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(72) Inventors:

- **MORI, Hiroyuki**  
Kitamoto-shi, Saitama 364-0028 (JP)
- **MATSUNAGA Hirotaka**  
Kitamoto-shi, Saitama 364-0028 (JP)

(74) Representative: **Hoffmann Eitle**

**Patent- und Rechtsanwälte PartmbB**  
**Arabellastraße 30**  
**81925 München (DE)**

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(71) Applicant: **Mitsubishi Materials Corporation**  
**Tokyo 100-8117 (JP)**

(54) **PURE COPPER PLATE**

(57) This pure copper plate or sheet contains 99.96% by mass or greater of Cu, in which when an average crystal grain size of crystal grains in a rolled surface is represented by X  $\mu\text{m}$  and an amount of Ag is represented by Y mass ppm, an expression of  $1 \times 10^{-8} \leq X^{-3}Y^{-1} \leq 1 \times 10^{-5}$  is satisfied, and when a ratio of J3, in which all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain

boundary triple junctions is defined as  $NF_{J3}$  and a ratio of J2, in which two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $NF_{J2}$ , an expression of  $0.30 < (NF_{J2}/(1-NF_{J3}))^{0.5} \leq 0.48$  is satisfied.

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**Description**

## TECHNICAL FIELD

**[0001]** The present invention relates to a pure copper plate or sheet suitable as electric or electronic components such as a heat sink, a thick copper circuit, or the like and particularly the present invention relates to a pure copper plate or sheet in which coarsening of crystal grains during being heated is suppressed.

**[0002]** The present application claims priority on Japanese Patent Application No. 2019-176835 filed on September 27, 2019, the content of which is incorporated herein by reference.

## BACKGROUND ART

**[0003]** In the related art, copper or a copper alloy with excellent electrical conductivity has been used for electric or electronic components such as a heat sink, a thick copper circuit, or the like.

**[0004]** Recently, with an increase in current of electronic devices and electric devices, in order to reduce the current density and diffuse heat due to Joule heat generation, an increase in size and an increase in thickness of electric or electronic components used for such electronic devices and electric devices have been attempted.

**[0005]** In a semiconductor device, for example, an insulating circuit substrate or the like in which a copper plate or sheet material is bonded to a ceramic substrate and the copper plate or sheet material is provided as the heat sink or the thick copper circuit has been used.

**[0006]** In a case where a ceramic substrate and a copper plate or sheet are bonded to each other, the bonding temperature is frequently set to 800°C or higher, and there is a concern that the crystal grains of the copper material constituting the heat sink or the thick copper circuit may be coarsened during the bonding. In particular, in a copper plate or sheet formed of pure copper having particularly excellent electrical conductivity and heat dissipation property, crystal grains tend to be coarsened. Further, in a case where the copper plate or sheet material to be bonded is produced press working, the burr height increases as the thickness of the plate or sheet increases.

**[0007]** In a case where the crystal grains are coarsened in the heat sink or the thick copper circuit after the bonding, the coarsening of the crystal grains may cause a problem in appearance.

**[0008]** For example, Patent Document 1 suggests a pure copper plate or sheet material in which the growth of crystal grains is suppressed.

**[0009]** Patent Document 1 describes that in a case where the copper plate or sheet contains 0.0006 to 0.0015 wt% of S, crystal grains can be adjusted to have a certain size even when subjected to a heat treatment at a temperature of a recrystallization temperature or higher.

**[0010]** Meanwhile, in Patent Document 1, the coarsening of crystal grains is suppressed by specifying the amount of S, but the effect of suppressing coarsening of crystal grains cannot be sufficiently obtained only by specifying the amount of S depending on the heat treatment conditions. In addition, after the heat treatment, the crystal grains are locally coarsened, and this results in non-uniformity of the crystal structure in some cases.

**[0011]** Further, in a case where the amount of S is increased in order to suppress the coarsening of the crystal grains, there is a problem in that the hot workability is greatly lowered and the production yield of the pure copper plate or sheet is greatly lowered.

## PRIOR ART DOCUMENTS

Patent Document

**[0012]** Patent Document 1: Japanese Unexamined Patent Application, First Publication No. H06-002058

## DISCLOSURE OF INVENTION

## Problems to be Solved by the Invention

**[0013]** The present invention has been made in consideration of the above-described circumstances, and an object thereof is to provide a pure copper plate or sheet which has high electrical conductivity and is capable of suppressing coarsening and non-uniformity of crystal grains even after a heat treatment.

## Solutions for Solving the Problems

**[0014]** As a result of intensive research conducted by the present inventors in order to solve the above-described

problem, it was found that the coarsening and non-uniformity of crystal grains can be suppressed even after a heat treatment by adjusting the average crystal grain size of crystal grains in a rolled surface and the amount of Ag and appropriately controlling grain boundaries constituting a grain boundary triple junction.

**[0015]** Hereinafter, in the present specification, suppression of the growth of crystal grains has the same definition as suppression of the coarsening of crystal grains.

**[0016]** The present invention has been made in consideration of the above-described knowledge, and there is provided a pure copper plate or sheet according to an aspect of the present invention including: 99.96% by mass or greater of Cu, in which when an average crystal grain size of crystal grains in a rolled surface is represented by  $X \mu\text{m}$  and an amount of Ag is represented by  $Y$  mass ppm, a relational expression of  $1 \times 10^{-8} \leq X^{-3}Y^{-1} \leq 1 \times 10^{-5}$  is satisfied, and in which a surface orthogonal to a rolling width direction is used as an observation surface, measurement regarding a matrix is performed on a measurement area of  $10000 \mu\text{m}^2$  or greater at every measurement intervals of  $0.25 \mu\text{m}$  by an EBSD method, measured results are analyzed by data analysis software OIM to obtain a CI value in each measurement point, a measurement point in which a CI value is 0.1 or less is removed, an orientation difference between crystal grains is analyzed, a boundary having  $15^\circ$  or more of an orientation difference between neighboring measuring points is assigned as a grain boundary, an average grain size  $A$  is acquired according to Area Fraction, measurement regarding the matrix is performed at every measurement intervals which are  $1/10$  or less of the average grain size  $A$  by the EBSD method, measured results are analyzed by the data analysis software OIM with a measurement area of  $10000 \mu\text{m}^2$  or greater in a plurality of visual fields such that a total of 1000 or more crystal grains are included to obtain a CI value in each measurement point, a measurement point in which a CI value is 0.1 or less is removed, an orientation difference between crystal grains is analyzed, and a boundary having  $15^\circ$  or more of an orientation difference between neighboring measuring points is assigned as a grain boundary, a coincidence boundary with  $\Sigma 29$  or less is defined as a special grain boundary, and the other grain boundaries are defined as random grain boundaries, in grain boundary triple junctions analyzed by the OIM, when a ratio of  $J_3$ , in which all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain boundary triple junctions is defined as  $NF_{J_3}$  and a ratio of  $J_2$ , in which two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $NF_{J_2}$ , an expression of  $0.30 < (NF_{J_2}/(1-NF_{J_3}))^{0.5} \leq 0.48$  is satisfied.

**[0017]** Further, the EBSD method denotes an electron backscatter diffraction patterns (EBSD) method using a scanning electron microscope provided with a backscattered electron diffraction image system, and the OIM denotes data analysis software (orientation imaging microscopy: OIM) for analyzing crystal orientation using data measured by EBSD. Further, the CI value denotes a confidence index, which is a numerical value displayed as a numerical value showing the reliability of crystal orientation determination when analyzed using analysis software OIM Analysis (Ver. 7.3.1) of an EBSD device (for example, "EBSD Reader: Using OIM (Revised 3rd Edition)" written by Seiichi Suzuki, September 2009, published by TSL Solutions Inc.).

**[0018]** In a case where the structure of the measurement point measured by the EBSD method and analyzed by OIM is a deformed structure, the crystal pattern is not clear; and therefore, the reliability of crystal orientation determination is lowered, and the CI value is lowered. In particular, in a case where the CI value is 0.1 or less, it is determined that the structure of the measurement point is a deformed structure.

**[0019]** Further, the special grain boundary is defined as a coincidence boundary in which a  $\Sigma$  value satisfies a relationship of  $3 \leq \Sigma \leq 29$ , and the  $\Sigma$  value is crystallographically defined based on CSL theory (Kronberg et al: Trans. Met. Soc. AIME, 185, 501 (1949)), and the coincidence boundary is a grain boundary in which the intrinsic corresponding site lattice orientation defect  $Dq$  satisfies a relationship of  $Dq \leq 15^\circ/\Sigma^{1/2}$  (D. G. Brandon: Acta. Metallurgica. Vol. 14, p. 1479, (1966)).

**[0020]** In addition, the random grain boundary is a grain boundary other than the special grain boundary having a coincidence orientation relationship in which a  $\Sigma$  value is 29 or less and satisfies  $Dq \leq 15^\circ/\Sigma^{1/2}$ . That is, the special grain boundary has a coincidence orientation relationship in which a  $\Sigma$  value is 29 or less and satisfies  $Dq \leq 15^\circ/\Sigma^{1/2}$ , and the grain boundary other than the special grain boundary is the random grain boundary.

**[0021]** Further, as the grain boundary triple junctions, four kinds of grain boundary triple junctions,  $J_0$  where all three grain boundaries are random grain boundaries,  $J_1$  where one grain boundary is a special grain boundary and two grain boundaries are random grain boundaries,  $J_2$  where two grain boundaries are special grain boundaries and one grain boundary is a random grain boundary, and  $J_3$  where all three grain boundaries are special grain boundaries, are present.

**[0022]** Therefore, the ratio  $NF_{J_3}$  of  $J_3$ , where all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain boundary triple junctions (the ratio of the number of  $J_3$  to the number of all grain boundary triple junctions) is defined by  $NF_{J_3} = \Sigma J_3 / (\Sigma J_0 + \Sigma J_1 + \Sigma J_2 + \Sigma J_3)$  when the total number of  $J_0$  is represented by  $\Sigma J_0$ , the total number of  $J_1$  is represented by  $\Sigma J_1$ , the total number of  $J_2$  is represented by  $\Sigma J_2$ , and the total number of  $J_3$  is represented by  $\Sigma J_3$ .

**[0023]** Further, the ratio  $NF_{J_2}$  of  $J_2$ , where two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to

all grain boundary triple junctions (the ratio of the number of J2 to the number of all grain boundary triple junctions) is defined by  $NF_{J2} = \Sigma J2 / (\Sigma J0 + \Sigma J1 + \Sigma J2 + \Sigma J3)$ .

**[0024]** According to the pure copper plate or sheet with the above-described configuration, the amount of Cu is set to 99.96% by mass or greater, and when the average crystal grain size of the crystal grains on the rolled surface is represented by X ( $\mu\text{m}$ ) and the amount of Ag is represented by Y (mass ppm), an expression of  $1 \times 10^{-8} \leq X^{-3}Y^{-1} \leq 1 \times 10^{-5}$  is satisfied. Therefore, since a part of Ag is segregated at the grain boundaries, the grain boundary energy is lowered due to the segregation, and thus the coarsening of the crystal grains can be suppressed. In addition, the electrical conductivity of the pure copper plate or sheet can be ensured, and thus the pure copper plate or sheet can be used as the material of a member for electric or electronic devices used for high-current applications and a member for heat dissipation.

**[0025]** Further, a surface orthogonal to a rolling width direction is used as an observation surface, measurement regarding a matrix is performed on a measurement area of 10000  $\mu\text{m}^2$  or greater at every measurement intervals of 0.25  $\mu\text{m}$  by an EBSD method. The measured results are analyzed by data analysis software OIM to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The average grain size A is obtained by Area Fraction. Measurement regarding the matrix is performed at every measurement intervals which are 1/10 or less of the average grain size A by the EBSD method. The measured results are analyzed by the data analysis software OIM with a total measurement area of 10000  $\mu\text{m}^2$  or greater in a plurality of visual fields such that a total of 1000 or more crystal grains are included to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The coincidence boundary with  $\Sigma 29$  or less is defined as a special grain boundary, and the other grain boundaries are defined as random grain boundaries. In grain boundary triple junctions analyzed by the OIM, the ratio of J3, where all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain boundary triple junctions is defined as  $NF_{J3}$  and the ratio of J2, where two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $NF_{J2}$ .

**[0026]** In the pure copper plate or sheet according to one aspect of the present invention, since an expression of  $0.30 < (NF_{J2} / (1 - NF_{J3}))^{0.5} \leq 0.48$  is satisfied and the grain boundary network is formed of special grain boundaries with low energy, the driving force for recrystallization during heating is small, and the grain growth can be suppressed.

**[0027]** In the pure copper plate or sheet according to one aspect of the present invention, it is preferable that a total amount of Mg and Sn is set to be in a range of 0.1 mass ppm or greater and 100 mass ppm or less.

**[0028]** In this case, since the pure copper plate or sheet contains Mg and Sn at a total amount of 0.1 mass ppm or greater, and Mg and Sn correspond to the elements that suppress the growth of crystal grains, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment. Further, the electrical conductivity can be sufficiently ensured by limiting the total amount of Mg and Sn to 100 mass ppm or less.

**[0029]** Further, in the pure copper plate or sheet according to one aspect of the present invention, it is preferable that an amount of S is set to be in a range of 1 mass ppm or greater and 20 mass ppm or less.

**[0030]** In this case, since the pure copper plate or sheet contains 1 mass ppm or greater of S corresponding to the element that suppresses the growth of crystal grains, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment. Further, the hot workability can be sufficiently ensured by limiting the amount of S to 20 mass ppm or less.

**[0031]** Further, in the pure copper plate or sheet according to one aspect of the present invention, it is preferable that a total amount of Pb, Se, and Te is 0.3 mass ppm or greater and 10 mass ppm or less.

**[0032]** Pb, Se, and Te, which may be contained as inevitable impurities, are elements that are segregated at the crystal grain boundaries and suppress the coarsening of the crystal grains. Therefore, in a case where the pure copper plate or sheet contains these elements at a total amount of 0.3 mass ppm or greater, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment. Further, in a case where a large amount of these elements are present, the elements also have an effect of suppressing segregation at the grain boundaries of Ag, and thus the hot workability is lowered. Therefore, in a case where the total amount of Pb, Se, and Te is set to 10 mass ppm or less, the effect of suppressing the grain growth can be sufficiently exhibited without impairing the effect of Ag.

**[0033]** Further, in the pure copper plate or sheet according to one aspect of the present invention, it is preferable that a total amount of Sr, Ba, Ti, Zr, Hf, and Y is 10 mass ppm or less.

**[0034]** Sr, Ba, Ti, Zr, Hf, and Y may be contained as inevitable impurities, and there is a concern that these elements are segregated at the crystal grain boundaries to prevent the segregation of Ag, and these elements generates compounds with elements (S, Se, Te, and the like) that suppress the coarsening of the crystal grains to impair the effect of elements that suppress the coarsening of the crystal grains. Therefore, the effect of the elements that suppress the growth of

crystal grains (the effect of suppressing the growth of crystal grains) can be sufficiently exhibited by limiting the total amount of Sr, Ba, Ti, Zr, Hf, and Y to 10 mass ppm or less, and thus the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment.

**[0035]** Further, in the pure copper plate or sheet according to one aspect of the present invention, it is preferable that a total amount of Al, Cr, P, Be, Cd, Ni, and Fe is 0.3 mass ppm or greater and 10 mass ppm or less.

**[0036]** The elements such as Al, Cr, P, Be, Cd, Ni, and Fe, which may be contained as inevitable impurities, have an effect of suppressing the grain growth due to solid solution in the copper matrix, segregation at the grain boundaries, and formation of oxides. Therefore, in a case where the pure copper plate or sheet contains these elements at a total amount of 0.3 mass ppm or greater, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment. Further, in a case where a large amount of such elements are present, there is a concern that these elements are segregated at the crystal grain boundaries to prevent the segregation of Ag. Therefore, the effect of the elements that suppress the growth of crystal grains (the effect of suppressing the growth of crystal grains) can be sufficiently exhibited by limiting the total amount of Al, Cr, P, Be, Cd, Ni, and Fe to 10 mass ppm or less, and thus the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment.

**[0037]** Further, in the pure copper plate or sheet according to one aspect of the present invention, it is preferable that a ratio  $d_{\max}/d_{\text{ave}}$  of a maximum crystal grain size  $d_{\max}$  to an average crystal grain size  $d_{\text{ave}}$  in a range of 50 mm  $\times$  50 mm after a heat treatment maintained at 800°C for 1 hour is 20 or less, and the average crystal grain size  $d_{\text{ave}}$  is 400  $\mu\text{m}$  or less.

**[0038]** In this case, even when the pure copper plate or sheet is heated under the above-described conditions, the coarsening and non-uniformity of the crystal grains can be reliably suppressed, and the occurrence of poor appearance can be further suppressed.

**[0039]** Further, in the pure copper plate or sheet according to one aspect of the present invention, it is preferable that a Vickers hardness is 150 Hv or less.

**[0040]** In a case where the Vickers hardness is 150 Hv or less, since the pure copper plate or sheet is sufficiently soft, and the characteristics as a pure copper plate or sheet are ensured, the pure copper plate or sheet is particularly suitable as a material for electric or electronic components used for high-current applications.

#### Effects of Invention

**[0041]** According to one aspect of the present invention, it is possible to provide a pure copper plate or sheet that has high electrical conductivity and is capable of suppressing coarsening and non-uniformity of crystal grains even after a heat treatment.

#### BRIEF DESCRIPTION OF DRAWINGS

**[0042]** Fig. 1 is a flow chart showing a method for producing a pure copper plate or sheet according to the present embodiment.

#### EMBODIMENTS FOR CARRYING OUT THE INVENTION

**[0043]** Hereinafter, a pure copper plate or sheet according to an embodiment of the present invention will be described.

**[0044]** The pure copper plate or sheet according to the present embodiment is used as a material for electric or electronic components such as a heat sink or a thick copper circuit and is used by being bonded to, for example, a ceramic substrate in a case of forming the above-described electric or electronic components.

**[0045]** The pure copper plate or sheet according to the present embodiment contains 99.96% by mass or greater of Cu, and when the average crystal grain size of crystal grains in a rolled surface is represented by X ( $\mu\text{m}$ ) and the amount of Ag is represented by Y (mass ppm), the following relational expression is satisfied.

$$1 \times 10^{-8} \leq X^{-3} \times Y^{-1} \leq 1 \times 10^{-5}$$

**[0046]** In the copper alloy for electric or electronic devices according to the embodiment of the present invention, a surface orthogonal to a rolling width direction is used as an observation surface, measurement regarding a matrix is performed on a measurement area of 10000  $\mu\text{m}^2$  or greater at every measurement intervals of 0.25  $\mu\text{m}$  by an EBSD method. The measured results are analyzed by data analysis software OIM to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The average grain size A is acquired by Area

Fraction using the data analysis software OIM. The measurement regarding the matrix is performed at every measurement intervals which are 1/10 or less of the average grain size A by the EBSD method. The measured results are analyzed by the data analysis software OIM with a total measurement area of 10000  $\mu\text{m}^2$  or greater in a plurality of visual fields such that a total of 1000 or more crystal grains are included to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The coincidence boundary with  $\Sigma 29$  or less is defined as a special grain boundary, and the other grain boundaries are defined as random grain boundaries. In grain boundary triple junctions analyzed by the OIM, when the ratio of J3, where all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain boundary triple junctions is defined as  $\text{NF}_{J3}$  and the ratio of J2, where two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $\text{NF}_{J2}$ , an expression of  $0.30 < (\text{NF}_{J2}/(1 - \text{NF}_{J3}))^{0.5} \leq 0.48$  is satisfied.

**[0047]** As described above, the matrix is measured twice by the EBSD method. In the first measurement, the average grain size A is obtained. The measurement interval in the second measurement is determined by the obtained average grain size A.

**[0048]** In the pure copper plate or sheet according to the present embodiment, it is preferable that the total amount of Mg and Sn is set to be in a range of 0.1 mass ppm or greater and 100 mass ppm or less.

**[0049]** Further, in the pure copper plate or sheet according to the present embodiment, it is preferable that the amount of S is set to be in a range of 1 mass ppm or greater and 20 mass ppm or less.

**[0050]** Further, in the pure copper plate or sheet according to the present embodiment, it is preferable that the total amount of Pb, Se, and Te is 0.3 mass ppm or greater and 10 mass ppm or less.

**[0051]** Further, in the pure copper plate or sheet according to the present embodiment, it is preferable that the total amount of Sr, Ba, Ti, Zr, Hf, Y (A element group) is 10 mass ppm or less.

**[0052]** Further, in the pure copper plate or sheet according to the present embodiment, it is preferable that the total amount of Al, Cr, P, Be, Cd, Ni, and Fe (M element group) is 0.3 mass ppm or greater and 10 mass or less.

**[0053]** The composition of the pure copper plate or sheet can also be described as follows.

**[0054]** The pure copper plate or sheet contains 99.96% by mass or greater of Cu, and Ag, with the balance being inevitable impurities.

**[0055]** It is preferable that the pure copper plate or sheet further contains either one or both of Mg and Sn in a total amount of 0.1 mass ppm or greater and 100 mass ppm or less.

**[0056]** It is preferable that the pure copper plate or sheet further contains 1 mass ppm or greater and 20 mass ppm or less of S.

**[0057]** It is preferable that the pure copper plate or sheet further contains one or more selected from Pb, Se, and Te in a total amount of 0.3 mass ppm or greater and 10 mass ppm or less.

**[0058]** It is preferable that the pure copper plate or sheet further contains at least one selected from Sr, Ba, Ti, Zr, Hf, and Y in a total amount of 10 mass ppm or less.

**[0059]** It is preferable that the pure copper plate or sheet further contains one or more selected from Al, Cr, P, Be, Cd, Ni, and Fe in a total amount of 0.3 mass ppm or greater and 10 mass ppm or less.

**[0060]** In the above-described elements other than Cu, the preferable ranges of the amounts thereof are as described above even in a case where the pure copper plate or sheet contains the elements as inevitable impurities or intentionally. Further, it can also be said that the elements other than Cu are inevitable impurities. It can also be said that the inevitable impurities as the balance are elements other than the elements whose amounts are specified above.

**[0061]** In the pure copper plate or sheet according to the present embodiment, it is preferable that a ratio  $d_{\text{max}}/d_{\text{ave}}$  of a maximum crystal grain size  $d_{\text{max}}$  to an average crystal grain size  $d_{\text{ave}}$  in a range of 50 mm  $\times$  50 mm after a heat treatment maintained at 800°C for 1 hour is 20 or less and the average crystal grain size  $d_{\text{ave}}$  is 400  $\mu\text{m}$  or less.

**[0062]** Further, in the pure copper plate or sheet according to the present embodiment, it is preferable that the Vickers hardness is preferably 150 Hv or less.

**[0063]** Further, in the pure copper plate or sheet according to the present embodiment, it is preferable that the electrical conductivity is 97% IACS or greater.

**[0064]** In the pure copper plate or sheet according to the present embodiment, the reasons for specifying the component composition, the crystal structure, and various characteristics as described above will be described.

(Purity of Cu: 99.96% by mass or greater)

**[0065]** The electric or electronic component for high-current applications is required to have excellent electrical conductivity and heat dissipation in order to suppress heat generation during electrical conduction, and pure copper with particularly excellent electrical conductivity and heat dissipation is preferably used. Further, in a case where the com-

ponent is bonded to a ceramic substrate or the like, it is preferable that the deformation resistance is small so that the thermal strain generated during a thermal cycle can be mitigated.

**[0066]** Therefore, in the pure copper plate or sheet according to the present embodiment, the purity of Cu is specified to 99.96% by mass or greater.

**[0067]** Further, the purity of Cu is preferably 99.965% by mass or greater and more preferably 99.97% by mass or greater. Further, the upper limit of the purity of Cu is not particularly limited, but in a case where the purity thereof is greater than 99.9999% by mass, a special refining step is required, and the production cost significantly increases. Therefore, the upper limit thereof is preferably set to 99.9999% by mass or less.

(Relational expression of average crystal grain size X of crystal grains in rolled surface and amount Y of Ag)

**[0068]** Ag has a narrow solid solution limit at a low temperature and thus Ag is unlikely to be dissolved into the Cu matrix. Therefore, a part of Ag that is dissolved into the matrix is segregated at the grain boundaries by performing the heat treatment at a high temperature so that Ag is dissolved into copper (the Cu matrix) and performing warm working at a temperature of 150°C or higher and 350°C or lower. As a result, the grain boundary energy is decreased, the coarsening of a part of crystal grains during being heated at a high temperature and abnormal grain growth due to secondary recrystallization are suppressed, and thus uniformity of the crystal grain size can be realized. In a case where the average crystal grain size is sufficiently small with respect to the amount of added Ag, a plurality of grain boundaries in which the segregation of Ag is relatively small or Ag is not segregated are present. In such grain boundaries, grains are coarsened or grow abnormally when heated at a high temperature, and thus the variation in grain size increases.

**[0069]** When the average crystal grain size of the crystal grains in the rolled surface is represented by X  $\mu\text{m}$  and the amount of Ag is represented by Y mass ppm, the amount of Ag is small and the average crystal grain size is small in some cases when the value of  $X^{-3}Y^{-1}$  is large. Therefore, the grain boundary area contained per unit volume increases, and Ag cannot be sufficiently segregated at the grain boundaries. Therefore, the crystal grains are coarsened when heated at a high temperature, and the variation in grain size increases.

**[0070]** On the contrary, the amount of Ag is large and the average crystal grain size is large in some cases when the value of  $X^{-3}Y^{-1}$  is small. In this case, the effect of suppressing the grain growth is high, but the amount of expensive Ag is large, and the heat treatment temperature is high for a long time, and thus this results in a significant cost increase.

**[0071]** Therefore, in the pure copper plate or sheet according to the present embodiment, an expression of  $1 \times 10^{-8} \leq X^{-3}Y^{-1} \leq 1 \times 10^{-5}$  is satisfied.

**[0072]** The upper limit of  $X^{-3}Y^{-1}$  is preferably  $7.5 \times 10^{-6}$  or less, more preferably  $5.0 \times 10^{-6}$  or less, and still more preferably  $3.0 \times 10^{-6}$  or less, and most preferably  $2.0 \times 10^{-6}$  or less. Further, the lower limit of  $X^{-3}Y^{-1}$  is preferably  $5.0 \times 10^{-8}$  or greater and more preferably  $1.0 \times 10^{-7}$  or greater.

**[0073]** The substantial amount of Ag to be added is 5 mass ppm or greater and 150 mass ppm or less. In a case where the amount of Ag is less than 5 mass ppm, the grain size is required to be further increased, which may cause a problem of a cost increase as well as a problem of poor appearance due to the relative increase in grain size after the heat treatment. Therefore, the substantial lower limit of Ag is 5 mass ppm or greater. The lower limit is preferably 6 mass ppm or greater and more preferably 7 mass ppm or greater.

**[0074]** It is desirable to add Ag from the viewpoint of suppressing the coarsening of crystal grains, but the cost increases and the electrical conductivity decreases as the added amount of Ag increases. Therefore, the substantial upper limit thereof is 150 mass ppm or less. The upper limit thereof is preferably 100 mass ppm or less, more preferably 60 mass ppm or less, still more preferably 50 mass ppm or less, even still more preferably 40 mass ppm or less, even still more preferably 30 mass ppm or less, and most preferably 25 mass ppm or less.

(Ratio of grain boundary triple junctions)

**[0075]** The crystal grain growth when the pure copper plate or sheet is subjected to a heat treatment at a high temperature is due to a high grain boundary movement speed of random grain boundaries with high grain boundary energy. Accordingly, by forming two or three of the three grain boundaries constituting a grain boundary triple junction into special grain boundaries with low grain boundary energy represented by  $\Sigma 29$  or less, grain growth at a high temperature is suppressed and the uniformity of the crystal grain size can be realized.

**[0076]** Therefore, a surface orthogonal to a rolling width direction is used as an observation surface, measurement regarding a matrix is performed on a measurement area of 10000  $\mu\text{m}^2$  or greater at every measurement intervals of 0.25  $\mu\text{m}$  by an EBSD method. The measured results are analyzed by data analysis software OIM to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The average grain size A is obtained by Area Fraction. The measurement regarding the matrix is performed at every measurement intervals

which are 1/10 or less of the average grain size A by the EBSD method. The measured results are analyzed by the data analysis software OIM with a total measurement area of 10000  $\mu\text{m}^2$  or greater in a plurality of visual fields such that a total of 1000 or more crystal grains are included to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The coincidence boundary with  $\Sigma 29$  or less is defined as a special grain boundary, and the other grain boundaries are defined as random grain boundaries. In grain boundary triple junctions analyzed by the OIM, when the ratio of J3, where all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain boundary triple junctions is defined as  $\text{NF}_{\text{J3}}$  and the ratio of J2, where two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $\text{NF}_{\text{J2}}$ , the numerical value of  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is specified.

**[0077]** From the viewpoint of suppressing the grain growth, the higher the value of  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is, the more preferable it is. In a case where  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is 0.30 or less, the number of random grain boundaries with respect to the grain boundary network is relatively large, and the network length also increases. Therefore, the effect of suppressing the grain growth is reduced, and the crystal grain size is also non-uniform. On the contrary, in a case where  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is greater than 0.48, the burr height during press working increases. Therefore, the burr is unlikely to be managed, and thus there is a concern that the production cost may increase.

Accordingly, in the present embodiment,  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is set to be greater than 0.30 and 0.48 or less.

**[0079]** The upper limit of  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is preferably 0.47 or less and more preferably 0.46 or less. Further, the lower limit of  $(\text{NF}_{\text{J2}}/(1-\text{NF}_{\text{J3}}))^{0.5}$  is preferably greater than 0.31 and more preferably greater than 0.32.

**[0080]** In consideration of the grain boundary network, the number of J2 increases according to the number of J3 in order for the random grain boundaries of J0 and J1 to form special grain boundaries constituting J3 and the network. That is,  $\text{NF}_{\text{J2}}$  increases as  $\text{NF}_{\text{J3}}$  increases. Therefore,  $\text{NF}_{\text{J3}}$  is preferably 0.007 or greater, more preferably 0.008 or greater, and still more preferably 0.010 or greater. Further, in order to suppress the burr height,  $\text{NF}_{\text{J3}}$  is preferably 0.036 or less, more preferably 0.034 or less, and still more preferably 0.030 or less.

(Total amount of Mg and Sn: 0.1 mass ppm or greater and 100 mass ppm or less)

**[0081]** Mg and Sn are elements having an effect of suppressing coarsening of crystal grains by being dissolved into the matrix of copper. Therefore, in a case where the total amount of Mg and Sn is set to 0.1 mass ppm or greater in the present embodiment, the effect of suppressing the coarsening of crystal grains using Mg and Sn can be exhibited, and the coarsening of crystal grains can be reliably suppressed even after the heat treatment. Meanwhile, since there is a concern of an increase in the production cost and a decrease in the electrical conductivity due to the addition more than necessary, the amount of either one or both of Mg and Sn is set to less than 100 mass ppm.

**[0082]** The lower limit of the amount of either one or both of Mg and Sn is set to preferably 0.5 mass ppm or greater and more preferably 1 mass ppm or greater. Further, the upper limit of the total amount of Mg and Sn is preferably less than 80 mass ppm, more preferably less than 60 mass ppm, and most preferably less than 10 mass ppm.

(Amount of S: 1 mass ppm or greater and 20 mass ppm or less)

**[0083]** S is an element that has an effect of suppressing coarsening of crystal grains by suppressing movement of crystal grain boundaries and lowers hot workability.

**[0084]** Therefore, in a case where the amount of S is set to 1 mass ppm or more in the present embodiment, the effect of suppressing the coarsening of the crystal grains due to S can be sufficiently exhibited, and the coarsening of the crystal grains can be reliably suppressed even after the heat treatment. Further, in a case where the amount of S is limited to 20 mass ppm or less, the hot workability can be ensured.

**[0085]** The lower limit of the amount of S is preferably 2 mass ppm or greater and more preferably 3 mass ppm or greater. Further, the upper limit of the amount of S is preferably 17.5 mass ppm or less and more preferably 15 mass ppm or less.

(Total amount of Pb, Se, and Te: 0.3 mass ppm or greater and 10 mass ppm or less)

**[0086]** Pb, Se, and Te have a low solid solution limit in Cu and have an effect of suppressing coarsening of the crystal grains by being segregated at grain boundaries. Further, Pb, Se and Te are elements that also have an effect of suppressing segregation of Ag at grain boundaries by existing in a large amount and lower the hot workability.

**[0087]** Therefore, in the present embodiment, it is preferable to limit the total amount of Pb, Se, and Te to 10 mass ppm or less in order to exhibit the effect of suppressing coarsening and to ensure hot workability at the same time. In a



case where the total amount of Pb, Se, and Te is less than 0.3 mass ppm, the effect of suppression is reduced and the cost increases due to refining. Therefore, the lower limit of the total amount of Pb, Se, and Te is preferably set to 0.3 mass ppm or greater.

**[0088]** In order to further improve the hot workability, the upper limit of the total amount of Pb, Se, and Te is set to preferably 9 mass ppm or less, more preferably 8 mass ppm or less, and still more preferably 7 mass ppm or less. Further, the lower limit of the total amount of Pb, Se, and Te is set to preferably 0.4 mass ppm or greater and more preferably 0.5 mass ppm or greater.

(Total amount of Sr, Ba, Ti, Zr, Hf, and Y (A element group): 10 mass ppm or less)

**[0089]** Sr, Ba, Ti, Zr, Hf, and Y (A element group) contained as inevitable impurities are segregated at the crystal grain boundaries to generate compounds with elements (S, Se, Te, and the like) that suppress the coarsening of the crystal grains and thus may impair the effect of elements that suppress the coarsening of the crystal grains.

**[0090]** Therefore, in order to reliably suppress the coarsening of the crystal grains after heat treatment, it is preferable that the total amount of Sr, Ba, Ti, Zr, Hf, and Y (A element group) is set to 10 mass ppm or less.

**[0091]** The total amount of Sr, Ba, Ti, Zr, Hf, and Y (A element group) is preferably 7.5 mass ppm or less and more preferably 5 mass ppm or less. The lower limit is not particularly specified, but the cost may increase due to refining in a case where the total amount of Sr, Ba, Ti, Zr, Hf, and Y (A element group) is less than 0.01 mass ppm, and thus the total amount of Sr, Ba, Ti, Zr, Hf, and Y (A element group) is preferably 0.01 mass ppm or greater and more preferably 0.05 mass ppm or greater.

(Total amount of Al, Cr, P, Be, Cd, Ni, and Fe (M element group): 0.3 mass ppm or greater and 10 mass or less)

**[0092]** Al, Cr, P, Be, Cd, Ni, and Fe (M element group) have an effect of suppressing grain growth by being dissolved into the matrix of copper, being segregated at grain boundaries, and forming oxides.

**[0093]** Therefore, in order to reliably suppress the coarsening of crystal grains after the heat treatment, the total amount of Al, Cr, P, Be, Cd, Ni, and Fe (M element group) is preferably set to 0.3 mass ppm or greater. In a case where the pure copper plate or sheet intentionally contains Al, Cr, P, Be, Cd, Ni, and Fe (M element group), the lower limit of the total amount of Al, Cr, P, Be, Cd, Ni, and Fe (M element group) is set to more preferably 1.0 mass ppm or greater, still more preferably 1.5 mass ppm or greater, even still more preferably 2.0 mass ppm or greater, and most preferably 2.5 mass ppm or greater.

**[0094]** Further, since there is a concern that the segregation of Ag at grain boundaries is impaired and the electrical conductivity is decreased in a case where the pure copper plate or sheet contains Al, Cr, P, Be, Cd, Ni, and Fe (M element group) more than necessary, the upper limit of the total amount of Al, Cr, P, Be, Cd, Ni, and Fe (M element group) is set to preferably 10 mass ppm or less, more preferably less than 8 mass ppm, and still more preferably less than 5 mass ppm.

(Other inevitable impurities)

**[0095]** Examples of inevitable impurities other than the above-described elements include B, Bi, Ca, Sc, rare earth elements, V, Nb, Ta, Mo, W, Mn, Re, Ru, Os, Co, Rh, Ir, Pd, Pt, Au, Zn, Hg, Ga, In, Ge, As, Sb, Tl, N, C, Si, Li, H, and O. Since these inevitable impurities may decrease the electrical conductivity, it is preferable that the amount thereof is as small as possible.

(Average crystal grain size  $d_{ave}$  after heat treatment maintained at 800°C for 1 hour: 400  $\mu\text{m}$  or less)

**[0096]** In the pure copper plate or sheet according to the present embodiment, in a case where the average crystal grain size after heat treatment maintained at 800°C for 1 hour is 400  $\mu\text{m}$  or less, since the coarsening of crystal grains can be reliably suppressed even when the pure copper plate or sheet is heated at a temperature of 800°C or higher, the pure copper plate or sheet is particularly suitable as a material for a thick copper circuit and a heat sink to be bonded to a ceramic substrate.

**[0097]** Further, the upper limit of the average crystal grain size after the heat treatment maintained at 800°C for 1 hour is preferably 380  $\mu\text{m}$  or less and more preferably 350  $\mu\text{m}$  or less.

**[0098]** The lower limit of the average crystal grain size after the heat treatment maintained at 800°C for 1 hour is not particularly limited, but is usually 200  $\mu\text{m}$  or greater.

( $d_{\max}/d_{\text{ave}}$  after heat treatment maintained at 800°C for 1 hour: 20 or less)

**[0099]** In the pure copper plate or sheet according to the present embodiment, in a case where the ratio  $d_{\max}/d_{\text{ave}}$  of the maximum crystal grain size  $d_{\max}$  to the average crystal grain size  $d_{\text{ave}}$  in a range of 50 mm × 50 mm after the heat treatment maintained at 800°C for 1 hour is 20 or less, since the non-uniformity of crystal grains can be reliably suppressed even when the pure copper plate or sheet is heated at 800°C or higher, the pure copper plate or sheet is particularly suitable as a material for a thick copper circuit and a heat sink to be bonded to a ceramic substrate.

**[0100]** The ratio  $d_{\max}/d_{\text{ave}}$  of the maximum crystal grain size  $d_{\max}$  to the average crystal grain size  $d_{\text{ave}}$  in a range of 50 mm × 50 mm after the heat treatment maintained at 800°C for 1 hour is preferably 18 or less and more preferably 16 or less.

(Vickers hardness: 150Hv or less)

**[0101]** In the pure copper plate or sheet according to the present embodiment, in a case where the Vickers hardness is set to 150 Hv or less, the characteristics as a pure copper plate or sheet are ensured, and thus the pure copper plate or sheet is particularly suitable as a material for electric or electronic components for high-current applications. Further, since the pure copper plate or sheet is sufficiently soft, the thermal strain generated by the deformation of the pure copper plate or sheet can be released even in a case where the pure copper plate or sheet is bonded to another member such as a ceramic substrate and a thermal cycle is loaded.

**[0102]** The Vickers hardness is preferably 140 Hv or less, more preferably 120 Hv or less, still more preferably 100 Hv or less, and even still more preferably 95 Hv or less.

**[0103]** The lower limit of the Vickers hardness is not particularly limited, but is preferably 60 Hv or greater.

(Electrical conductivity: 97% IACS or greater)

**[0104]** In the pure copper plate or sheet according to the present embodiment, in a case where the electrical conductivity is set to 97% IACS or greater, the characteristics as a pure copper plate or sheet are ensured, and thus the pure copper plate or sheet is particularly suitable as a material of a member for electric or electronic devices used for high-current applications and a member for heat dissipation.

**[0105]** The electrical conductivity is preferably 98% IACS or greater, more preferably 99% IACS or greater, and even still more preferably 100% IACS or greater.

**[0106]** The upper limit of the electrical conductivity is not particularly limited, but is usually 103% IACS or less.

**[0107]** Next, a method of producing the pure copper plate or sheet according to the present embodiment having these configurations will be described with reference to the flow chart of Fig. 1.

(Melting and casting step S01)

**[0108]** First, the above-described elements are added to molten copper obtained by melting the copper raw material to adjust components; and thereby, a molten copper alloy is produced. Further, a single element, a base alloy, or the like can be used for addition of various elements. In addition, raw materials containing the above-described elements may be melted together with the copper raw material. Further, a recycled material or a scrap material of the alloy according to the present embodiment may be used. As the molten copper, so-called 4 NCu having a purity of 99.99% by mass or greater or so-called 5 NCu having a purity of 99.999% by mass or greater is preferably used. In the melting step, in order to suppress oxidation of additive elements and reduce the hydrogen concentration, atmosphere-controlled melting is performed using an inert gas atmosphere (for example, Ar gas or N<sub>2</sub> gas) in which the vapor pressure of H<sub>2</sub>O is low and the holding time during melting is set to the minimum.

**[0109]** Further, the molten copper alloy in which the components have been adjusted is injected into a mold to produce an ingot. In consideration of mass production, it is preferable to use a continuous casting method or a semi-continuous casting method.

**[0110]** The cooling rate of the molten metal is set to preferably 0.1 °C/sec or greater and more preferably 0.5°C/sec or greater.

(Hot working step S02)

**[0111]** Next, hot working is performed to make the structure uniform. The hot working temperature is not particularly limited, but is preferably set to be in a range of 500°C or higher and 1000°C or lower.

**[0112]** The total working rate of hot working is preferably 50% or greater, more preferably 60% or greater, and still more preferably 70% or greater.

**[0113]** Further, a cooling method after the hot working is not particularly limited, but it is preferable to perform air cooling or water cooling.

**[0114]** Further, the working method in the hot working step S02 is not particularly limited, and examples of the method which can be employed include rolling, extruding, groove rolling, forging, and pressing.

(Rough working step S03)

**[0115]** In order to work the pure copper plate or sheet in a predetermined shape, rough working is performed. In this rough working step S03, warm working is carried out at a temperature of 150°C or higher and 350°C or lower. By carrying out warm working at a temperature of 150°C or higher and 350°C or lower, Ag can be segregated in the vicinity of the grain boundaries, and the grain boundary energy can be lowered. In this step, warm working may be combined with cold working. In that case, warm working may be performed in a plurality of passes before the final working. For example, in a case of rolling, the final 3 or more passes may be defined as warm working.

(Recrystallization heat treatment step S04)

**[0116]** Next, a heat treatment is performed on the copper material after the rough working step S03 for the objective of recrystallization. The grain size of the recrystallized grains is preferably 10 μm or greater. In a case where the recrystallized grains are fine, the growth of the crystal grains and the non-uniformity of the structure may be promoted when the recrystallized grains are subsequently heated to a temperature of 800°C or higher. The crystal grain size after recrystallization is preferably 15 μm or greater, more preferably 20 μm or greater, and still more preferably 25 μm or greater.

**[0117]** The heat treatment conditions in the recrystallization heat treatment step S04 are not particularly limited, but it is preferable that the heat treatment is performed at a heat treatment temperature of 200°C or higher and 900°C or lower for a holding time of 1 second or longer and 10 hours or shorter.

**[0118]** Further, in order to obtain a desired shape, the rough working step S03 and the recrystallization heat treatment step S04 may be repeatedly performed two or more times.

(Temper deforming step S05)

**[0119]** Next, in order to adjust the strength of the material, the copper material after the recrystallization heat treatment step S04 may be subjected to temper deforming. The working rate of the temper deforming is not particularly limited, but it is preferable that the temper deforming is performed at a working rate of greater than 0% and 50% or less in order to adjust the strength of the material. It is more preferable to limit the working rate to 3% or greater and 40% or less.

**[0120]** Further, as necessary, the heat treatment may be further performed after the temper deforming in order to remove the residual strain.

**[0121]** By performing each of the above-described steps, the pure copper plate or sheet according to the present embodiment is produced.

**[0122]** According to the pure copper plate or sheet of the present embodiment with the above-described configuration, when the average crystal grain size of the crystal grains in the rolled surface is represented by X (μm) and the amount of Ag is represented by Y (mass ppm), a relational expression of  $1 \times 10^{-8} \leq X^{-3}Y^{-1} \leq 1 \times 10^{-5}$  is satisfied. Therefore, a part of Ag is segregated at the grain boundaries to reduce the grain boundary energy, and thus the coarsening of the crystal grains can be suppressed.

**[0123]** Further, a surface orthogonal to a rolling width direction is used as an observation surface, measurement regarding a matrix is performed on a measurement area of 10000 μm<sup>2</sup> or greater at every measurement intervals of 0.25 μm by an EBSD method. The measured results are analyzed by data analysis software OIM to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The average grain size A is obtained by Area Fraction. The measurement regarding the matrix is performed at every measurement intervals which are 1/10 or less of the average grain size A by the EBSD method. The measured results are analyzed by the data analysis software OIM with a total measurement area of 10000 μm<sup>2</sup> or greater in a plurality of visual fields such that a total of 1000 or more crystal grains are included to obtain a CI value in each measurement point. The measurement point in which a CI value is 0.1 or less is removed. The orientation difference between crystal grains is analyzed by the data analysis software OIM, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The coincidence boundary with Σ29 or less is defined as a special grain boundary, and the other grain boundaries are defined as random grain boundaries. In grain boundary triple junctions analyzed by the OIM, when the ratio of J3, where all three grain boundaries constituting a grain boundary triple junction

are special grain boundaries, to all grain boundary triple junctions is defined as  $NF_{J3}$  and the ratio of  $J2$ , where two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $NF_{J2}$ , an expression of  $0.30 \leq (NF_{J2}/(1 - NF_{J3}))^{0.5} \leq 0.48$  is satisfied. Therefore, the grain boundary network is formed of special grain boundaries with low energy, the driving force for recrystallization during heating is small, and the grain growth can be suppressed. The burr height during press working can also be suppressed.

**[0124]** In the present embodiment, in a case where the amount of Mg and Sn corresponding to the elements that suppress the growth of crystal grains is 0.1 mass ppm or greater, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment. Further, in a case where the total amount of Mg and Sn is limited to 100 mass ppm or less, the electrical conductivity can be sufficiently ensured.

**[0125]** Further, in the present embodiment, in a case where the amount of S is set to be in a range of 1 mass ppm or greater and 20 mass ppm or less, S, which is a kind of element that suppresses the growth of crystal grains, is segregated at the grain boundaries, and the coarsening and non-uniformity of the crystal grains during heating can be reliably suppressed. In addition, the hot workability can be ensured.

**[0126]** Further, in the present embodiment, in a case where the total amount of Pb, Se, and Te, which are elements that are segregated at the crystal grain boundaries to suppress the coarsening of the crystal grains, is set to 0.3 mass ppm or greater, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment. In addition, in a case where the total amount of Pb, Se, and Te is set to 10 mass ppm or less, the effect of suppressing the grain growth can be sufficiently exhibited without impairing the effect of Ag.

**[0127]** Further, in the present embodiment, in a case where the total amount of Sr, Ba, Ti, Zr, Hf, and Y (A element group) is set to 10 mass ppm or less, the elements of the A element group do not impair the effect of Ag which is an element that suppresses the growth of crystal grains and can suppress reaction of the elements in the A element group with S, Se, Te, and the like to generate compounds. Therefore, the effect of the elements that suppress the growth of crystal grains can be sufficiently exhibited. Therefore, the coarsening and non-uniformity of the crystal grains during heating can be reliably suppressed.

**[0128]** Further, in the present embodiment, in a case where the total amount of Al, Cr, P, Be, Cd, Ni, and Fe (M element group) is set to 0.3 mass ppm or greater, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment by dissolving into the matrix of copper, segregation at grain boundaries, and formation of oxides. In addition, in a case where the total amount of Al, Cr, P, Be, Cd, Ni, and Fe is limited to 10 mass ppm or less, the effect of suppressing the growth of crystal grains without suppressing the effect of Ag can be sufficiently exhibited, and the coarsening and non-uniformity of the crystal grains during heating can be reliably suppressed.

**[0129]** Further, in the present embodiment, in a case where the ratio  $d_{\max}/d_{\text{ave}}$  of the maximum crystal grain size  $d_{\max}$  to the average crystal grain size  $d_{\text{ave}}$  in a range of 50 mm  $\times$  50 mm after the heat treatment maintained at 800°C for 1 hour is 20 or less and the average crystal grain size  $d_{\text{ave}}$  is 400  $\mu\text{m}$  or less, the coarsening and non-uniformity of the crystal grains can be reliably suppressed even after the heat treatment, and the occurrence of poor appearance can be further suppressed.

**[0130]** Further, in the present embodiment, in a case where the Vickers hardness is 150 Hv or less, since the pure copper plate or sheet is sufficiently soft and the characteristics as a pure copper plate or sheet are ensured, the pure copper plate or sheet is particularly suitable as a material for electric or electronic components for high-current applications.

**[0131]** Hereinbefore, the pure copper plate or sheet which is an embodiment of the present invention has been described, but the present invention is not limited thereto this and can be appropriately modified without departing from the technical features of the present invention.

**[0132]** For example, in the above-described embodiment, the example of the method of producing the pure copper plate or sheet has been described, but the method of producing the pure copper plate or sheet is not limited to the description of the embodiment, and the pure copper plate or sheet may be produced by appropriately selecting a production method of the related art.

**[0133]** The average crystal grain size  $X$  of the crystal grains in the rolled surface, and the maximum crystal grain size  $d_{\max}$  and the average crystal grain size  $d_{\text{ave}}$  after the heat treatment maintained at 800°C for 1 hour are measured by the methods described in the following examples.

## EXAMPLES

**[0134]** Hereinafter, results of a verification test conducted to verify the effects of the present invention will be described.

**[0135]** A copper raw material formed of pure copper having a purity of 99.999% by mass or greater was prepared, the copper raw material was put into a high-purity graphite crucible, and subjected to high-frequency induction heating in a furnace in which the atmosphere was set to an Ar gas atmosphere so that the material was melted.

**[0136]** Each element was added to the obtained molten copper and poured into a carbon mold to produce an ingot

having the component composition listed in Tables 1 and 3. Thereafter, a part of the ingot was cut and machined to obtain an ingot having a thickness of 50 mm, a width of 100 mm, and a length of 100 mm.

[0137] Thereafter, the ingot was heated in an electric furnace at 800°C for 4 hours in an Ar gas atmosphere and subjected to a homogenization treatment.

[0138] The ingot after the homogenization heat treatment was hot-forged by free forging such that the forging ratio reached 4 or greater to obtain a plate or sheet material having a height of approximately 25 mm and a width of approximately 150 mm. The ingot was hot-forged at 500°C or higher, the ingot was reheated in an electric furnace maintained at 800°C when the surface temperature reached 500°C or lower, and the ingot was hot-forged again when the surface temperature reached approximately 600°C. The temperature when the hot forging was completed was 500°C or higher. After the completion of hot forging, a solutionizing heat treatment was performed for 1 minute in an electric furnace heated to 800°C.

[0139] The forged plate or sheet material was subjected to surface grinding to remove the oxide film on the surface.

[0140] Thereafter, the rolling roll was heated to 300°C, and rough rolling (warm rolling) was carried out at the rolling rate listed in the tables. The copper plate or sheet material after the warm rolling was subjected to the recrystallization heat treatment at the heat treatment temperature listed in Tables 2 and 4 using an electric furnace to adjust the crystal grain size to 10  $\mu\text{m}$  or greater and 150  $\mu\text{m}$  or less.

[0141] Next, the copper material after the recrystallization heat treatment was subjected to temper rolling under the conditions listed in Tables 2 and 4; and thereby, a strip for characteristic evaluation (test piece for characteristic evaluation) having a width of 60 mm and the thickness listed in Tables 2 and 4 were produced.

[0142] Next, the following items were evaluated.

(Composition analysis)

[0143] Measurement specimens were collected from the obtained ingot, and the amount of each element was measured using a glow discharge mass spectrometer (GD-MS). The measurement was performed at two sites, the center portion of the specimen and the end portion of the specimen in the width direction, and the larger amount was defined as the amount of the sample. The measured results are listed in Tables 1 and 3.

(Ratio of grain boundary triple junctions)

[0144] The crystal grain boundaries (special grain boundaries and random grain boundaries) and the grain boundary triple junctions were measured by an EBSD measuring device and OIM analysis software using a cross section orthogonal to the rolling width direction, that is, a transverse direction (TD) surface as an observation surface. Mechanical polishing was performed using waterproof abrasive paper and diamond abrasive grains. Next, finish polishing was performed using a colloidal silica solution. Thereafter, measurement regarding a matrix was performed on a measurement area of 10000  $\mu\text{m}^2$  or greater at every measurement intervals of 0.25  $\mu\text{m}$  at an electron beam acceleration voltage of 20 kV by an EBSD method using an EBSD measuring device (Quanta FEG 450, manufactured by FEI, OIM Data Collection, manufactured by EDAX/TSL (currently AMETEK)) and analysis software (OIM Data Analysis ver. 7.3.1, manufactured by EDAX/TSL (currently AMETEK)). The measured results were analyzed by the data analysis software OIM to obtain CI values at each measurement point. The measurement points in which a CI value was 0.1 or less were removed. The orientation difference between crystal grains was analyzed by the data analysis software OIM. A boundary having 15° or more of an orientation difference between neighboring measuring points was assigned as a grain boundary. The average grain size A was acquired by Area Fraction. Thereafter, measurement regarding the matrix was performed at every measurement intervals which were 1/10 or less of the average grain size A by the EBSD method. The measured results were analyzed by the data analysis software OIM with a measurement area where the total area of a plurality of visual fields was 10000  $\mu\text{m}^2$  or greater such that a total of 1000 or more crystal grains were included, to obtain a CI value in each measurement point. The measurement points in which a CI value was 0.1 or less were removed. The orientation difference between crystal grains was analyzed by the data analysis software OIM. A boundary having 15° or more of an orientation difference between neighboring measuring points was assigned as a grain boundary. Further, for the three grain boundaries constituting each grain boundary triple junction, the special grain boundary and the random grain boundary were identified by using the CSL sigma value calculated by the Neighboring grid point. The coincidence grain boundaries with greater than  $\Sigma 29$  were regarded as random grain boundaries.

(Press workability)

[0145] A plurality of circular holes ( $\phi 8$  mm) were punched out from the strip for characteristic evaluation using a metal die, the burr height was measured, and the press workability was evaluated.

[0146] The clearance of the metal die was set to approximately 3% with respect to the thickness of the plate or sheet,

and punching was performed at a punching speed of 50 spm (stroke per minute). The cut surface on the punched hole side was observed, the burr heights at 10 or more points were measured, and the ratio of the burr height to the thickness of the plate or sheet was acquired.

**[0147]** A case where the ratio of the highest value of the burr height to the thickness of the plate or sheet was 3.0% or less was evaluated as "A" (good). A case where the ratio of the highest value of the burr height to the thickness of the plate or sheet was greater than 3.0% was evaluated as "B" (poor). The evaluation results are listed in Tables 5 and 6.

(Vickers hardness)

**[0148]** The Vickers hardness was measured with a test load of 0.98 N in conformity with the micro Vickers hardness test method specified in JIS Z 2244. Further, the rolled surface of the test piece for characteristic evaluation was used as the measurement position. The evaluation results are listed in Tables 5 and 6.

(Electrical conductivity)

**[0149]** Test pieces having a width of 10 mm and a length of 60 mm were collected from each strip for characteristic evaluation and the electrical resistance was acquired according to a 4 terminal method. Further, the dimension of each test piece was measured using a micrometer and the volume of the test piece was calculated. In addition, the electrical conductivity was calculated from the measured electrical resistance value and volume. The evaluation results are listed in Tables 5 and 6.

**[0150]** Further, the test pieces were collected such that the longitudinal directions thereof were parallel to the rolling direction of each strip for characteristic evaluation.

(Crystal grain size before heat treatment)

**[0151]** A 20 mm × 20 mm sample was cut out from the obtained strip for characteristic evaluation, and the average crystal grain size was measured by an electron backscatter diffraction patterns (SEM-EBSD) measuring device.

**[0152]** The rolled surface was mechanically polished using waterproof abrasive paper and diamond abrasive grains. Next, finish polishing was performed using a colloidal silica solution. Thereafter, measurement regarding the matrix was performed on a measurement area of 10000  $\mu\text{m}^2$  or greater at every measurement intervals of 0.25  $\mu\text{m}$  at an electron beam acceleration voltage of 20 kV by an EBSD method using an EBSD measuring device (Quanta FEG 450, manufactured by FEI, OIM Data Collection, manufactured by EDAX/TSL (currently AMETEK)) and analysis software (OIM Data Analysis ver. 7.3.1, manufactured by EDAX/TSL (currently AMETEK)). The measured results were analyzed by the data analysis software OIM to obtain CI values at each measurement point. The measurement points in which a CI value was 0.1 or less were removed. The orientation difference between crystal grains was analyzed by the data analysis software OIM. A boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary. The average grain size A was acquired by Area Fraction. Thereafter, measurement regarding the matrix was performed at every measurement intervals which were 1/10 or less of the average grain size A by the EBSD method. The measured results were analyzed by the data analysis software OIM with a measurement area where the total area of a plurality of visual fields was 10000  $\mu\text{m}^2$  or greater such that a total of 1000 or more crystal grains were included, to obtain a CI value in each measurement point. The measurement points in which a CI value was 0.1 or less were removed. The orientation difference between crystal grains was analyzed by the data analysis software OIM. A boundary having 15° or more of an orientation difference between neighboring measuring points was assigned as a large-angle grain boundary, and a boundary having less than 15° of an orientation difference between neighboring measuring points was assigned as a small-angle grain boundary. A crystal grain boundary map was created using a large-angle grain boundary, and five line segments having a predetermined length were drawn at predetermined intervals in the longitudinal direction and the transverse direction on the crystal grain boundary map in conformity with the cutting method of JIS H 0501. The number of crystal grains that were completely cut was counted, and the average value of the lengths of the cut grains was calculated as the average crystal grain size before the heat treatment. The evaluation results are listed in Tables 5 and 6.

**[0153]** The average crystal grain size before the heat treatment is also the average crystal grain size X  $\mu\text{m}$  of the crystal grains in the rolled surface. The values of  $X^{-3}Y^{-1}$  in which the average crystal grain size of the crystal grains in the rolled surface was represented by X  $\mu\text{m}$  and the amount of Ag was represented by Y mass ppm were calculated and listed in Tables 5 and 6. In a case where the calculated value is " $a \times 10^{-b}$ ", the value is described as " $aE-b$ " in Tables 5 and 6. For example, "1.2E-08" denotes " $1.2 \times 10^{-8}$ ".

(Crystal grain size after heat treatment)

**[0154]** A 60 mm × 60 mm sample was cut out from the strip for characteristic evaluation described above and subjected to a heat treatment maintained at 800°C for 1 hour. A 50 mm × 50 mm sample was cut out from this test piece, and the rolled surface was mirror-polished and etched. Thereafter, the surface was imaged with an optical microscope such that the rolling direction was on the side of the photograph. Among the observation sites, the site where the crystal grains were the finest and the field of view of approximately 1 mm<sup>2</sup> or greater was formed with a uniform grain size was selected, and observation and measurement were performed in the field of view of approximately 1 mm<sup>2</sup> or greater. Thereafter, five line segments having a predetermined length were drawn at predetermined intervals in the longitudinal direction and the transverse direction of the photograph according to the cutting method of JIS H 0501. The number of crystal grains that were completely cut was counted, and the average value of the lengths of the cut grains was calculated as the average crystal grain size  $d_{ave}$  after the heat treatment. The evaluation results are listed in Tables 5 and 6.

(Variation in grain size after heat treatment)

**[0155]** As described above, in the samples collected from the test piece that had been subjected to the heat treatment, the average value of the major axis and the minor axis of the coarsest crystal grains was defined as the maximum crystal grain size  $d_{max}$ , excluding twin crystals in a range of 50 mm × 50 mm. The major axis is the length of the longest line segment among the line segments connecting two points on the grain boundary (contour of the crystal grain), and the minor axis is the length of longest line segment among the line segments cut by the grain boundaries when a line is drawn perpendicularly to the major axis. A case where the ratio  $d_{max}/d_{ave}$  of the maximum crystal grain size to the above-described average crystal grain size  $d_{ave}$  was 20 or less was evaluated as "A" (good), and a case where the ratio  $d_{max}/d_{ave}$  thereof was greater than 20 was evaluated as "B" (poor). The evaluation results are listed in Tables 5 and 6.

Table 1

|                    |    | Component composition (mass ratio) |           |          |                   |                        |                              |                              |
|--------------------|----|------------------------------------|-----------|----------|-------------------|------------------------|------------------------------|------------------------------|
|                    |    | Cu<br>%                            | Ag<br>ppm | S<br>ppm | Mg +<br>Sn<br>ppm | Pb + Se +<br>Te<br>ppm | A<br>element<br>group<br>ppm | M<br>element<br>group<br>ppm |
| Invention Examples | 1  | 99.96 or greater                   | 52        | 0.9      | 0.06              | 0.23                   | 0.03                         | 0.16                         |
|                    | 2  | 99.96 or greater                   | 51        | 0.5      | 0.01              | 0.12                   | 0.03                         | 0.14                         |
|                    | 3  | 99.96 or greater                   | 50        | 0.9      | 0.07              | 0.25                   | 0.01                         | 0.14                         |
|                    | 4  | 99.96 or greater                   | 49        | 0.8      | 0.03              | 0.18                   | 0.01                         | 0.17                         |
|                    | 5  | 99.96 or greater                   | 143       | 0.8      | 0.02              | 0.18                   | 0.02                         | 0.20                         |
|                    | 6  | 99.96 or greater                   | 105       | 0.5      | 0.06              | 0.28                   | 0.02                         | 0.11                         |
|                    | 7  | 99.96 or greater                   | 39        | 0.7      | 0.05              | 0.19                   | 0.03                         | 0.14                         |
|                    | 8  | 99.96 or greater                   | 29        | 0.6      | 0.03              | 0.11                   | 0.03                         | 0.16                         |
|                    | 9  | 99.96 or greater                   | 24        | 0.8      | 0.01              | 0.21                   | 0.02                         | 0.18                         |
|                    | 10 | 99.96 or greater                   | 21        | 0.8      | 0.02              | 0.28                   | 0.03                         | 0.12                         |
|                    | 11 | 99.96 or greater                   | 21        | 0.9      | 0.04              | 0.21                   | 0.01                         | 0.19                         |
|                    | 12 | 99.96 or greater                   | 16        | 0.5      | 0.07              | 0.30                   | 0.03                         | 0.11                         |
|                    | 13 | 99.96 or greater                   | 11        | 0.7      | 0.07              | 0.16                   | 0.02                         | 0.17                         |
|                    | 14 | 99.96 or greater                   | 8         | 0.9      | 0.03              | 0.12                   | 0.01                         | 0.18                         |
|                    | 15 | 99.96 or greater                   | 6         | 0.5      | 0.10              | 0.20                   | 0.02                         | 0.11                         |
|                    | 16 | 99.96 or greater                   | 49        | 0.6      | 0.09              | 0.28                   | 0.01                         | 0.13                         |
|                    | 17 | 99.96 or greater                   | 39        | 0.8      | 0.04              | 0.16                   | 0.02                         | 0.15                         |
|                    | 18 | 99.96 or greater                   | 28        | 0.5      | 0.06              | 0.27                   | 0.03                         | 0.13                         |
|                    | 19 | 99.96 or greater                   | 26        | 0.7      | 0.03              | 0.24                   | 0.02                         | 0.16                         |
|                    | 20 | 99.96 or greater                   | 18        | 0.7      | 0.05              | 0.25                   | 0.01                         | 0.19                         |

A element group: one or two or more selected from Sr, Ba, Ti, Zr, Hf, and Y

M element group: one or two or more selected from Al, Cr, P, Be, Cd, Ni, and Fe



Table 2

|                    |    | Production step   |                      |                                     |                     | Thickness<br>mm |
|--------------------|----|-------------------|----------------------|-------------------------------------|---------------------|-----------------|
|                    |    | Hot working       | Rough<br>working     | Recrystallization<br>heat treatment | Temper<br>deforming |                 |
|                    |    | Temperature<br>°C | Rolling<br>rate<br>% | Temperature<br>°C                   | Rolling rate<br>%   |                 |
| Invention Examples | 1  | 800               | 95                   | 900                                 | 5                   | 1.0             |
|                    | 2  | 800               | 95                   | 850                                 | 5                   | 1.0             |
|                    | 3  | 800               | 95                   | 850                                 | 5                   | 1.0             |
|                    | 4  | 800               | 95                   | 800                                 | 5                   | 1.0             |
|                    | 5  | 800               | 95                   | 800                                 | 5                   | 1.0             |
|                    | 6  | 800               | 95                   | 800                                 | 5                   | 1.0             |
|                    | 7  | 800               | 95                   | 850                                 | 5                   | 1.0             |
|                    | 8  | 800               | 95                   | 900                                 | 5                   | 1.0             |
|                    | 9  | 800               | 95                   | 850                                 | 5                   | 1.0             |
|                    | 10 | 800               | 95                   | 800                                 | 5                   | 1.0             |
|                    | 11 | 800               | 95                   | 900                                 | 5                   | 1.0             |
|                    | 12 | 800               | 95                   | 800                                 | 5                   | 1.0             |
|                    | 13 | 800               | 95                   | 850                                 | 5                   | 1.0             |
|                    | 14 | 800               | 95                   | 900                                 | 5                   | 1.0             |
|                    | 15 | 800               | 95                   | 900                                 | 5                   | 1.0             |
|                    | 16 | 800               | 95                   | 850                                 | 10                  | 1.0             |
|                    | 17 | 800               | 95                   | 850                                 | 10                  | 1.0             |
|                    | 18 | 800               | 95                   | 850                                 | 10                  | 1.0             |
|                    | 19 | 800               | 95                   | 850                                 | 10                  | 1.0             |
|                    | 20 | 800               | 95                   | 800                                 | 10                  | 1.0             |

Table 3

|                                                                                                                                                                |    | Component composition (mass ratio) |        |       |             |                  |                     |                     |
|----------------------------------------------------------------------------------------------------------------------------------------------------------------|----|------------------------------------|--------|-------|-------------|------------------|---------------------|---------------------|
|                                                                                                                                                                |    | Cu %                               | Ag ppm | S ppm | Mg + Sn ppm | Pb + Se + Te ppm | A element group ppm | M element group ppm |
| Invention Examples                                                                                                                                             | 21 | 99.96 or greater                   | 20     | 0.7   | 0.03        | 0.21             | 0.03                | 0.12                |
|                                                                                                                                                                | 22 | 99.96 or greater                   | 7      | 0.9   | 0.03        | 0.15             | 0.03                | 0.17                |
|                                                                                                                                                                | 23 | 99.96 or greater                   | 8      | 0.8   | 0.06        | 0.20             | 0.03                | 0.16                |
|                                                                                                                                                                | 24 | 99.96 or greater                   | 6      | 0.7   | 0.07        | 0.28             | 0.01                | 0.13                |
|                                                                                                                                                                | 25 | 99.96 or greater                   | 5      | 0.8   | 0.07        | 0.29             | 0.03                | 0.13                |
|                                                                                                                                                                | 26 | 99.96 or greater                   | 7      | 3.9   | 1.50        | 1.20             | 0.50                | 2.70                |
|                                                                                                                                                                | 27 | 99.96 or greater                   | 11     | 15.0  | 0.03        | 0.30             | 0.02                | 1.50                |
|                                                                                                                                                                | 28 | 99.96 or greater                   | 21     | 1.9   | 80.00       | 0.29             | 0.10                | 1.60                |
|                                                                                                                                                                | 29 | 99.96 or greater                   | 25     | 3.0   | 0.06        | 9.30             | 0.01                | 0.16                |
|                                                                                                                                                                | 30 | 99.96 or greater                   | 9      | 3.2   | 0.07        | 0.19             | 0.50                | 1.08                |
|                                                                                                                                                                | 31 | 99.96 or greater                   | 14     | 3.5   | 0.02        | 0.29             | 8.60                | 1.24                |
|                                                                                                                                                                | 32 | 99.96 or greater                   | 19     | 3.5   | 0.50        | 0.70             | 0.02                | 9.70                |
|                                                                                                                                                                | 33 | 99.96 or greater                   | 17     | 7.0   | 0.05        | 0.19             | 0.03                | 1.31                |
| Comparative Examples                                                                                                                                           | 1  | 99.96 or greater                   | 2      | 0.7   | 0.07        | 0.21             | 0.02                | 1.40                |
|                                                                                                                                                                | 2  | 99.96 or greater                   | 7      | 0.8   | 0.02        | 0.15             | 0.02                | 1.31                |
|                                                                                                                                                                | 3  | 99.96 or greater                   | 5      | 0.4   | 0.08        | 0.28             | 0.02                | 1.09                |
|                                                                                                                                                                | 4  | 99.96 or greater                   | 1      | 0.6   | 0.05        | 0.20             | 0.01                | 1.30                |
| A element group: one or two or more selected from Sr, Ba, Ti, Zr, Hf, and Y<br>M element group: one or two or more selected from Al, Cr, P, Be, Cd, Ni, and Fe |    |                                    |        |       |             |                  |                     |                     |

Table 4

|                         |    | Production step   |                   |                                     |                     | Thickness<br>mm |
|-------------------------|----|-------------------|-------------------|-------------------------------------|---------------------|-----------------|
|                         |    | Hot working       | Rough<br>working  | Recrystallization heat<br>treatment | Temper<br>deforming |                 |
|                         |    | Temperature<br>°C | Rolling rate<br>% | Temperature °C                      | Rolling rate %      |                 |
| Invention<br>Examples   | 21 | 800               | 95                | 800                                 | 10                  | 1.0             |
|                         | 22 | 800               | 95                | 800                                 | 10                  | 1.0             |
|                         | 23 | 800               | 95                | 800                                 | 10                  | 1.0             |
|                         | 24 | 800               | 95                | 800                                 | 10                  | 1.0             |
|                         | 25 | 800               | 95                | 800                                 | 10                  | 1.0             |
|                         | 26 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 27 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 28 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 29 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 30 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 31 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 32 | 800               | 95                | 800                                 | 15                  | 1.0             |
|                         | 33 | 800               | 95                | 900                                 | 15                  | 1.0             |
| Comparative<br>Examples | 1  | 800               | 94                | 150                                 | 15                  | 1.0             |
|                         | 2  | 800               | 50                | 500                                 | 90                  | 1.0             |
|                         | 3  | 800               | 95                | 500                                 | 1                   | 1.0             |
|                         | 4  | 800               | 95                | 900                                 | 1                   | 1.0             |

Table 5

|                    | X <sup>3</sup> Y <sup>-1</sup> | (NF <sub>12</sub> /(1-NF <sub>13</sub> )) <sup>0.5</sup> | Press workability | Vickers hardness Hv | Electrical conductivity % IACS | Before heat treatment                    |                                          | After heat treatment                     |                         |
|--------------------|--------------------------------|----------------------------------------------------------|-------------------|---------------------|--------------------------------|------------------------------------------|------------------------------------------|------------------------------------------|-------------------------|
|                    |                                |                                                          |                   |                     |                                | Average crystal grain size $\mu\text{m}$ | Average crystal grain size $\mu\text{m}$ | Average crystal grain size $\mu\text{m}$ | Variation of grain size |
| Invention Examples | 1                              | 1.2E-08                                                  | 0.43              | A                   | 76                             | 101                                      | 116                                      | 275                                      | A                       |
|                    | 2                              | 5.5E-08                                                  | 0.43              | A                   | 78                             | 101                                      | 71                                       | 266                                      | A                       |
|                    | 3                              | 9.7E-08                                                  | 0.42              | A                   | 79                             | 101                                      | 59                                       | 274                                      | A                       |
|                    | 4                              | 9.3E-07                                                  | 0.42              | A                   | 79                             | 101                                      | 28                                       | 286                                      | A                       |
|                    | 5                              | 2.9E-07                                                  | 0.41              | A                   | 82                             | 100                                      | 29                                       | 271                                      | A                       |
|                    | 6                              | 8.9E-07                                                  | 0.44              | A                   | 80                             | 101                                      | 22                                       | 275                                      | A                       |
|                    | 7                              | 1.2E-07                                                  | 0.43              | A                   | 78                             | 101                                      | 60                                       | 272                                      | A                       |
|                    | 8                              | 7.0E-08                                                  | 0.41              | A                   | 75                             | 101                                      | 79                                       | 270                                      | A                       |
|                    | 9                              | 1.4E-07                                                  | 0.42              | A                   | 79                             | 101                                      | 66                                       | 281                                      | A                       |
|                    | 10                             | 6.9E-07                                                  | 0.43              | A                   | 76                             | 101                                      | 41                                       | 288                                      | A                       |
|                    | 11                             | 1.0E-07                                                  | 0.42              | A                   | 72                             | 101                                      | 77                                       | 289                                      | A                       |
|                    | 12                             | 6.0E-07                                                  | 0.45              | A                   | 75                             | 101                                      | 47                                       | 294                                      | A                       |
|                    | 13                             | 6.5E-07                                                  | 0.46              | A                   | 73                             | 101                                      | 52                                       | 297                                      | A                       |
|                    | 14                             | 1.8E-07                                                  | 0.43              | A                   | 73                             | 101                                      | 89                                       | 283                                      | A                       |
|                    | 15                             | 4.8E-08                                                  | 0.40              | A                   | 71                             | 101                                      | 151                                      | 288                                      | A                       |
|                    | 16                             | 1.0E-07                                                  | 0.41              | A                   | 85                             | 101                                      | 58                                       | 271                                      | A                       |
|                    | 17                             | 1.2E-07                                                  | 0.41              | A                   | 82                             | 101                                      | 60                                       | 275                                      | A                       |
|                    | 18                             | 1.2E-07                                                  | 0.36              | A                   | 81                             | 101                                      | 67                                       | 269                                      | A                       |
|                    | 19                             | 1.2E-07                                                  | 0.41              | A                   | 84                             | 101                                      | 68                                       | 271                                      | A                       |
|                    | 20                             | 1.0E-06                                                  | 0.40              | A                   | 76                             | 101                                      | 38                                       | 293                                      | A                       |

X: average crystal grain size ( $\mu\text{m}$ ) of crystal grains on rolled surface

Y: amount of Ag (mass ppm)

[0156]

Table 6

|                    |    | X-3Y-1   | (NF <sub>J2</sub> /(1-NF <sub>J3</sub> )) <sup>0.5</sup> | Press workability | Vickers hardness Hv | Electrical conductivity % IACS | Before heat treatment         |                               | After heat treatment          |                            |
|--------------------|----|----------|----------------------------------------------------------|-------------------|---------------------|--------------------------------|-------------------------------|-------------------------------|-------------------------------|----------------------------|
|                    |    |          |                                                          |                   |                     |                                | Average crystal grain size μm | Average crystal grain size μm | Average crystal grain size μm | Variation of grain size μm |
| Invention Examples | 21 | 6.3E-06  | 0.40                                                     | A                 | 79                  | 101                            | 20                            | 344                           | A                             |                            |
|                    | 22 | 2.2E-06  | 0.35                                                     | A                 | 79                  | 101                            | 40                            | 303                           | A                             |                            |
|                    | 23 | 1.6E-06  | 0.36                                                     | A                 | 78                  | 101                            | 43                            | 299                           | A                             |                            |
|                    | 24 | 5.1 E-06 | 0.37                                                     | A                 | 77                  | 101                            | 32                            | 319                           | A                             |                            |
|                    | 25 | 9.1E-06  | 0.36                                                     | A                 | 78                  | 101                            | 28                            | 361                           | A                             |                            |
|                    | 26 | 2.8E-06  | 0.32                                                     | A                 | 83                  | 100                            | 37                            | 289                           | A                             |                            |
|                    | 27 | 1.8E-06  | 0.31                                                     | A                 | 84                  | 101                            | 37                            | 281                           | A                             |                            |
|                    | 28 | 9.4E-07  | 0.35                                                     | A                 | 87                  | 100                            | 37                            | 263                           | A                             |                            |
|                    | 29 | 3.4E-07  | 0.34                                                     | A                 | 86                  | 101                            | 49                            | 259                           | A                             |                            |
|                    | 30 | 1.6E-06  | 0.36                                                     | A                 | 82                  | 101                            | 41                            | 284                           | A                             |                            |
|                    | 31 | 6.5E-07  | 0.33                                                     | A                 | 88                  | 101                            | 48                            | 266                           | A                             |                            |
|                    | 32 | 6.2E-07  | 0.34                                                     | A                 | 86                  | 101                            | 44                            | 267                           | A                             |                            |
|                    | 33 | 1.0E-07  | 0.34                                                     | A                 | 85                  | 101                            | 83                            | 245                           | A                             |                            |

(continued)

|                                                                                                      |   | X <sup>3</sup> Y <sup>-1</sup> | (NF <sub>J2</sub> /(1-NF <sub>J3</sub> )) <sup>0.5</sup> | Press workability | Vickers hardness Hv | Electrical conductivity % IACS | Before heat treatment         | After heat treatment          |                            |
|------------------------------------------------------------------------------------------------------|---|--------------------------------|----------------------------------------------------------|-------------------|---------------------|--------------------------------|-------------------------------|-------------------------------|----------------------------|
|                                                                                                      |   |                                |                                                          |                   |                     |                                | Average crystal grain size μm | Average crystal grain size μm | Variation of grain size μm |
| Comparative Examples                                                                                 | 1 | 5.0E-04                        | 0.31                                                     | A                 | 77                  | 101                            | 10                            | 452                           | B                          |
|                                                                                                      | 2 | 9.1E-06                        | 0.21                                                     | A                 | 154                 | 99                             | 25                            | 532                           | B                          |
|                                                                                                      | 3 | 8.1E-07                        | 0.51                                                     | B                 | 54                  | 101                            | 63                            | -                             | -                          |
|                                                                                                      | 4 | 9.3E-09                        | -                                                        |                   | -                   | -                              | 475                           | -                             | -                          |
| X: average crystal grain size (μm) of crystal grains on rolled surface<br>Y: amount of Ag (mass ppm) |   |                                |                                                          |                   |                     |                                |                               |                               |                            |

[0157] In Comparative Example 1,  $X^{-3}Y^{-1}$  was greater than the range of the present embodiment, the variation in the grain size after the heat treatment was evaluated as "B" (poor), and the grain size after the heat treatment was also greater than 400  $\mu\text{m}$ .

[0158] In Comparative Example 2,  $(\text{NF}_{\text{J}2}/(1 - \text{NF}_{\text{J}3}))^{0.5}$  was smaller than the range of the present embodiment, the variation in the grain size after the heat treatment was evaluated as "B" (poor), and the grain size after the heat treatment was also greater than 400  $\mu\text{m}$ .

[0159] In Comparative Example 3,  $(\text{NF}_{\text{J}2}/(1 - \text{NF}_{\text{J}3}))^{0.5}$  was greater than the range of the present embodiment, and the press workability was evaluated as "B" (poor). Therefore, the crystal grain size after the heat treatment was not evaluated.

[0160] In Comparative Example 4,  $X^{-3}Y^{-1}$  was smaller than the range of the present embodiment, and the crystal grain size before the heat treatment was greater than 400  $\mu\text{m}$ . Therefore, other evaluations were not performed.

[0161] On the contrary, in Invention Examples, the average crystal grain size after the heat treatment was small, and the variation in the grain size was small. In addition, the electrical conductivity was also 97% IACS or greater.

[0162] As described above, according to Invention Examples, it was confirmed that a pure copper plate or sheet which has excellent electrical conductivity and is capable of suppressing coarsening and non-uniformity of crystal grains even after heat treatment can be provided.

#### Industrial Applicability

[0163] The pure copper plate or sheet of the present embodiment can be suitably applied to electric or electronic components such as an insulating circuit substrate provided with a copper plate or sheet material as a heat sink or a thick copper circuit.

#### Claims

##### 1. A pure copper plate or sheet comprising:

99.96% by mass or greater of Cu,

wherein when an average crystal grain size of crystal grains in a rolled surface is represented by  $X \mu\text{m}$  and an amount of Ag is represented by  $Y$  mass ppm, a relational expression of  $1 \times 10^{-8} \leq X^{-3}Y^{-1} \leq 1 \times 10^{-5}$  is satisfied, a surface orthogonal to a rolling width direction is used as an observation surface, measurement regarding a matrix is performed on a measurement area of 10000  $\mu\text{m}^2$  or greater at every measurement intervals of 0.25  $\mu\text{m}$  by an EBSD method, measured results are analyzed by data analysis software OIM to obtain a CI value in each measurement point, a measurement point in which a CI value is 0.1 or less is removed, an orientation difference between crystal grains is analyzed, a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary, an average grain size  $A$  is acquired according to Area Fraction, measurement regarding the matrix is performed at every measurement intervals which are 1/10 or less of the average grain size  $A$  by the EBSD method, measured results are analyzed by the data analysis software OIM with a measurement area of 10000  $\mu\text{m}^2$  or greater in a plurality of visual fields such that a total of 1000 or more crystal grains are included to obtain a CI value in each measurement point, a measurement point in which a CI value is 0.1 or less is removed, an orientation difference between crystal grains is analyzed, and a boundary having 15° or more of an orientation difference between neighboring measuring points is assigned as a grain boundary, a coincidence boundary with  $\Sigma 29$  or less is defined as a special grain boundary, and the other grain boundaries are defined as random grain boundaries, in grain boundary triple junctions analyzed by the OIM, when a ratio of  $J_3$ , in which all three grain boundaries constituting a grain boundary triple junction are special grain boundaries, to all grain boundary triple junctions is defined as  $\text{NF}_{\text{J}3}$  and a ratio of  $J_2$ , in which two grain boundaries constituting a grain boundary triple junction are special grain boundaries and one grain boundary constituting the grain boundary triple junction is a random grain boundary, to all grain boundary triple junctions is defined as  $\text{NF}_{\text{J}2}$ , an expression of  $0.30 < (\text{NF}_{\text{J}2}/(1 - \text{NF}_{\text{J}3}))^{0.5} \leq 0.48$  is satisfied.

##### 2. The pure copper plate or sheet according to Claim 1,

wherein a total amount of Mg and Sn is set to be in a range of 0.1 mass ppm or greater and 100 mass ppm or less.

##### 3. The pure copper plate or sheet according to Claim 1 or 2,

wherein an amount of S is set to be in a range of 1 mass ppm or greater and 20 mass ppm or less.

##### 4. The pure copper plate or sheet according to any one of Claims 1 to 3,

wherein a total amount of Pb, Se, and Te is set to be in a range of 0.3 mass ppm or greater and 10 mass ppm or less.

- 5      5. The pure copper plate or sheet according to any one of Claims 1 to 4,  
wherein a total amount of Sr, Ba, Ti, Zr, Hf, and Y is 10 mass ppm or less.

6. The pure copper plate or sheet according to any one of Claims 1 to 5,  
wherein a total amount of Al, Cr, P, Be, Cd, Ni, and Fe is set to be in a range of 0.3 mass ppm or greater and 10  
mass ppm or less.

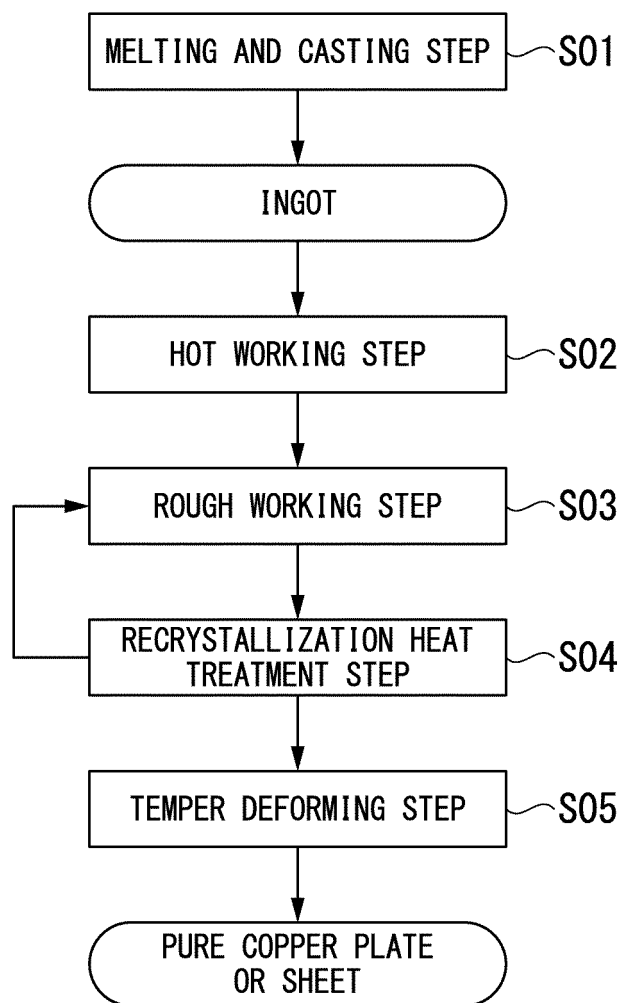
- 10      7. The pure copper plate or sheet according to any one of Claims 1 to 6,

wherein a ratio  $d_{\max}/d_{\text{ave}}$  of a maximum crystal grain size  $d_{\max}$  to an average crystal grain size  $d_{\text{ave}}$  in a range  
of 50 mm  $\times$  50 mm after a heat treatment maintained at 800°C for 1 hour is 20 or less, and  
the average crystal grain size  $d_{\text{ave}}$  is 400  $\mu\text{m}$  or less.

- 15      8. The pure copper plate or sheet according to any one of Claims 1 to 7,  
wherein a Vickers hardness is 150 Hv or less.



FIG. 1



## INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/034462

## A. CLASSIFICATION OF SUBJECT MATTER

Int.Cl. C22C9/00(2006.01)i, C22F1/00(2006.01)n, C22F1/08(2006.01)i  
 FI: C22C9/00, C22F1/08B, C22F1/00604, C22F1/00623, C22F1/00691B, C22F1/00691C,  
 C22F1/00630K, C22F1/00661A, C22F1/00651A, C22F1/00650F, C22F1/00682,  
 C22F1/00683, C22F1/00684C, C22F1/00685A, C22F1/00686A, C22F1/00694A,  
 C22F1/00694B, C22F1/00692A, C22F1/00685Z

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)

Int.Cl. C22C9/00, C22F1/00, C22F1/08

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

|                                                          |           |
|----------------------------------------------------------|-----------|
| Published examined utility model applications of Japan   | 1922-1996 |
| Published unexamined utility model applications of Japan | 1971-2020 |
| Registered utility model specifications of Japan         | 1996-2020 |
| Published registered utility model applications of Japan | 1994-2020 |

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages    | Relevant to claim No. |
|-----------|---------------------------------------------------------------------------------------|-----------------------|
| A         | WO 2016/158589 A1 (FURUKAWA ELECTRIC CO., LTD.) 06 October 2016 (2016-10-06)          | 1-8                   |
| A         | JP 2015-061950 A (JX NIPPON MINING AND METALS CORPORATION) 02 April 2015 (2015-04-02) | 1-8                   |
| A         | JP 2015-048521 A (JX NIPPON MINING AND METALS CORPORATION) 16 March 2015 (2015-03-16) | 1-8                   |
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| A         | JP 2012-094292 A (JX NIPPON MINING AND METALS CORPORATION) 17 May 2012 (2012-05-17)   | 1-8                   |



Further documents are listed in the continuation of Box C.



See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

"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

"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

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&" document member of the same patent family

Date of the actual completion of the international search  
11 November 2020

Date of mailing of the international search report  
24 November 2020

Name and mailing address of the ISA/  
Japan Patent Office  
3-4-3, Kasumigaseki, Chiyoda-ku,  
Tokyo 100-8915, Japan

Authorized officer

Telephone No.

INTERNATIONAL SEARCH REPORT  
Information on patent family members

International application No.

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|                   |                  | KR 10-2014-0057584 A |
| JP 2012-094292 A  | 17 May 2012      | (Family: none)       |

**REFERENCES CITED IN THE DESCRIPTION**

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- **KRONBERG et al.** *Trans. Met. Soc. AIME*, 1949, vol. 185, 501 [0019]
- **D. G. BRANDON.** *Acta. Metallurgica.*, 1966, vol. 14, 1479 [0019]