), and 3 sheets of photographs were arbitrarily taken at a magnification of 100,000 times. An average particle size of the precipitates (the number of precipitates is approximately 100) were determined

using the photographs.

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f2. Solder wetting test (meniscograph)

[0108] It is based on JIS C 600068-2-54.

The size of a test piece was 10x25 mm, and the 10-mm width side of the test piece was immersed into a prepared solder bath of Pb-free solder (Sn-3.0Ag-0.5Cu). The condition in this case was such that a test of immersing the test piece down to 10 mm at an immersion speed of 10 mm/sec was carried out using a rosin-based R100-40 as a flux. The temperature of the solder bath was controlled to 245° C ($\pm 2^{\circ}$ C). The test was carried out with a test material number of n=5, and the wetting time and wetting load were measured, while the evaluation was made on the basis of the wetting time. In this case, the test material having a wetting time of 2 seconds or less was rated as "good (o)"; the test material having a wetting time of 3 seconds or less as "acceptable (Δ)"; and the test material having a wetting time of longer than 3 seconds as "poor (x). The average time for n=5 was evaluated.

g2. Evaluation of solder adhesive strength

[0109] The evaluation of the solder adhesive strength was carried out by the following method. Pb-free solder (Sn-3.0Ag-0.5Cu) was used as the solder kind, and a material was subjected in advance to electrolytic degreasing and washing with a 10% sulfuric acid solution for approximately one minute, followed by sufficient drying. Thereafter, the material was cut to a size of 25 mm \times 25 mm, and the solder with ϕ 6 mm was placed on one of the surfaces of the copper alloy material used as the test piece using an instrument for exclusive use, to thereby fix an EF line (a steel wire coated with pure copper: copper-coated steel wire) with ϕ 1 mm. This state is shown in Fig. 1. In Fig. 1, reference numeral 1 represents an EF line, reference numeral 2 represents solder, and reference numeral 3 represents a test piece.

[0110] Subsequently, the EF line was grabbed, and a tensile test was carried out to measure the mechanical strength at which the solder was peeled off from the material. The speed of the tensile test in that case was 10 mm/minute, and the test was carried out with a test material number of n=5. Thus, an average value was determined.

[0111] On the other hand, in regard to the changes over time, the material, having the EF line fixed thereon, was left to stand for 500 hours in an atmospheric high temperature bath at 150°C to simulate an acceleration test, and then the material was spontaneously cooled to room temperature. After cooling, the tensile test was carried out 5 times as described above, and an average value was determined. The change over time in the peeling strength was determined by the following formula (1).

[0112]

Formula (1):

Ratio of change over time = (Peeling strength after 500 hours/initial peeling strength) \times 100 (%).

[0113] In the formula (1), ratio of change over time $\geq 50\%$ was rated as "excellent (oo)"; ratio of change over time $\geq 30\%$ was rated as "good (o)"; ratio of change over time $\geq 10\%$ was rated as "acceptable (Δ)"; and ratio of change over time of < 10% was rated as "poor (x)".

45 {Table 3}

[0114]

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Table 3

No.	Со	Si	Other element	Temp.*1	Temp.*2	Time*3	GS4*4	Size*5	Density*6	Ra	Rt	SW*8	SAS*9	Ratio*10	TS*11	EC*12	BP*14
		(mass	5%)	(°C)	(°C)	(h)	(μm)	(nm)	(num.)* ⁷	(μm)	(µm)			(%)	(MPa)	(%)*13	R/t
1c	0.6	0.15		850	550	2	20	22	4×10 ⁸	0.12	1.15	0	Δ	20	600	62	0
2c	0.9	0.22		875	550	1.5	18	29	7×10 ⁸	0.13	1.18	0	Δ	15	648	63	0.5
3c	1.2	0.29		900	525	4	17	28	3×10 ⁹	0.11	1.07	0	Δ	10	697	63	1
4c	1.4	0.34		975	550	2	22	19	5×10 ⁹	0.13	1.20	0	Δ	10	729	63	1.5
5c	0.65	0.16	Sn=0.13, Zn=0.3, Mg=0.1	850	550	3	24	31	5×10 ⁸	0.10	0.90	0	0	20	608	63	0
6c	0.95	0.24	Zn=0.15	875	525	4	16	33	8×10 ⁸	0.08	0.71	0	00	15	656	62	0.5
7c	1.15	0.29	Mg=0.08, Zn=0.5	900	550	3	21	25	2×10 ⁹	0.07	0.67	0	0	15	689	64	1
8c	1.35	0.34	Sn=0.1, Zn=0.3, Mg=0.2	950	550	2	30	32	4×10 ⁹	0.05	0.52	0	0	10	721	57	1.5
9с	1.95	0.48	Zn=0.2, Sn=0.1	975	525	4	34	27	6×10 ⁹	0.05	0.40	0	00	5	749	62	2
10c	0.6	0.15	Fe=0.2, Zn=0.3	850	550	3	27	25	4×10 ⁸	0.13	1.31	0	0	20	600	62	0
11c	0.92	0.23	Cr=0.15, Zn=0.5	875	525	4	27	30	6×10 ⁸	0.18	1.84	0	0	10	652	63	0.5
12c	1.22	0.30	Ni=0.3, Sn=0.1, Zn=0.4	900	550	3	33	19	3×10 ⁹	0.18	1.81	0	0	15	700	63	1
13c	1.42	0.35	Sn=0.12,	950	550	2	31	25	4×10 ⁹	0.13	1.28	0	Δ	10	732	64	1.5

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No.	Со	Si	Other element	Temp.*1	Temp.*2	Time*3	GS4*4	Size*5	Density*6	Ra	Rt	SW*8	SAS*9	Ratio*10	TS*11	EC*12	BP*14
		(mass	s%)	(°C)	(°C)	(h)	(μm)	(nm)	(num.)* ⁷	(μm)	(μm)			(%)	(MPa)	(%)*13	R/t
14c	1.82	0.45	Cr=0.2, Ni=0.2, Zn=0.2	1000	550	4	32	33	5×10 ⁹	0.11	1.05	0	00	5	797	63	2
15c	0.9	0.22	Mg=0.1	875	525	4	15	24	5×10 ⁸	0.12	1.10	0	0	10	620	67	0
16c	1.4	0.33	Mg=0.15	945	550	2	21	25	3 × 10 ⁹	0.17	1.30	0	00	15	720	61	
17c	0.88	0.20	Mg=0.11, Zn=0.2	865	525	2	12	21	4 × 10 ⁸	0.14	1.30	0	00	10	641	63	0
18c	1.38	0.34	Mg=0.1, Zn=0.3	935	550	3	18	28	2 × 10 ⁹	0.13	1.20	0	0	15	710	60	1.3
19c	0.92	0.31	Mg=0.1,	885	550	2	11	29	7 × 10 ⁸	0.12	1.10	0	0	10	655	62	0
20c	1.4	0.51	Ni=0.8	975	525	4	13	21	4 × 10 ⁹	0.11	1.00	0	00	15	752	57	1.3
21c	0.67	0.17 Cr=0.	Zn=0.3, 1	875	550	2	26	38	4 × 10 ⁸	0.09	0.82	0	0	15	611	62	0
22c	0.93	0.23	Sn=0.15, Fe=0.2, Zn=0.5	900	525	4	31	23	7 × 10 ⁸	0.20	2.00	0	0	10	653	62	0.5
23c	1.2	0.30	Mg=0.1, Ni=0.25	925	550	1	29	33	3 × 10 ⁹	0.20	1.89	0	Δ	15	697	63	1
24c	1.44	0.36	Sn=0.2, Fe=0.3, Zn=0.5	950	525	4	30	26	5 × 10 ⁹	0.17	1.68	0	0	10	726	55	1.5

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No.	Со	Si	Other element	Temp.*1	Temp.*2	Time*3	GS4*4	Size*5	Density*6	Ra	Rt	SW*8	SAS*9	Ratio*10	TS*11	EC*12	BP*14
		(mass	5%)	(°C)	(°C)	(h)	(μm)	(nm)	(num.)* ⁷	(µm)	(µm)			(%)	(MPa)	(%)*13	R/t
25c	1.8	0.44	Sn=0.1, Zn=0.5, Cr-0.1	975	550	2	28	35	7 × 10 ⁹	0.17	1.67	0	00	5	734	56	2
26c	1.6	0.39	Zn=0.05	940	575	2	22	11	6 × 10 ⁹	0.1	1.1	0	0	20	698	55	2

*1: Temperature of recrystalization heat treatment

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- *2: Temperature of aging heat treatment
- *3: Time of aging heat treatment
- *4: Grain size
- *5: Size of precipitate

- *6: Density of precipitate
- *7: (number/mm²)
- *8: Solder wettability
- *9: Solder adhesive strength
- *10: Working ratio
- *11: Tensile strength
- *12: Electrical conductivity
- *13: (%IACS)
- *14: Bending property

		EP 2 319 947 A1
	{Table 4}	
	[0115]	
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Table 4

									T GDIO T								
No.	Со	Si	Other Element	Temp.*1	Temp.*2	Time*3	GS*4	Size*5	Density*6	Ra	Rt	SW**8	SAS**9	Ratio*10	TS*11	EC*12	BP*14
		(mass	s%)	(°C)	(°C)	(h)	(μm)	(nm)	(num.)* ⁷	(µm)	(µm)			(%)	(MPa)	(%)*13	R/t
1d	0.35	0.09		750	525	2	22	20	5 × 10 ⁶	0.12	1.3	0	0	15	477	78	0.5
2d	2.3	0.61		975	550	2	25	15	6 × 10 ¹⁰	0.18	1.6	Δ	Δ	10	720	48	3
3d	0.8	0.20		1 <i>035</i>	550	2	52	12	6 × 10 ⁸	0.12	1.2	0	0	30	711	63	3
4d	1	0.24		750	550	3	mixed grain	21	8 × 10 ⁸	0.1	1.1	0	0	10	723	64	3
5d	0.9	0.23	Sn=0.1, Zn=0.5	880	575	3	24	23	7 × 10 ⁸	0.24	2.5	X		15	622	62	1.5
6d	1	0.25	Fe=0.2, Zn=0.7	900	500	2	19	12	9 × 10 ⁸	0.27	2.6	X		10	625	66	1
7d	0.8	0.20	Zn=0.02, Sn=0.02	890	450	3	22	2	6 × 10 ⁷	0.2	1.9	0	О	5	459	43	0.5
8d	1.2	0.23	Zn=2	760	625	3	22	62	9 × 10 ⁷	0.13 1.2		0	00	10	452	77	1.5
9d	0.85	0.22	Sn=1.5	830	575	3	29	14	7 × 10 ⁸	0.09	1	0	0	20	714	38	1.5
10d	2.3	0.56		900	525	2	2	7	7 × 10 ⁹	0.08	0.89	0	0	25	745	53	3
11d	0.5	0.13	Fe=2.2	900	575	3	mixed grain	1	2 × 10 ⁸	0.07	0.9	0	o	20	647	68	3
12d	0.9	0.23	Cr=1.7	925	575	2	mixed grain	6	4 × 10 ⁸	0.06	0.7	0	0	10	706	51	3

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No.	Со	Si	Other Element	Temp.*1	Temp.*2	Time*3	GS*4	Size*5	Density*6	Ra	Rt	SW**8	SAS**9	Ratio*10	TS*11	EC*12	BP*14
		(mass	s%)	(°C)	(°C)	(h)	(μm)	(nm)	(num.)* ⁷	(μm)	(µm)			(%)	(MPa)	(%)*13	R/t
13d	1.2	0.30	Ni=2.5	950	575	3	27	32	7 × 10 ⁸	0.19	1.8	0	0	15	714	43	2

^{*1:} Temperature of recrystalization heat treatment *6: Density of precipitate *11: Tensile strength

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^{*2:} Temperature of aging heat treatment *7: (number/mm²) *12: Electrical conductivity

^{*3:} Time of aging heat treatment *8: Solder wettability *13: (%IACS)

^{*4:} Grain size *9: Solder adhesive strength *14: Bending property

^{*5:} Size of precipitate *10: Working ratio

[0116] Examples are presented in Table 3 and Table 4, respectively. In Table 3, italic letters represent the number or the like outside the range defined in the second embodiment of the present invention. The examples described in Table 1 satisfied all of mechanical strength, electrical conductivity, solder wettability, solder adhesive strength, and bending property, with a good balance, and it was found that the examples are favorable as copper alloy materials for electric/ electronic parts where high electrical conductivity and high mechanical strength are particularly required. On the contrary, it was found that, in the examples described in Table 2, at least one item among mechanical strength, electrical conductivity, solder wettability, solder adhesive strength, and bending property, was not suitable for copper alloy materials for electric/electronic parts.

10 (Example 3)

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[0117] Alloys containing the components shown in Table 5, with the balance composed of Cu and inevitable impurities, were melted with the high-frequency melting furnace, followed by casting at a cooling speed from 10 to 30 K/sec, to obtain ingots with width 160 mm, thickness 30 mm, and length 180 mm, respectively. Cooling was carried out under the conditions of temperature, in which any crack or the like was generated in the ingots.

The thus-obtained ingots were kept at a temperature of $1,000^{\circ}$ C for 30 minutes, followed by hot rolling to produce hot rolled sheets with a sheet thickness t = 12 mm. After the hot rolling, both surfaces of the sheets were face-milled to reduce a thickness of 1 mm, respectively, to be a sheet thickness t = 10 mm, and then the sheets were finished to have a sheet thickness t = 0.3 mm by cold rolling. After the cold rolling, the sheets were subjected to a recrystallization heat treatment at a temperature from 800° C to $1,025^{\circ}$ C. The temperature of the recrystallization heat treatment was varied as described in Table 5 and Table 6, in accordance with the addition amount of Co or the like. The materials after the recrystallization heat treatment were subjected to the following two processes, and test materials corresponding to final products were produced.

Process A: recrystallization heat treatment - aging heat treatment (at a temperature of 525°C for 2 hours) - cold working (0 to 20%)

*Then, according to the necessity, strain-relieving annealing was conducted at a temperature from 300 to 400°C for 1 to 2 hours.

Process B: recrystallization heat treatment - cold rolling (0 to 20%) - aging heat treatment (at a temperature of 525°C for 2 hours)

[0118] With respect to the test materials, investigations of the following properties were conducted. Evaluation results for the alloy properties of the copper alloy materials are shown in Table 5, and the evaluation results for the mechanical strength and bending property of the copper alloy materials are shown in Table 6. Table 6 shows, for some of the examples of Table 5, the evaluation results obtained in the case where the alloy composition (Nos. 101 and 102) and/or the production method (Nos. 203 to 208) were outside the ranges defined in the third embodiment of the present invention, together with the evaluations including the bending property of some of the examples shown in Table 5.

a. tensile strength, b. measurement of electrical conductivity, and c. bending property were measured in the same manner as the example 1.

d3. Grain size (arithmetic average):

[0119] A cross-section perpendicular to the rolling direction of a test piece was finished into a mirror surface by wet polishing and buff polishing; the thus-polished surface was corroded with a liquid of chromic acid: water = 1:1 for several seconds; and then, a photograph of the resultant polished surface was taken with an optical microscope of 200 to 400 times magnification or using a secondary electronic image of a scanning electron microscope (SEM) at a magnification ratio from 500 to 2,000 times; to measure grain size on the cross-section, according to the cutting method of JIS-H-0501. The arithmetic mean was determined, with the measurement parameter set at 200, and this value was defined as the arithmetic mean value of the grain size. In the tables, this value is indicated as "average grain size".

e3. Deviation of grain size:

[0120] The grain size of one grain was measured by the same technique as that used for the measurement of grain size, and the standard deviation of the grain size was determined, with the measurement parameter set at 200.

{Table 5}

[0121]

Table 5

					Table 5							
Alloy No.	Test No.	Element**1		Other additive	Speed *2	Temp.*3	Average*4	Deviation*5	Size*6	Density*7	TS*8	EC*9
Alloy No.	restino.	Co (mass%)	Si (mass%)	element (mass%)	element (mass%)	Average						
1e	1e	0.9	0.22		50	875	12.0	7.0	22	4×10 ⁸	575	67
2e	2e	1.40	0.35		50	925	18.0	7.0	25	3×10 ⁸	625	64
1e	3e	0.9	0.22		30	875	12.2	6.9	25	5×10 ⁸	573	67
2e	4e	1.40	0.35		30	925	18.1	7.1	27	4×10 ⁹	626	64
1e	5e	0.9	0.22		150	875	11.5	7.2	19	6×10 ⁸	576	67
2e	6e	1.40	0.35		150	925	17.5	7.1	23	3×10 ⁹	628	64
3e	7e	0.9	0.22	Cr:0.1	50	875	6.0	2.0	21	6×10 ⁸	572	68
4e	8e	1.40	0.36	Cr:0.05	50	950	14.0	6.4	27	4×10 ⁹	630	65
5e	9e	0.9	0.22	Ti:0.03	50	875	12.0	5.8	16	4x10 ⁸	568	67
6e	10e	1.40	0.35	Ti:0.03	50	950	12.0	5.5	25	4×10 ⁸	631	64
7e	11e	0.9	0.24	Ni:0.2	50	875	8.5	4.5	15	6×10 ⁸	582	66
8e	12e	1.40	0.36	Ni:0.2	50	950	9.0	5.0	21	5×10 ⁹	643	63
9e	13e	0.9	0.22	Cr:0.006	50	875	12.2	6.2	22	4×10 ⁸	575	64
10e	14e	1.40	0.35	Cr:0.005	50	925	17.8	6.4	17	3×10 ⁹	633	67
11e	15e	0.9	0.22	Ti:0.002	50	875	12.2	6.8	22	4×10 ⁸	586	63
12e	16e	1.40	0.34	Ti:0.003	50	950	17.5	6.6	25	3×10 ⁹	633	67
13e	17e	0.9	0.23	Ni:0.002	50	875	12.2	6.8	22	4×10 ⁸	588	63
14e	18e	1.40	0.35	Ni 0.003	50	950	17.8	7.2	26	3×10 ⁹	633	67
101e	101e	0.9	0.15		50	875	15.0	16.0	17	2×10 ⁸	560	68
102e	102e	1.40	0.20		50	950	25.0	27.0	14	9×10 ⁸	612	66
103e	103e	0.90	0.40		50	875	10.8	6.5	31	5×10 ⁸	582	57
104e	104e	1.40	0.60		50	950	16.5	7.0	35	4×10 ⁹	642	53
105e	105e	0.9	0.22	Ti:0.4		Droduction	waa impacsih	olo duo to cuid	ation at th	o timo of sa	ating	
106e	106e	1.40	0.35	Ti:0.5	Production was impossible, due to oxidation at the time of casting							

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		Eleme	ent**1									
Alloy No.	Test No.		ı	Other additive element (mass%)	Speed *2	Temp.*3	Average*4	Deviation*5	Size*6	Density*7	TS*8	EC*9
		Co (mass%)	Si (mass%)	elefficht (mass /0)								
107e	107e	0.9	0.22	Cr.1.1	50	875	10.5	6.1	45	8×10 ⁷	525	59
108e	108e	1.40	0.35	Cr:1.3	50	925	12.0	6.6	75	7×10 ⁷	585	55
109e	109e	0.9	0.23	Ni:1.4	50	875	10.6	6.5	35	6×10 ⁹	582	50
110e	110e	1.40	0.36	Ni:1.3	50	950	14.5	6.2	65	4×10 ⁹	645	46
1e	201 e	0.9	0.22		5	875	11.0	13.2	65	3×10 ⁸	562	68
2e	202e	1.40	0.35		5	950	22.0	23.0	75	2×10 ⁹	616	64
1e	203e	0.9	0.24		500	875	14.0	15.2	25	5×10 ⁸	572	67
2e	204e	1.40	0.36		500	950	18.0	20.2	22	4×10 ⁹	631	64
1e	205e	0.9	0.22		50	750	2.8	1.8	20	4×10 ⁷	512	69
2e	206e	1.40	0.35		50	775	1.4	1.0	22	8×10 ⁷	568	65
1 e	207e	0.9	0.23		50	1035	80.0	22.5	20	5×10 ⁸	578	66
2e	208e	1.40	0.36		50	1040	52.0	11.5	18	5×10 ⁹	648	63

^{*1:} Essential additive Element

^{*2:} Temperature raising speed at the time of recrystalization heat treatment (K/s)

^{*3:} Temperature of recrystalization heat treatment (°C)

^{*4:} Arithmetic mean of grain size (μm)

^{*5:} Standard deviation of grain size (μm)

^{*6:} Size of precipitate (nm)

^{*7:} Density of precipitate (number/mm²)

^{*8:} Tensile strength (MPa)

^{*9:} Electrical conductivity (%IACS)

{Table 6}

[0122]

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Table 6

Allas Alla	Took No.	Bending pr	operty (R/t)	Tomaile atmoments (MDa)
Alloy No.	Test No.	GW	BW	Tensile strength (MPa)
1e	1e	0.3	0.4	632
2e	2e	1.0	1.4	722
1e	3e	0.3	0.4	633
2e	4e	1.0	1.4	720
1e	5e	0.3	0.4	628
2e	6e	1.0	1.4	727
3e	7e	0.2	0.3	638
4e	8e	0.8	1.2	725
5e	9e	0.2	0.3	631
6e	10e	0.8	1.2	715
7e	11e	0.4	0.5	642
8e	12e	1.0	1.5	733
101e	101e	0.4	0.6	612
102e	102e	1.2	1.6	702
1e	203e	0.4	0.6	611
2e	204e	1.2	1.6	705
1e	205e	0.4	0.6	622
2e	206e	1.2	1.6	715
1 e	207e	0.6	0.7	648
2e	208e	1.4	2.0	745

[0123] As described in Table 5 and Table 6, the examples according to the third embodiment of the present invention satisfied all of mechanical strength, electrical conductivity and bending property with a good balance. Specifically, when the electrical conductivity was 60 %IACS or more and the tensile strength was 570 MPa to 650 MPa, the value of R/t was 0.5 or less; when the electrical conductivity was 60 %IACS or more and the tensile strength was more than 650 MPa to 700 MPa, the value of R/t was 1.0 or less; and when the electrical conductivity was 60 %IACS or more and the tensile strength was more than 700 MPa, the value of R/t was 1.5 or less. On the contrary, the examples that were not conforming to the third embodiment of the present invention showed results that did not satisfy the values described above.

[0124] Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

[0125] This application claims priority on Patent Application No. 2008-197672 filed in Japan on July 31, 2008, Patent Application No. 2008-197677 filed in Japan on July 31, 2008, and Patent Application No. 2008-202468 filed in Japan on August 5, 2008, each of which is entirely herein incorporated by reference.

Claims

1. A copper alloy material for an electric/electronic part, having a composition comprising Co (cobalt) 0.5 to 2.0 mass% and Si (silicon) 0.1 to 0.5 mass%, with the balance of Cu (copper) and inevitable impurities,

wherein a copper alloy of a matrix has a grain size of 3 to 35 μ m, wherein a precipitate composed of Co and Si has a particle size of 5 to 50 nm, and the precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and wherein the copper alloy material has a tensile strength of 550 MPa and an electrical conductivity of 50 %IACS or more.

- 5 2. The copper alloy material for an electric/electronic part according to Claim 1, comprising at least one of Sn (tin) and Mg (magnesium) 0.1 to 0.5 mass% in total.
 - 3. The copper alloy material for an electric/electronic part according to Claim 1 or 2, comprising at least one of Zn (zinc) and Mn (manganese) 0.1 to 0.5 mass% in total.
 - **4.** The copper alloy material for an electric/electronic part according to any one of Claims 1 to 3, comprising at least one selected from the group consisting of Fe (iron), Cr (chronium) and Ni (nickel) 0.1 to 1.0 mass% in total.
 - **5.** The copper alloy material for an electric/electronic part according to any one of Claims 1 to 4, wherein a stress relaxation ratio after a lapse of 1,000 hours in an air atmosphere at a temperature of 150°C is less than 40%.
 - 6. A method of producing a copper alloy material for an electric/electronic part, comprising the steps a and b of:
- step a: subjecting a copper alloy material having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities, to an aging heat treatment at 500 to 600°C for 1 to 4 hours; and
 - step b: after the step a, setting a cooling speed from the temperature at the time of the aging heat treatment to a temperature of the copper alloy material of 300°C to be in a range of 20 to 100 K/hour (K representing the absolute temperature),
 - whereby a copper alloy material is obtained, in which a copper alloy of a matrix has a grain size of 3 to 35 μ m, a precipitate containing Co and Si has a particle size of 5 to 50 nm, the precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and the copper alloy material has a tensile strength of 550 MPa or more and an electrical conductivity of 50 %IACS or more.
- 7. The copper alloy material for an electric/electronic part according to Claim 1, wherein the surface roughness as the copper alloy material is such that Ra is 0.2 μm or less and Rt is 2 μm or less.
 - **8.** The copper alloy material for an electric/electronic part according to Claim 7, comprising at least one selected from the group consisting of Zn, Sn and Mg 0.1 to 1.0 mass% in total.
 - **9.** The copper alloy material for an electric/electronic part according to Claim 7 or 8, comprising at least one selected from the group consisting of Fe, Cr and Ni 0.1 to 1.0 mass% in total.
 - 10. A method of producing a copper alloy material for an electric/electronic part, comprising the steps of:
 - subjecting a copper alloy material having a composition comprising Co 0.5 to 2.0 mass% and Si 0.1 to 0.5 mass%, with the balance of Cu and inevitable impurities, to an aging heat treatment; acid-dissolving the surface of the aged material; and
 - grinding the acid-dissolved surface,

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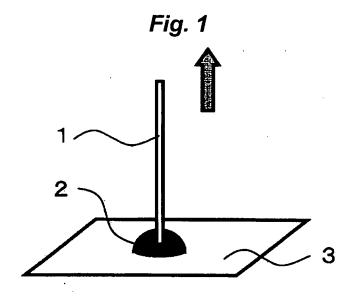
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- whereby a copper alloy material is obtained, in which a copper alloy of a matrix has a grain size of 3 to 35 μ m, a precipitate containing Co and Si has a particle size of 5 to 50 nm, the precipitate has a density of 1×10^8 to 1×10^{10} number/mm², and the copper alloy material has a surface roughness of 0.2 μ m or less in Ra and 2 μ m or less in Rt, and a tensile strength of 550 MPa or more, and an electrical conductivity of 50 %IACS or more.
- 11. The copper alloy material for an electric/electronic part according to Claim 1, wherein the Co content is 0.7 to 2.0 mass%, the mass ratio of Co to Si (Co/Si) is from 3 to 5, the arithmetic mean of the grain size of the copper alloy of a matrix is 3 to 20 μm, the standard deviation is 8 μm or less, and the standard deviation is smaller than the arithmetic mean.
- 12. The copper alloy material for an electric/electronic part according to Claim 11, further comprising at least one selected from the group consisting of Cr, Ni and Fe 0.01 to 1.0 mass% in total, with the balance of Cu and inevitable impurities.
 - 13. The copper alloy material for an electric/electronic part according to Claim 11 or 12, further comprising at least one

selected from the group consisting of Sn, Mg, Zn and Mn 0.01 to 1.0 mass% in total, with the balance of Cu and inevitable impurities. 14. The copper alloy material for an electric/electronic part according to any one of Claims 11 to 13, further comprising at least one selected from the group consisting of Zr (zirconium) and Ti (titanium) 0.01 to 1.0 mass% in total, with the balance of Cu and inevitable impurities.



INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2009/063616

A. CLASSIFICATION OF SUBJECT MATTER

 $\begin{array}{l} {\rm C22C9/06\,(2006.01)\,i,\ C22C9/00\,(2006.01)\,i,\ C22C9/02\,(2006.01)\,i,\ C22C9/04}\\ {\rm (2006.01)\,i,\ C22C9/05\,(2006.01)\,i,\ C22C9/10\,(2006.01)\,i,\ C22F1/08\,(2006.01)\,i,\ H01B1/02\,(2006.01)\,i,\ H01B13/00\,(2006.01)\,i,\ C22F1/00\,(2006.01)\,n}\\ {\rm According\ to\ International\ Patent\ Classification\ (IPC)\ or\ to\ both\ national\ classification\ and\ IPC} \end{array}$

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C9/06, C22C9/00, C22C9/02, C22C9/04, C22C9/05, C22C9/10, C22F1/08,
H01B1/02, H01B13/00, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922–1996 Jitsuyo Shinan Toroku Koho 1996–2009 Kokai Jitsuyo Shinan Koho 1971–2009 Toroku Jitsuyo Shinan Koho 1994–2009

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 Y	JP 2008-56977 A (Mitsubishi Electric Corp., Mitsubishi Electric Metecs Co., Ltd.), 13 March 2008 (13.03.2008), claims; paragraphs [0001], [0015] to [0023], [0025]; tables 1 to 3 & US 2008/0056930 A1 & DE 10 2007 040 822 A1	1-6 7-14
Y	JP 2005-243821 A (Dowa Mining Co., Ltd.), 08 September 2005 (08.09.2005), claims; paragraphs [0012], [0013] (Family: none)	7-10
Υ	JP 11-12714 A (Dowa Mining Co., Ltd.), 19 January 1999 (19.01.1999), claim 1 (Family: none)	7-9

×	Further documents are listed in the continuation of Box C.		See patent family annex.			
* "A"	Special categories of cited documents: document defining the general state of the art which is not considered to be of particular relevance	"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			
"E" earlier application or patent but published on or after the international filing date "L" document which may throw doubts on priority claim(s) or which is		"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 document of particular relevance; the claimed invention cannot be			
"O" "P"	special reason (as specified) locument referring to an oral disclosure, use, exhibition or other means locument published prior to the international filing date but later than the priority date claimed		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			
	of the actual completion of the international search 22 October, 2009 (22.10.09)	Date	c of mailing of the international search report 02 November, 2009 (02.11.09)			
Name and mailing address of the ISA/ Japanese Patent Office			norized officer			
Facs	imile No.	Telephone No.				

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/063616

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C (Continuation)	. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relev	ant passages	Relevant to claim No.
Y	JP 2008-7839 A (Nippon Mining & Metals (Ltd.), 17 January 2008 (17.01.2008), claim 1; paragraphs [0004], [0008] & WO 2008/001852 A1 & KR 10-2009-002 & CN 101479396 A		11-14
Y	<pre>JP 2007-177274 A (Kobe Steel, Ltd.), 12 July 2007 (12.07.2007), claim 1; paragraph [0015] & WO 2007/007517 A1 & US 2009/008447 & EP 1918390 A1 & KR 10-2008-001</pre>		11-14
A	<pre>JP 2007-169765 A (The Furukawa Electric Ltd.), 05 July 2007 (05.07.2007), claims (Family: none)</pre>	Co.,	1-14
A	JP 9-20943 A (The Furukawa Electric Co. Ltd.), 21 January 1997 (21.01.1997), claims (Family: none)		1-14

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 61087838 A [0009]
- JP 63307232 A [0009]
- JP 2129326 A **[0009]**
- JP 2277735 A [0009]
- JP 2008088512 A **[0009]**

- JP 2008056977 A [0009]
- JP 2008197672 A [0125]
- JP 2008197677 A [0125]
- JP 2008202468 A [0125]