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

(11) EP 2 256 219 A1

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

(43) Date of publication:
01.12.2010 Bulletin 2010/48

(21) Application number: **09712614.8**

(22) Date of filing: **17.02.2009**

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

(86) International application number:
PCT/JP2009/052718

(87) International publication number:
WO 2009/104615 (27.08.2009 Gazette 2009/35)

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

(30) Priority: **18.02.2008 JP 2008036694**

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(54) COPPER ALLOY MATERIAL

(57) A copper alloy material, containing Ni 1.8 to 5.0 mass% and Si 0.3 to 1.7 mass%, at a ratio of contents of Ni and Si, Ni/Si, of 3.0 to 6.0, and having a content of S of less than 0.005 mass%, with the balance of being Cu and inevitable impurities, wherein the copper alloy material satisfies formulae (1) to (4):

$$130 \times C + 300 \leq TS \leq 130 \times C + 650 \quad \cdots (1)$$

$$0.001 \leq d \leq 0.020 \quad \cdots (2)$$

$$W \leq 150 \quad \cdots (3)$$

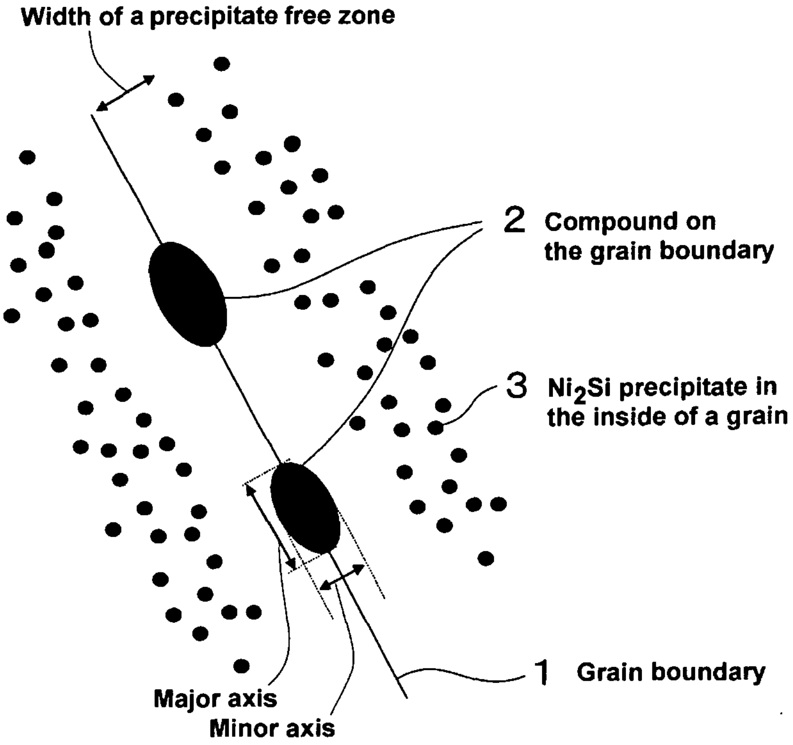
$$10 \leq L \leq 800 \quad \cdots (4)$$

wherein TS represents a tensile strength (MPa) of the copper alloy material in a direction parallel to rolling; C represents the content (mass%) of Ni in the copper alloy material; d represents an average grain diameter (mm) of the copper alloy material; W represents a width (nm) of a precipitate free zone; and L represents a particle diameter (nm) of a compound on a grain boundary.

Printed by Jouve, 75001 PARIS (FR)

(Cont. next page)

Fig. 2


Width of a precipitate free zone
2 Compound on the grain boundary
3 Ni_2Si precipitate in the inside of a grain
1 Grain boundary
Major axis
Minor axis

Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy material.

BACKGROUND ART

[0002] Conventionally, as materials for electric / electronic equipments in general, not only materials of iron-based but also materials of copper-based that are excellent in electrical conductivity and thermal conductivity, such as phosphor bronze, red brass, brass, or the like, are made use as widely. In recent years, a demand is increased in smaller size and lighter mass of the electric / electronic equipments, and then for a packaging to be higher density in mounting that is accompanied by those. Hence various kinds of properties are required as well for the materials of copper-based that are to be applied to these. As the properties mainly required of copper-based materials, mechanical properties, an electrical conductivity, and bending property and formability are required in order to achieve product functions, while a stress relaxation resistance and a fatigue property are required in order to obtain reliability upon the use of products. Hitherto, high-mechanical strength alloys favorable in fatigue strength, such as titanium-copper or beryllium-copper, have been used in members where reliability, such as the fatigue property, is required.

[0003] Since the high mechanical strength alloys, such as titanium-copper and beryllium-copper, are expensive as compared with copper alloys, such as phosphor bronze, and the beryllium-copper contains metallic beryllium which is harmful to human bodies, substitution materials are desired from the viewpoints of production process and environmental considerations.

In recent years, a Cu-Ni-Si-based alloy (Corson alloy), which is relatively not expensive in the production cost and which is excellent in the balance between mechanical strength and electrical conductivity, has attracted attention and has come to be used as a copper alloy for connectors. The Cu-Ni-Si-based alloy is a precipitation-type alloy in which a precipitate, which is comprised of Ni and Si, is to be formed and the resultant alloy is hardened, and the hardening ability is very high.

[0004] In general, the fatigue property is enhanced concomitantly with an increase in tensile strength. However, in the Cu-Ni-Si-based alloy, it is difficult to maintain a bending property as the tensile strength increases. Further, there is a problem that the stress relaxation resistance deteriorates, when a high processing rate is introduced for a material in order to obtain a tensile strength. Therefore, in order to obtain a mechanical strength and a bending property needed for achieving product functions, and to obtain reliability upon the use of products, there has been a demand to develop a Cu-Ni-Si alloy that satisfies both of a favorable stress relaxation resistance and a favorable fatigue property.

[0005] In connection with the Corson alloy, high-mechanical strength copper alloys having improved mechanical strength and bending property as well as those having improved mechanical strength and fatigue property, have been proposed, for example, in Patent Literatures 1 and 2. However, as described above, there is a demand for a copper alloy material having all of a proof stress, a bending property, a stress relaxation resistance, and a fatigue property, each of which is further enhanced.

Patent Literature 1: Publication of Japanese Patent No. 3520034
Patent Literature 2: JP-A-2005-48262 ("JP-A" means unexamined published Japanese patent application)

DISCLOSURE OF INVENTION

TECHNICAL PROBLEM

[0006] In view of the problems as described above, the present invention is contemplated for providing a copper alloy material, which has a high mechanical strength, is excellent in the bending property and the stress relaxation resistance, and is also excellent in the fatigue property, and which is suitable for terminals, connectors, switches, relays, and the like, for electric / electronic equipments.

SOLUTION TO PROBLEM

[0007] The inventors have conducted investigations on copper alloy materials suitable for the use in electric / electronic parts, and have found that, upon an aging treatment, a precipitate free zone (PFZ) is formed in the vicinity of a grain boundary in a copper alloy, and since this precipitate free zone is lower in mechanical strength as compared with that of the inside of grains, when the copper alloy is subjected to processing or repeated stress, deformation occurs dominantly, causing deterioration of a bending property and a fatigue property, but when the width of the precipitate free zone is narrowed, the precipitate free zone can be rendered harmless. Further, in addition to the above, by controlling the grain diameter and the particle diameter of a compound present on the grain boundary, we have attained our invention of a copper alloy material which has high mechanical strength, is excellent in the bending property and the stress relaxation resistance, and is also excellent in the fatigue property.

[0008] According to the present invention, there is provided the following means:

<1> A copper alloy material, comprising Ni 1.8 to 5.0 mass% and Si 0.3 to 1.7 mass%, at a ratio of contents of Ni and Si, Ni/Si, of 3.0 to 6.0, and having a content of S of less than 0.005 mass%, with the balance of being Cu and inevitable impurities, wherein the copper alloy material satisfies the following formulae (1) to (4):

$$130 \times C + 300 \leq TS \leq 130 \times C + 650 \quad \cdots (1)$$

$$0.001 \leq d \leq 0.020 \quad \cdots (2)$$

$$W \leq 150 \quad \cdots (3)$$

$$10 \leq L \leq 800 \quad \cdots (4)$$

wherein TS represents a tensile strength (MPa) of the copper alloy material in a direction parallel to rolling (LD); C represents the content (mass%) of Ni in the copper alloy material; d represents an average grain diameter (mm) of the copper alloy material; W represents a width (nm) of a precipitate free zone (PFZ); and L represents a particle diameter (nm) of a compound on a grain boundary;

<2> The copper alloy material as described in item <1>, further comprising Mg 0.01 to 0.20 mass%;

<3> The copper alloy material as described in item <1> or <2>, further comprising Sn 0.05 to 1.5 mass%;

<4> The copper alloy material as described in any one of items <1> to <3>, further comprising Zn 0.2 to 1.5 mass%; and

<5> The copper alloy material as described in any one of items <1> to <4>, further comprising any one or two or more in the following (I) to (IV) in 0.005 to 2.0 mass% in total:

(I) one or two or more selected from the group consisting of Sc, Y, Ti, Zr, Hf, V, Mo, and Ag in 0.005 to 0.3 mass%;
(II) Mn 0.01 to 0.5 mass%;
(III) Co 0.05 to 2.0 mass%; and
(IV) Cr 0.005 to 1.0 mass%.

ADVANTAGEOUS EFFECTS OF INVENTION

[0009] The Cu-Ni-Si-based copper alloy material of the present invention is a copper alloy material which has a high mechanical strength and is excellent in all of the bending property, the stress relaxation resistance, and the fatigue property, as compared with conventional copper alloy materials.

[0010] 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

[0011]

{Fig. 1}

Fig. 1 is a transmission electron microscopic photograph showing the vicinity of a grain boundary including a precipitate free zone of an example of the copper alloy material of the present invention.

{Fig. 2}

Fig. 2 is an explanatory diagram showing a method of determining the width W of the precipitate free zone and the particle diameter L of a compound on the grain boundary, as defined in the present invention.

DESCRIPTION OF REFERENCE NUMERALS

[0012]

1 Grain boundary
2 Compound on the grain boundary
3 Ni_2Si precipitate in the inside of a grain

BEST MODE FOR CARRYING OUT THE INVENTION

[0013] With respect to a composition and an alloy structure of the copper alloy material of the present invention, preferable embodiments will be described in detail below. In the present invention, the copper alloy material means a copper alloy processed into a particular shape, for example, a sheet material, a strip material, or a foil, by rolling.

[0014] Nickel (Ni) and silicon (Si) in a copper alloy form mainly a Ni_2Si phase via an aging treatment, to enhance the mechanical strength and improve the electrical conductivity of the resultant copper alloy. The content of Ni is 1.8 to 5.0 mass%, and preferably 2.0 to 4.8 mass%. The reason for defining as such is that, if the content is less than 1.8 mass%, a sufficient mechanical strength required of a copper alloy for the use in connectors cannot be obtained. On the other hand, in the case where the content is more than 5.0 mass%, a compound is formed that is not to contribute to enhancement of the mechanical strength upon casting or hot-working, which results in arising such problems that it is not able to obtain the mechanical strength corresponding to the added content, and that a hot workability becomes to be worsened and the same becomes to affect as negatively.

[0015] The content of Si is 0.3 to 1.7 mass%, and preferably 0.35 to 1.6 mass%. The reason for defining as such is that, if the amount of Si is less than 0.3 mass%, the enhancement of mechanical strength by the aging treatment is insufficiently achieved, and a sufficient mechanical strength cannot be obtained. On the other hand, in the case where the content of Si is more than 1.7 mass%, it becomes a cause of lowering of electrical conductivity, in addition to occurrence of the above problems that are similar to the case where the amount of Ni is too large.

Since Ni and Si form mainly the Ni_2Si phase, there is an optimal ratio between Ni and Si in order to enhance the mechanical strength. A ratio, Ni / Si, between Ni (mass%) and Si (mass%) is determined to be 4.2, in the case where the Ni_2Si phase is formed regarding the amount of Si. Further, it is preferable to control the Ni/Si to be within a range of 3.0 to 6.0 with the above-mentioned value to be a central value, and more preferably within a range of 3.8 to 4.6.

[0016] Sulfur (S) is contained with a very small amount in a copper alloy in general. In the case where the amount is 0.005 mass% or more, the same becomes a cause of worsening hot workability. The content is specified to be less than 0.005 mass%, particularly preferably less than 0.002 mass%.

[0017] Further, it is preferable to add magnesium (Mg) into the copper alloy. The amount is 0.01 to 0.20 mass%. Mg is able to improve the stress relaxation property largely, but affects as negatively to the bending property. The amount of Mg is 0.01 mass% or more in order to improve the stress relaxation property, and the more the amount is, the better the improvement becomes to be. However, in the case where the amount is more than 0.20 mass%, it becomes unable to satisfy the required level of bending property. The amount is preferably 0.05 to 0.15 mass%.

[0018] Further, it is preferable to add tin (Sn) into the copper alloy. The amount is 0.05 to 1.5 mass%. Sn co-relating to Mg each other is able to improve the stress relaxation property further, but the effect is not so large with comparing to that according to Mg. In the case where Sn is less than 0.05 mass%, it is not able to obtain the effect sufficiently. On the other hand, in the case where the amount is more than 1.5 mass%, the electrical conductivity lowers conspicuously. The amount is preferably 0.1 to 0.7 mass%.

[0019] Further, it is preferable to add zinc (Zn) into the copper alloy. The amount is 0.2 to 1.5 mass%. Zn is able to improve the bending property slightly. By containing Zn in an amount of 0.2 to 1.5 mass%, it becomes possible to obtain the bending property corresponding to the standard without any problem for a practical use even adding Mg with 0.20 mass% at the maximum. In addition to the above, Zn is able to improve, for example, adherence or migration of Sn plating or solder plating. In the case where the amount of Zn is less than 0.2 mass%, it is not able to obtain the effect sufficiently, and on the other hand, in the case where the amount is more than 1.5 mass%, the electrical conductivity becomes lowered. The amount is preferably 0.3 to 1.0 mass%.

[0020] Further, the copper alloy can contain any one or two or more selected from the group consisting of scandium (Sc), yttrium (Y), titanium (Ti), zirconium (Zr), hafnium (Hf), vanadium (V), molybdenum (Mo), and silver (Ag), in an amount of 0.005 to 0.3 mass% in total. Any of Sc, Y, Ti, Zr, Hf, V, and Mo respectively forms a compound together with Ni or Si, which is effective to restrict coarsening of grains in the grain size. With respect to the addition amount, those may be added singly or in combination of two or more, within the above-mentioned range by which the properties, for example, mechanical strength or electrical conductivity, would not be worsened.

Ag is able to improve heat resistance and enhance mechanical strength, and is effective to restrict coarsening of grains in the grain size to improve the bending property. In the case where the amount of Ag is less than 0.005 mass%, it is not able to obtain the effect sufficiently. On the other hand, in the case where the amount is more than 0.3 mass%, it becomes a cause of a high cost of production, although there is no affect as negatively to be given to the properties of the resultant copper alloy. The content of Ag is preferably within the above-mentioned range, from the viewpoints of those.

[0021] Manganese (Mn) has an effect to improve hot workability. The addition in an amount of 0.01 to 0.5 mass% is effective in such a level that no deterioration would occur to the electrical conductivity.

Cobalt (Co) forms a compound with Si, which is similar to Ni, and has an effect to enhance the mechanical strength. Thus, it is preferable to contain Co in an amount of 0.05 to 2.0 mass%. In the case where the content is less than 0.05 mass%, it is not able to obtain the effect sufficiently. On the other hand, in the case where the amount is more than 2.0 mass%, a crystallized and/or precipitated product occurs even after a solution treatment which does not contribute to enhancement of the mechanical strength, thereby resulting in deterioration of the bending property.

Chromium (Cr) is precipitated finely into the copper, to contribute to enhancement of the mechanical strength, and Cr forms a compound with Si or with Ni and Si, which is effective to restrict coarsening of grains in the grain size, similar to the above-mentioned group of Sc, Y, Ti, Zr, Hf, V, and Mo. When added, in the case where the amount is less than 0.005 mass%, it is not able to obtain the effect sufficiently. On the other hand, in the case where the amount is more than 1.0 mass%, the bending property is deteriorated.

[0022] When adding two or more of the above-mentioned Sc, Y, Ti, Zr, Hf, V, Mo, Ag, Mn, Co, and Cr, the respective amount is determined within the range of 0.005 to 2.0 mass% in total, according to the required characteristics.

[0023] In the present invention, the tensile strength TS is defined, which is in the direction parallel to rolling (LD) of the copper alloy material having the composition mentioned above. Herein, since a hot-rolling and a cold-rolling are all conducted in the same direction in the process for producing the present copper alloy material, the rolling direction is identical.

In regard to the use in terminals, connectors, relays, and the like, a mechanical strength of the copper alloy material is required in order to maintain a springiness or spring property, but when the mechanical strength is markedly enhanced by working or the like, the bending property deteriorates. Further, when the Ni and Si contents in the Cu-Ni-Si-based alloy are increased, the mechanical strength is increased; however, even in the case of the contents of Ni and Si described above, if the contents are increased to no purpose, the cost is raised. From that point of view, it was revealed that even when the contents of Ni and Si fall within the range described above, contents of Ni and Si appropriate for various levels of the mechanical strength would exist. Thus, the formula (1) was eventually deduced. In this case, the Si content has a region that is optimal for the ratio of contents of Ni and Si as described above, and the Si content can be representatively defined by the Ni content, C. If the tensile strength TS is too small, this implies that the contents of Ni and Si are large relative to the mechanical strength, and the cost increases. If the tensile strength TS is too large, this implies that the mechanical strength is markedly increased by working or the like, and thus the bending property deteriorates.

$$130 \times C + 300 \leq TS \leq 130 \times C + 650 \quad \cdots (1)$$

In the present invention, TS is a value determined according to JIS Z 2241. TS is preferably such that $(130 \times C+350) \leq TS \leq (130 \times C+600)$.

[0024] In the present invention, the average grain diameter d (mm) of the grains of the matrix of the copper alloy material is such that $0.001 \leq d \leq 0.020$. The reason for defining the average grain diameter d to be 0.001 mm or more and 0.020 mm or less is because, if the average grain diameter d is less than 0.001 mm, the recrystallized structure is apt to have mixed grains (which is a structure in which grains with different sizes are co-exist), and the bending property and stress relaxation resistance are deteriorated. On the other hand, if the average grain diameter d exceeds 0.020 mm, stress concentration at the vicinity of the grain boundary is accelerated at the time of bending working, and the grains interact with the precipitate free zone (PFZ) that will be described below and the compound on the grain boundary, thereby deteriorating the bending property. The grain diameter d is a value measured based on JIS H 0501 (cutting method). The number of measurements for determining the grain diameter d is set at 1,000 or more. The average grain diameter d (mm) is preferably such that $0.001 \leq d \leq 0.015$.

[0025] The precipitate free zone (PFZ) is formed at the vicinity of the grain boundary in the course of the aging treatment, and is a region where no precipitate is present. Fig. 1 is a transmission electron microscopic photograph at the vicinity of the grain boundary including the precipitate free zone of one example of the copper alloy material of the present invention. Since the precipitate free zone (PFZ) is a region where no precipitate is present, the precipitate free zone (PFZ) is relatively softer than the inside of grains. Therefore, when the copper alloy material is subjected to deformation or loaded with repeated stress, deformation progresses dominantly and the PFZ serves as an origin of cracks, and the PFZ serves as an origin of fatigue fracture due to accumulation of dislocations. Thus, when the width W of the PFZ is narrower, brittleness of the copper alloy structure is alleviated. We found from the results of detailed investigations that when the width W (nm) of the precipitate free zone is such that $W \leq 150$ (150 nm or less), the width does not much affect the deterioration in the bending property and fatigue property.

[0026] According to the present invention, the width W of the PFZ is obtained, by taking transmission electron microscopic photographs of two visual fields at the vicinity of the grain boundary of a copper alloy sheet, with the incident direction of the beam aligned to the (100) plane, at a magnification of 50,000 times, measuring the width of PFZ at 5 sites per one visual field, and calculating an average value of 10 sites in total. W is preferably from 0 to 100 nm.

[0027] The compound on the grain boundary is mainly an intermetallic compound, and is harder as compared with the inner part of the grain and the precipitate free zone. When the copper alloy material is subjected to deformation or repeated stress, there occurs a difference in mechanical strength between the hard compound and the structure surrounding the compound, and thus dislocations are apt to accumulate in the copper alloy structures near the compound and serve as the origin of cracks and the origin of fatigue fracture. Therefore, when the compound on the grain boundary is smaller, brittleness of the copper alloy structure is alleviated. In the present invention, the average particle diameter L (nm) of the compound on the grain boundary is such that $10 \leq L \leq 800$. When the average particle diameter L of the compound is 800 nm or less, the compound does not much affect the deterioration of bending property and fatigue property. The average particle diameter L of the compound is preferably 500 nm or less. However, the compound present on the grain boundary has an effect of suppressing the movement of grains and thereby maintaining the grain diameter fine. For that reason, the particle diameter L is 10 nm or more, and preferably 30 nm or more.

In the present invention, the average particle diameter L of the compound on the grain boundary is determined, by taking transmission electron microscopic photographs of five visual fields of the grain boundary of the copper alloy material, with the incident direction of the beam aligned to (100) plane, at a magnification of 50,000 times, measuring the major axis and the minor axis for an individual compound to take an average of the axes as the particle diameter of the compound, and averaging the particle diameters of 20 pieces of compounds.

[0028] Fig. 2 is an explanatory diagram schematically showing the method of determining the width W of the precipitate free zone and the particle diameter L of the compound on the grain boundary, according to the present invention. In the figure, reference numeral 1 represents the grain boundary, reference numeral 2 represents the compound on the grain boundary, and reference numeral 3 represents a Ni_2Si precipitate in the grain. As shown in the diagram, the width W of the precipitate free zone can be determined, by measuring the distance from the grain boundary 1 to the boundary of a region (where no precipitates are present) formed by one grain. The average particle diameter L of the compound on the grain boundary can be determined, by measuring the major axis and the minor axis of the compound 2 on the grain boundary, calculating the average of the axes as the particle diameter of the compound, and averaging the particle diameters of 20 compounds.

[0029] The grain, the precipitate free zone, and the grain boundary compound interact with each other when the copper alloy is subjected to deformation or repeated stress. Thus, it is not sufficient merely if the average grain diameter d, the width W of the precipitate free zone, or the average particle diameter L of the grain boundary compound respectively satisfy the definitions described above, and only when all of the definitions are satisfied, brittleness of the copper alloy structure can be alleviated.

[0030] Next, a preferable method for producing the copper alloy material according to the present invention will be explained.

Casting is conducted by a general semi-continuous casting method, a so-called DC (direct chill) casting method, or the like. Then, the resultant ingot is subjected to a homogenization treatment, for example, at a temperature of 850 to 1,000˚C for 0.5 to 6 hours, and then the resultant homogenized ingot is immediately subjected to a hot-rolling at a temperature of 600 to 1,000˚C. After the hot-rolling, a cold-rolling is conducted appropriately. The precipitate formed upon cooling after the hot-rolling is apt to become coarse, and coarse compounds of size 1,000 nm or more may often remain on the grain boundary of the final products, causing deterioration of bending property and fatigue property. In order to prevent precipitation upon cooling from occurring, it is preferable to conduct water cooling after the hot-rolling. After cooling, it is preferable to conduct cloth rolling after face milling the oxide layer. The cloth rolling is preferably conducted such that said rolling would be conducted to a sheet thickness with which a predetermined working ratio in the cold-rolling of the subsequent steps can be given.

[0031] Subsequently, a solution treatment is conducted by determining the temperature according to the Ni content, C. It is preferable that the solution treatment is conducted to the extent that the actual (substance's) temperature Tst (˚C) of the material satisfies the formula (5).

$$54 \times C + 625 \leq Tst \leq 54 \times C + 725 \qquad \cdots(5)$$

As the temperature of the solution treatment is raised, the average particle diameter L of the precipitate on the grain boundary is decreased, and the width W of the precipitate free zone is narrowed. Then, a satisfactory solid solution state can be obtained, and it is possible to obtain a high mechanical strength upon the aging treatment in the subsequent steps. However, when the Tst is in a range that exceeds the upper limit of the formula shown above, the grains are coarsened and the average grain diameter d does not fall in the above range, possibly resulting in deterioration of bending property. When the Tst is below the lower limit of the formula, dislocation structures resulting from a cold-working of plain rolling may remain behind, possibly causing deterioration of bending property.

[0032] Subsequently, an aging treatment causes the Ni_2Si compound uniformly dispersed and precipitated in the copper alloy, thereby enhancing the mechanical strength and the electrical conductivity. It is preferable to maintain the copper alloy at an actual substance temperature of 350 to 600˚C for 0.5 to 12 hours, using a batch-type furnace. If the temperature at the aging treatment is lower than 350˚C, a longer period of time is required to obtain a sufficient precipitation amount of Ni_2Si, and the costs increase, or the tensile strength and electrical conductivity may become insufficient. If the temperature at the aging treatment is higher than 600˚C, coarsened Ni_2Si is formed at the inside of the grains, thus lowering the mechanical strength, and since the width W of the precipitate free zone is broadened at the vicinity of the grain boundary, the bending property and the fatigue property may deteriorate. Regarding the treatment period of time, if it is less than 0.5 hours, sufficient properties may not be obtained, and if it is longer than 12 hours, not only the costs increase but also the width W of the precipitate free zone is broadened, possibly causing deterioration of the bending property and fatigue property.

For the purpose of further enhancing the tensile strength, a cold-rolling may be conducted in mid course of from the solution treatment to the aging treatment. The dislocations introduced by this cold-rolling serve to accelerate precipitation of the Ni_2Si compound, and also have a function of decreasing the width of the precipitate free zone W. If the cold-working ratio at this is too high, the bending property deteriorates, and thus it is preferable to conduct the cold-rolling at 50% or less.

[0033] Further, since the aging treatment functions to reduce the width W of the precipitate free zone, the aging treatment may also be conducted twice. In order to reduce the width W of the precipitate free zone through the two aging treatments, it is preferable to conduct the aging treatments, by dividing the aging treatment temperature mentioned above into a temperature region 1: 350 to 450˚C and a temperature region 2: 450 to 600˚C, and conducting the treatment once each at the temperature region 1 and at the temperature region 2. In this case, the order of conducting the treatments at the temperature region 1 and the temperature region 2 may be such that any one temperature region may precede the other. It is preferable to conduct the aging treatment for a relatively longer period of time at the temperature region 1 from 4 to 12 hours, and for a relatively shorter period of time at the temperature region 2 from 0.5 to 6 hours. In mid curse of the two aging treatments, a cold-rolling may be carried out at 50% or less, to accelerate precipitation of the Ni_2Si compound.

[0034] Subsequent to the aging treatment, a finish cold-rolling is conducted for the purpose of enhancing the tensile strength. When the tensile strength obtainable after the aging treatment is satisfactory, the finish cold-rolling may not be introduced. If the rolling ratio of the finish cold-rolling is too high, the bending property deteriorates, and the stress relaxation resistance also deteriorates. Therefore, it is preferable to set the rolling ratio of the finish rolling at 50% or less.

[0035] Subsequent to the finish rolling, a low-temperature annealing is conducted for the purpose of restoring the elongation, the bending property, and the spring limit value, while maintaining the mechanical strength to a certain extent. When the finish rolling is not conducted, the step of low-temperature annealing may be omitted. It is preferable to conduct the annealing at an actual substance temperature of 300 to 600˚C for a short time period of 5 to 60 seconds. If the temperature at the annealing is lower than 300˚C, restoration of the elongation, the bending property, and the spring limit value may be insufficient.

If the temperature at the annealing is higher than 600˚C, a decrease in mechanical strength may occur.

EXAMPLES

[0036] Hereinafter, the present invention is explained in more detail by way of the examples based on the present invention in comparison to comparative examples, but the invention is not intended to be limited to these examples.

Each of the copper alloy materials in the Examples according to the present invention and the Comparative Examples, was formed of a copper alloy (Alloy Nos. 1 to 25) which had a chemical composition (the balance of Cu), as shown in Table 1, respectively. Each of those copper alloys was dissolved with a high-frequency melting furnace, and then the melt was cast into an ingot of thickness 30 mm, width 120 mm, and length 150 mm. Then, each of those ingots were heated to 980˚C, and maintained at this temperature for one hour, followed by a hot-rolling to thickness 12 mm, and a cooling quickly.

At this time, regarding Alloy No. 19 due to the too high amount of Ni, regarding Alloy No. 20 due to the too high amount of S, regarding Alloy No. 21 due to the too high amount of Si, regarding Alloy No. 23 due to the too high amount of Cr, regarding Alloy Nos. 24 and 25 due to the too high total amounts of Zr, Ti, and Hf, and of V, Mo, and Y, respectively, cracks occurred upon the hot-rolling, and the subsequent steps were stopped in the production of those.

{Table 1}

[0037]

Table 1

Alloy No.	Ni (mass%)	Si (mass%)	Mg (mass%)	Sn (mass%)	Zn (mass%)	S (mass%)	Others (mass%)
1	3.7	0.89	0.11	0.16	0.48	0.001	Cr: 0.19
2	2.4	0.57	0.19	0.15	0.48	0.001	Cr: 0.15
3	3.3	0.78	0.10	0.15	0.49	0.001	Cr: 0.20
4	4.8	1.14	0.10	0.14	0.50	0.001	Cr: 0.21
5	3.2	0.75	0.14	-	-	0.001	-
6	3.8	0.88	0.11	-	-	0.001	Mn: 0.12
7	3.3	0.78	0.10	-	-	0.001	Co: 0.12
8	3.3	0.77	0.10	0.14	0.49	0.001	Ag: 0.05
9	3.3	0.77	0.09	0.15	0.45	0.001	Co: 0.19
10	3.8	0.91	0.10	0.14	0.51	0.001	Cr: 0.87
11	3.3	0.77	0.15	0.14	0.47	0.001	Zr: 0.006, Ti: 0.005, Hf: 0.005
12	3.3	0.77	0.15	0.15	0.49	0.001	Sc: 0.005, Y: 0.01
13	3.2	0.76	0.13	0.15	0.50	0.001	V: 0.007, Mo: 0.005
14	0.8	0.18	0.08	0.34	0.50	0.002	
15	3.3	0.77	0.23	0.15	0.49	0.001	
16	3.3	0.76	0.11	0.14	0.53	0.001	Mn: 0.7
17	3.3	0.77	0.10	0.16	1.86	0.001	
18	3.3	0.77	-	-	-	0.001	Co: 2.1
19	5.5	1.68	0.10	0.15	0.52	0.001	
20	3.3	0.77	0.10	0.16	0.50	0.007	
21	3.3	2.02	0.11	0.15	0.48	0.001	
22	3.3	0.77	0.10	1.90	0.40	0.001	
23	3.3	0.76	0.12	-	-	0.001	Cr: 1.5
24	3.2	0.76	0.09	0.14	0.50	0.001	Zr: 0.20, Ti: 0.10, Hf: 0.10
25	3.2	0.77	0.09	0.15	0.50	0.001	V: 0.20, Mo: 0.10, Y: 0.20

[0038] Then, the oxide layer was removed by face-milling the both sides at 1.5 mm each. Then, the resultant respective alloy was worked to thickness 0.16 to 0.50 mm by a cold-rolling. At this time, regarding Alloy No. 22 due to the too high amount of Sn, cobber cracks occurred upon the cold-rolling, and the subsequent steps were stopped in the production of this. Then, the resultant respective alloy was subjected to a heat treatment at 800˚C to 950˚C for 30 sec, followed immediately by a cooling with a cooling rate of 15˚C/sec or more.

[0039] The thus-cooled respective alloy was subjected to a cold-rolling at various rolling ratios of 0 to 50% (when the rolling ratio was 0%, without conducting any cold-rolling) before an aging treatment, and the thus-rolled alloy was subjected to the aging treatment at 500˚C for 2 hours under an inert gas atmosphere. Herein, a rolling ratio of 0% means that no rolling was conducted. As the heat treatment, instead of the aging treatment described above, the copper alloy sheet was either subjected to a heat treatment of applying the two aging treatments, or subjected to a heat treatment of heating at 400˚C for 4 hours and then heating at 500˚C for 2 hours in an inert gas atmosphere, or subjected to a heat treatment of heating at 500˚C for 2 hours and then heating at 400˚C for 4 hours. The details on those will be described in the below.

Then, a finish rolling was conducted at various rolling ratios, and finally the sheet thickness was adjusted to 0.15 mm. After the finish rolling, the copper alloy sheet was subjected to a low-temperature annealing at 400 to 600°C for 30 seconds. In the above-manner, copper alloy materials of Examples and Comparative Examples were produced, and the following various property evaluations were carried out thereon.

[0040] With respect to the various copper alloy sheets produced in Examples and Comparative Examples, examinations were made on: (a) an average grain diameter, (b) a width of a precipitate free zone, (c) an average particle diameter of a precipitate on a grain boundary, (d) a tensile strength, (e) an electrical conductivity, (f) a bending property, (g) a stress relaxation resistance, and (h) a fatigue property.

[0041]

(a) The average grain diameter was determined, by measuring the grain diameters according to the cutting method as specified in JIS (JIS H 0501), and calculating based on the resultant values. In regard to the cross-section used for the measurement of the grain diameter, measurement was made with a cross-section that was parallel to the direction of the finally-conducted cold-rolling. A photograph of the crystalline structure of the copper alloy sheet was taken, with a scanning electron microscope with a magnification of 1,000 times. Then, a line segment with length 200 mm was drawn on the photograph. The number of grains (n) was counted, which were cut by the line segment. The average grain diameter was determined from a formula of: {200 [mm]/(n × 1,000)}. In a case where the number of grains cut by the line segment, was less than twenty, a photograph was taken with a magnification of 500 times. Then, the number of grains (n) was counted, which were cut by the line segment of length 200 mm. The average grain diameter was determined from the formula of: {200 [mm]/(n × 500)}. The grain diameter d is shown as an average which was determined from each four values of the major axes and the minor axes measured on the cross sections A and B, and which was rounded off to an integral multiple of 0.005 mm.

(b) The width of the precipitate free zone was determined, by taking transmission electron micrographs of two visual fields of the vicinity of grain boundary of each of the copper alloy sheets, with the incident direction of the beam aligned to (100) plane, at a magnification of 50,000 times, measuring the width of the PFZ at 5 sites per one visual field, and taking the average value of 10 sites in total as the width W of the precipitate free zone, in which the width is indicated as a value rounded off to an integral multiple of 10 nm.

(c) The particle diameter of the compound on the grain boundary was determined in the following manner. Transmission electron micrographs of five visual fields of the grain boundary of each of the copper alloy sheets were taken, with the incident direction of the beam aligned to (100) plane, at a magnification of 50,000 times, and the particle diameters of 20 pieces of compounds in total were measured, respectively. The major axis and the minor axis were measured for one compound, and the average was taken as the particle diameter of the compound. Further, the particle diameters of the 20 compounds were averaged and designated as the average particle diameter L of the compound on the grain boundary of the copper alloy sheet, and this value is indicated as a value rounded off to an integral multiple of 10 nm.

[0042]

(d) The tensile strength was determined, with a No. 5 test piece as stipulated in JIS Z 2201, according to JIS Z 2241. The test was conducted to the test piece in a parallel direction to the rolling direction.

(e) The electrical conductivity was determined according to JIS H 0505.

(f) The bending property was evaluated, by dividing the level according to the tensile strength. With respect to the copper alloys having the tensile strength of less than 750 MPa, 180° bending was conducted, with an inner bending radius of 0 mm. According to the results, a sample which did not have any crack occurred at the bent portion was judged to be "good" (○), and a sample which had cracks occurred was judged to be "poor" (×). With respect to the copper alloys having the tensile strength of 750 MPa or more, a 90° W-bending test was conducted, with a 90°-bending jig with an inner bending radius of 0.15 mm, such that a ratio, R/t, between the bending radius (mm) and the sheet thickness (mm) would be 1.0. According to the results, a sample which did not have any crack occurred at the bent portion was judged to be "good" (○), and a sample which had cracks occurred was judged to be "poor" (×).

(g) The stress relaxation resistance was evaluated with a stress relaxation ratio which was determined in the following manner. A sample was kept in a thermostat bath at 150°C for 1,000 hours, with the cantilever block method according to the technical standard as stipulated by Japan Copper and Brass Association (JBMA-T309), in which a stress load to the sample was set such that a maximum stress on the surface would be an 80% amount of the proof stress.

(h) The fatigue property was collected, by conducting a completely reversed plane bending fatigue test according to JIS Z 2273. A test piece was prepared into a strip with width 10 mm, and the parallel to the rolling direction was brought into line with the longitudinal direction of the test piece. In regard to the test conditions, the test piece was set so that the sheet thickness t (mm) of the test piece, a maximum bending stress σB (MPa) applied to the surface of the test piece, a half amplitude δ (mm) applied to the test piece, a Young's modulus E of the alloy (130 GPa), and the distance l (mm) between the supporting point (fulcrum) and the site of action of stress, would satisfy the relationship of:

$$l = \sqrt{(3Et\delta/(2\sigma B))},$$

in which the test was conducted with the maximum bending stress σB of 500 (MPa), and the number N of sample fractures occurred was measured. The test and measurement were carried out by repeating four times, and the average value of the number N was determined to be defined as the fatigue life of each test piece.

[0043] The evaluation results are shown in Table 2. Herein, Examples 1-1 to 1-6 and Comparative Examples 1-7 to 1-10 are the cases in which Alloy No. 1 was subjected to the heat treatment and rolling in the different conditions each other within the ranges mentioned above, and Examples 2-1 to 2-2 are the cases in which Alloy No. 2 was subjected to those similarly in the above. Further, Nos. 3 to 18 are samples produced from Alloys Nos. 3 to 18, respectively.

[0044] In the following, the conditions taken for Examples 1-1 to 1-6 and Comparative Examples 1-7 to 1-10 are described. In addition, the conditions not described in Examples 1-2 to 1-6 and Comparative Examples 1-7 to 1-10 were the same as the corresponding conditions utilized in Example 1-1.

<Steps in Examples>

[0045]

Example 1-1: After a solution treatment at 875˚C, without conducting any cold-rolling, an aging treatment was conducted at 500˚C for 2 hours, and a finish rolling at 5% and a low-temperature annealing were subsequently carried out.
Example 1-2: Instead of the aging treatment in Example 1-1, two aging treatments of one at 500˚C for 2 hours after the other at 400˚C for 4 hours were carried out.
Example 1-3: Instead of the aging treatment in Example 1-1, two aging treatments of one at 400˚C for 4 hours after the other at 500˚C for 2 hours were carried out.
Example 1-4: The solution treatment was carried out at 885˚C.
Example 1-5: After the solution treatment, a cold-rolling at 5% was carried out before the aging treatment.
Example 1-6: After the solution treatment, a cold-rolling at 10% was carried out before the aging treatment.

<Steps in Comparative Examples>

[0046]

Comparative Example 1-7: The solution treatment was carried out at 950˚C.
Comparative Example 1-8: The solution treatment was carried out at 800˚C.
Comparative Example 1-9: The solution treatment was carried out at a treating temperature of 800˚C with a small rate of the temperature raising.
Comparative Example 1-10: The finish rolling ratio was set at 60%.

{Table 2}

[0047]

Table 2

	No.	TS (MPa)	EC (%IACS)	d (mm)	W of PFZ (nm)	L (nm)	Bending property	SRR (%)	Fatigue life (x 10^3)
Example according to this invention	1-1	854	33	0.005	40	210	○	8	670
	1-2	857	35	0.005	20	180	○	8	783
	1-3	856	35	0.005	20	170	○	8	821
	1-4	845	30	0.010	20	170	○	8	793
	1-5	867	33	0.005	40	180	○	8	839
	1-6	903	33	0.005	40	190	○	8	816
	2-1	806	38	0.005	60	160	○	16	504
	2-2	798	38	0.005	30	150	○	16	406
	3	832	34	0.005	50	260	○	9	462
	4	974	28	0.005	20	380	○	6	358
	5	832	44	0.010	50	160	○	11	686
	6	824	34	0.010	50	180	○	8	703
	7	837	33	0.005	50	280	○	10	406
	8	831	34	0.005	60	230	○	10	558
	9	840	32	0.005	70	400	○	9	398
	10	833	31	0.005	50	370	○	10	432
	11	833	32	0.005	80	460	○	10	468
	12	838	32	0.005	70	410	○	10	395
	13	835	32	0.005	70	420	○	9	423
Comparative example	1-7	852	33	0.030	20	70	×	8	679
	1-8	843	32	0.005	170	260	×	8	42
	1-9	824	36	0.005	150	880	×	9	46
	1-10	1150	30	0.005	40	200	×	13	835
	14	480	51	0.005	80	60	○	34	132
	15	834	31	0.005	40	260	×	9	408
	16	832	25	0.005	40	210	○	11	531
	17	836	24	0.005	50	200	○	10	412
	18	824	31	0.005	40	930	×	9	201

Note: "TS" (MPa) means tensile strength.
"EC" (%IACS) means electrical conductivity.
"d" (mm) means the grain diameter (GS).
"W of PFZ" (nm) the width of the precipitate free zone.
"L" (nm) means the diameter of the compound on the grain boundary.
"SRR" (%) means the stress relaxation ratio.

[0048] The copper alloy materials of Examples 1-1 to 1-6, 2-1, 2-2, and 3 to 13 each are high in the mechanical strength and good in the bending property, and are excellent in the fatigue property.

[0049] In Comparative Example 1-7, since the value of the grain diameter d was too large, the bending property was poor. In Comparative Example 1-8, since the value of the width W of the precipitate free zone was too large, the bending property and fatigue property were poor. In Comparative Example 1-9, since the particle diameter L of the compound on the grain boundary was too large, the bending property and fatigue property were poor. In Comparative Example 1-10, since the tensile strength was too high, the bending property was poor.

[0050] In Comparative Example 14, since the Ni concentration and the Si concentration were too low, the fatigue life was conspicuously short, and the stress relaxation resistance was also poor. In Comparative Example 15, since the Mg concentration was too high, the bending property was poor. In Comparative Example 16 and 17, since the Mg concentration or the Zn concentration was too high, respectively, the electrical conductivity was poor. In Comparative Example 18, since the Co concentration was too high, the bending property was poor, and the fatigue life was also poor.

INDUSTRIAL APPLICABILITY

[0051] The copper alloy material of the present invention can be favorably used as a material, for example, for lead frames, connectors, terminal materials, relays, and switches, of electric / electronic equipments.

[0052] 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.

[0053] This application claims priority on Patent Application No. 2008-036694 filed in Japan on February 18, 2008, of which is entirely herein incorporated by reference.

Claims

1. A copper alloy material, comprising Ni 1.8 to 5.0 mass% and Si 0.3 to 1.7 mass%, at a ratio of contents of Ni and Si, Ni/Si, of 3.0 to 6.0, and having a content of S of less than 0.005 mass%, with the balance of being Cu and inevitable impurities, wherein the copper alloy material satisfies the following formulae (1) to (4):

$$130 \times C + 300 \leq TS \leq 130 \times C + 650 \quad \cdots (1)$$

$$0.001 \leq d \leq 0.020 \quad \cdots (2)$$

$$W \leq 150 \quad \cdots (3)$$

$$10 \leq L \leq 800 \qquad \cdots (4)$$

wherein TS represents a tensile strength (MPa) of the copper alloy material in a direction parallel to rolling (LD); C represents the content (mass%) of Ni in the copper alloy material; d represents an average grain diameter (mm) of the copper alloy material; W represents a width (nm) of a precipitate free zone (PFZ); and L represents a particle diameter (nm) of a compound on a grain boundary.

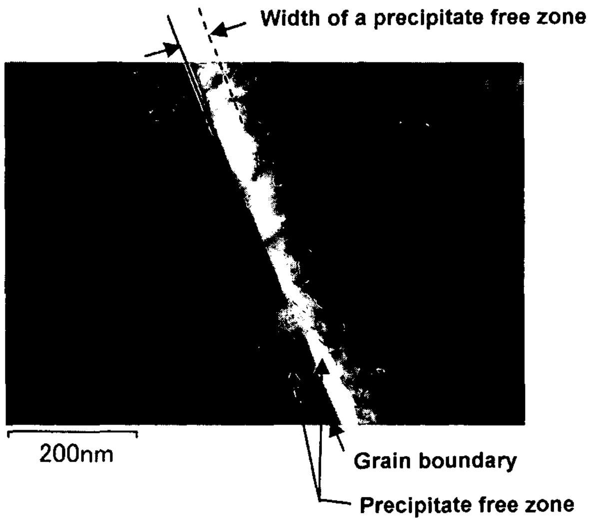
2. The copper alloy material according to claim 1, further comprising Mg 0.01 to 0.20 mass%.

3. The copper alloy material according to claim 1 or 2, further comprising Sn 0.05 to 1.5 mass%.

4. The copper alloy material according to any one of claims 1 to 3, further comprising Zn 0.2 to 1.5 mass%.

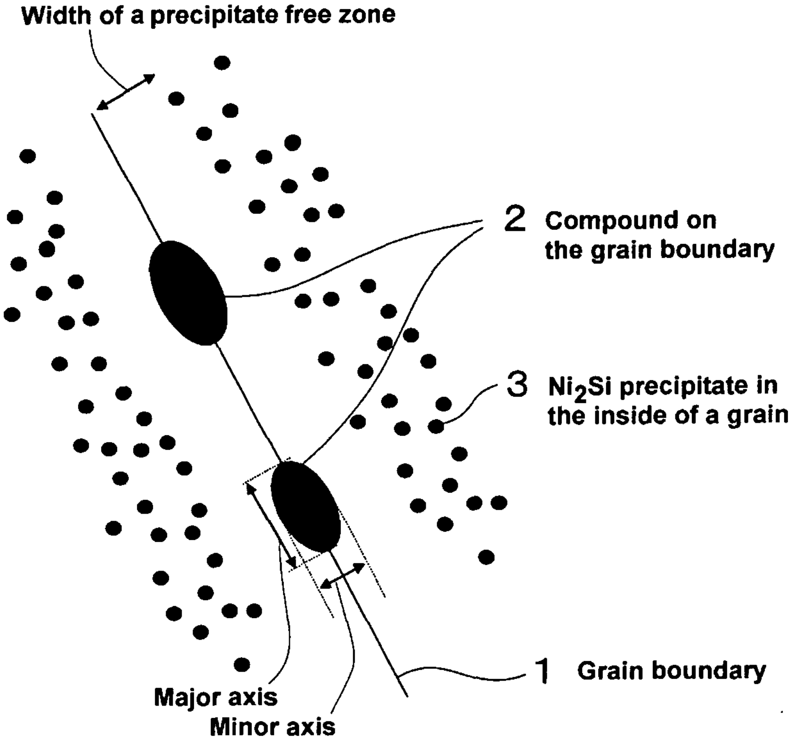
5. The copper alloy material according to any one of claims 1 to 4, further comprising any one or two or more in the following (I) to (IV) in 0.005 to 2.0 mass% in total:

(I) one or two or more selected from the group consisting of Sc, Y, Ti, Zr, Hf, V, Mo, and Ag in 0.005 to 0.3 mass%;
(II) Mn 0.01 to 0.5 mass%;
(III) Co 0.05 to 2.0 mass%; and
(IV) Cr 0.005 to 1.0 mass%.



Width of a precipitate free zone
200nm
Grain boundary
Precipitate free zone

Fig. 1



Width of a precipitate free zone
2 Compound on the grain boundary
3 Ni_2Si precipitate in the inside of a grain
1 Grain boundary
Major axis
Minor axis

Fig. 2

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/052718

A. CLASSIFICATION OF SUBJECT MATTER
C22C9/06(2006.01)i, *H01B1/02*(2006.01)i, *C22F1/00*(2006.01)n, *C22F1/08*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

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

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

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
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	JP 2006-9137 A (The Furukawa Electric Co., Ltd.), 12 January, 2006 (12.01.06), Claims 1 to 13; Par. Nos. [0040] to [0052] & US 2005/0263218 A1 & WO 2005/116282 A1 & DE 112005001197 T5 & CN 1950525 A	1-5
Y	JP 2002-266042 A (Kobe Steel, Ltd.), 18 September, 2002 (18.09.02), Claims 1 to 5; Par. Nos. [0015], [0018], [0021] (Family: none)	1-5
Y	Chihiro WATANABE et al., "Cu-4.0mass%Ni-0.95mass%Si-0.02mass%P Gokin no Kikaiteki Tokusei no Kaizen", Copper and Copper Alloy, 01 August, 2006 (01.08.06), Vol.45, pages 16 to 22	1-5

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

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

Date of the actual completion of the international search 08 May, 2009 (08.05.09)	Date of mailing of the international search report 19 May, 2009 (19.05.09)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2009/052718

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	JP 2008-24999 A (Dowa Holdings Co., Ltd.), 07 February, 2008 (07.02.08), Claims 1, 2; Par. No. [0029] (Family: none)	1-5
A	JP 2007-169764 A (The Furukawa Electric Co., Ltd.), 05 July, 2007 (05.07.07), Claims 1 to 3 (Family: none)	1-5
A	JP 2006-200042 A (Kobe Steel, Ltd.), 03 August, 2006 (03.08.06), Claims 1 to 5; Par. No. [0017] (Family: none)	1-5
P,A	JP 2008-75172 A (Nippon Mining & Metals Co., Ltd.), 03 April, 2008 (03.04.08), Claims 1 to 6 & WO 2008/038593 A1	1-5

Form PCT/ISA/210 (continuation of second sheet) (April 2007)

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- JP 2005048262 A **[0005]**
- JP 2008036694 A **[0053]**