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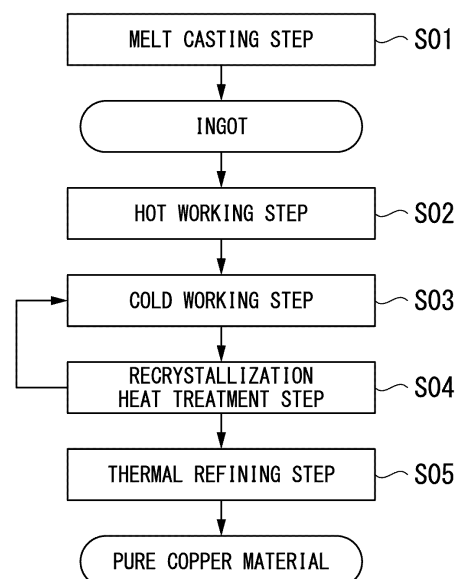
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(54) **COPPER MATERIAL AND HEAT-DISSIPATING MEMBER**

(57) Provided are a copper material capable of suppressing coarsening and non-uniformity of crystal grains even after heating, and a heat-dissipating member made of the copper material. A copper material has a composition in which a amount of Ca is in a range of 3 mass ppm or more and 400 mass ppm or less with the remainder being Cu and inevitable impurities, in a case in which the amount of Ca is defined as X (mass ppm) and the total amount of O, S, Se, and Te contained as inevitable impurities is defined as Y (mass ppm), $X/Y > 2$ is satisfied, and after heat treatment of holding the copper material at 800°C for 1 hour, the average crystal grain size is 200 μm or less and the area ratio of crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more.

FIG. 1



Description

TECHNICAL FIELD

[0001] The present invention relates to a copper material and a heat-dissipating member suitable for an electric and electronic component such as a heat sink or a thick copper circuit, and particularly to a copper material and a heat-dissipating member in which coarsening of crystal grains at the time of heating is suppressed.

[0002] Priority is claimed on Japanese Patent Application No. 2019-068349, filed March 29, 2019, the content of which is incorporated herein by reference.

BACKGROUND ART

[0003] In the related art, copper or copper alloys having high conductivity have been used for electric and electronic components such as heat sinks or thick copper circuits.

[0004] Recently, as the current of electronic devices or electric devices has increased, the size and the thickness of the electric and electronic component used in the electronic device or the electric device has increased to reduce the current density and the diffusion of heat due to Joule heat generation.

[0005] Here, in a semiconductor device, for example, an insulating circuit substrate is used in which a copper material is bonded to a ceramic substrate to form the heat sink or the thick copper circuit described above.

[0006] In a case in which the ceramic substrate is bonded to a copper sheet, in many cases, the bonding temperature is set to 800°C or higher, and there is a possibility for the crystal grains of the copper material forming the heat sink or the thick copper circuit to coarsen at the time of bonding. In particular, for copper material made of pure copper having particularly excellent conductivity and heat radiation, the crystal grains tend to be coarsened.

[0007] In a case in which the crystal grains of the heat sink or the thick copper circuit coarsen after bonding, there is a possibility of a problem in appearance caused by the coarsening of the crystal grains.

[0008] Therefore, for example, Patent Document 1 proposes a copper material with an objective of suppressing the growth of the crystal grains in a case of heating the copper material at a high temperature.

[0009] In Patent Document 1, it is disclosed that by containing 0.0006 wt% to 0.0015 wt% of S, the crystal grains can be adjusted to a fixed size even in a case in which heat treatment is carried out at recrystallization temperature or higher.

[Citation List]

[Patent Document]

[0010] [Patent Document 1]
Japanese Unexamined Patent Application, First Publication No. H06-002058

SUMMARY OF INVENTION

Technical Problem

[0011] Incidentally, in Patent Document 1, the coarsening of the crystal grains is suppressed by specifying the amount of S, but with simply specifying the amount of S, sufficient effect of suppressing the coarsening of the crystal grains cannot be obtained. Also, after heating, the crystal grains may be locally coarsened and the crystal structure may become non-uniform.

[0012] Further, in a case in which the amount of S is increased in order to suppress the coarsening of the crystal grains, there are problems in that the hot workability is greatly decreased and the producing yield of the copper material is greatly decreased.

[0013] The present invention has been made in view of the circumstances described above, with the objective to provide a copper material capable of suppressing coarsening and non-uniformity of crystal grains even after heating, and a heat-dissipating member made of the copper material.

Solution to Problem

[0014] As a result of diligent studies by the present inventors in order to solve the above problems, the following findings have been obtained.

[0015] In a case in which the copper material is plastically worked and then heated, during primary recrystallization, which occurs at low temperature range, uniform structure is formed as strain is released, and during secondary recryst-

tallization, which occurs at high temperature range (for example, 800°C or higher), non-uniform structure is formed as the crystal grains are partly coarsened. Therefore, by suppressing the secondary recrystallization at the high temperature range, the coarsening and the non-uniformity of the crystal grains can be suppressed.

[0016] Then, in the copper material to which an appropriate amount of Ca is added, Ca produces compounds with S, Se, and Te contained as inevitable impurities (hereinafter referred to as Ca compound), and a part of the Ca compound decomposes at a temperature of 800°C or higher, and Ca, S, Se, and Te dissolves into the matrix, so that the growth of the crystal grains can be suppressed by Ca, S, Se, and Te.

[0017] The present invention has been made based on the findings described above, and a copper material according to the present invention has a composition in which the amount of Ca is in a range of 3 mass ppm or more and 400 mass ppm or less with the remainder being Cu and inevitable impurities, and in a case in which the amount of Ca is defined as X (mass ppm) and the total amount of O, S, Se, and Te contained as inevitable impurities is defined as Y (mass ppm), $X/Y > 2$ is satisfied, and after heat treatment of holding the copper material at 800°C for 1 hour, the average crystal grain size A is 200 μm or less and the area ratio of crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more.

[0018] With the copper material having the above configuration, since the amount of Ca is in a range of 3 mass ppm or more and 400 mass ppm or less, at the time of casting, Ca reacts with S, Se, and Te contained as inevitable impurities to produce the Ca compound. In a case in which the Ca compound is heated at a high temperature, the Ca compound is decomposed into Ca, S, Se, and Te dissolves into the matrix, and the dissolved Ca, S, Se, and Te inhibit the growth of the crystal grains. Therefore, the secondary recrystallization that occurs in the high temperature range (for example, 800°C or higher) can be sufficiently suppressed, and the coarsening and the non-uniformity of the crystal grains can be suppressed even after heating.

[0019] Further, in a case in which the amount of Ca is defined as X (mass ppm) and a total amount of O, S, Se, and Te contained as inevitable impurities is defined as Y (mass ppm), $X/Y > 2$ is satisfied. Therefore, even in a case in which Ca is preferentially oxidized and consumed, Ca that reacts with S, Se, and Te can be assured, and the Ca compound can be sufficiently produced.

[0020] In addition, the average crystal grain size A after heat treatment of holding the copper material at 800°C for 1 hour is 200 μm or less, and the area ratio of crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more. Therefore, even in a case in which the copper material is heated to 800°C or higher, the coarsening and the non-uniformity of the crystal grains can be reliably suppressed.

[0021] Here, in the copper material according to the present invention, it is preferable that, in a case in which the average crystal grain size after the heat treatment of holding the copper material at 800°C for 1 hour is defined as A and the average crystal grain size after heat treatment of holding the copper material at 1000°C for 1 hour is defined as B, $B/A \leq 2$ be satisfied.

[0022] In this case, a difference between the average crystal grain size B after the heat treatment of holding the copper material at 1000°C for 1 hour and the average crystal grain size A after the heat treatment of holding the copper material at 800°C for 1 hour is small, and even in a case in which the copper material is heated at a high temperature, the coarsening and the non-uniformity of the crystal grains can be sufficiently suppressed.

[0023] Further, in the copper material according to the present invention, it is preferable that the total amount of inevitable impurities described above excluding O, S, Se, and Te described above be 0.1 mass% or less.

[0024] A heat-dissipating member according to the present invention is made of the copper material described above.

[0025] With the heat-dissipating member having the above configuration, since the heat-dissipating member is made of the copper material described above, the coarsening and the non-uniformity of the crystal grains can be suppressed even in a case in which the heat-dissipating member is heated to a high temperature of 800°C or higher at the time of the bonding.

Advantageous Effects of Invention

[0026] According to the present invention, it is possible to provide a copper material capable of suppressing coarsening and non-uniformity of crystal grains even after heating, and a heat-dissipating member made of the copper material.

BRIEF DESCRIPTION OF DRAWINGS

[0027] Fig. 1 is a flowchart of a production method of a copper material according to the present embodiment.

DESCRIPTION OF EMBODIMENTS

[0028] A copper material according to an embodiment of the present invention will be described below.

[0029] The copper material according to the present embodiment is used as a material for an electric and electronic

component such as a heat sink and a thick copper circuit, and is used, for example, by being bonded to a ceramic substrate in a case of forming the electric and electronic component described above.

[0030] The copper material according to the present embodiment has a composition in which a amount of Ca is in a range of 3 mass ppm or more and 400 mass ppm or less with the remainder being Cu and inevitable impurities, and in a case in which the amount of Ca is defined as X (mass ppm) and the total amount of O, S, Se, and Te contained as inevitable impurities is defined as Y (mass ppm), a relationship of $X/Y > 2$ is satisfied.

[0031] Further, in the copper material according to the present embodiment, an average crystal grain size A after heat treatment of holding the copper material at 800°C for 1 hour is 200 μm or less, and an area ratio of crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more.

[0032] Further, in the copper material according to the present embodiment, it is preferable that, in a case in which the average crystal grain size after the heat treatment of holding the copper material at 800°C for 1 hour is defined as A and the average crystal grain size after heat treatment of holding the copper material at 1000°C for 1 hour is defined as B, $B/A \leq 2$ be satisfied.

[0033] Further, in the copper material according to the present embodiment, the total amount of the inevitable impurities excluding O, S, Se, and Te is 0.1 mass% or less.

[0034] Here, in the copper material according to the present embodiment, the reason why the component composition and the crystal grain size after the heat treatment are specified as described above will be described below.

(Amount of Ca: 3 mass ppm or More and 400 mass ppm or Less)

[0035] Ca produces Ca compounds with S, Se, and Te contained as inevitable impurities. Since a part of the compound is decomposed at a high temperature and Ca, S, Se, and Te dissolves, the growth of the crystal grains can be suppressed by the dissolved Ca, S, Se, and Te.

[0036] Here, in a case in which the amount of Ca is less than 3 mass ppm, there is a possibility that the Ca compound cannot be sufficiently produced. On the other hand, in a case in which the amount of Ca exceeds 400 mass ppm, there is a possibility that a coarse Ca compound is produced and the workability is significantly lowered.

[0037] Therefore, in the present embodiment, the amount of Ca is set in a range of 3 mass ppm or more and 400 mass ppm or less.

[0038] Note that a lower limit of the amount of Ca is preferably 3.5 mass ppm or more, and more preferably 4 mass ppm or more. An upper limit of the amount of Ca is preferably 350 mass ppm or less, and more preferably 300 mass ppm or less. The upper limit of the amount of Ca is still more preferably 100 mass ppm or less.

(Ratio of Amount X of Ca and Total Amount Y of O, S, Se, and Te: $X/Y > 2$)

[0039] Ca described above has higher reactivity with O than S, Se, and Te, and Ca is preferentially oxidized and consumed.

[0040] Therefore, by setting a ratio X/Y of the amount X of Ca to the total amount Y of O, S, Se, and Te contained as inevitable impurities larger than 2, a sufficient amount of residual Ca is assured after Ca is consumed by oxidation, and by residual Ca reacting with S, Se, and Te, the Ca compound can be sufficiently produced.

[0041] Note that the ratio X/Y of the amount X of Ca and the total amount Y of O, S, Se, and Te is preferably 2.2 or more, and more preferably 2.5 or more. The upper limit of X/Y is not particularly limited, but is substantially 50 or less.

(Other Inevitable Impurities)

[0042] Exemplary examples of other inevitable impurities other than the elements described above include Ag, B, Bi, Sc, rare earth elements (excluding Sc and Y), V, Nb, Ta, Cr, Mg, Sr, Ba, Ti, Zr, Hf, Y, Mo, W, Mn, Re, Fe, Ru, Os, Co, Rh, Ir, Ni, Pb, Pd, Pt, Au, Zn, Cd, Hg, Al, Ga, In, Ge, Sn, As, Sb, Tl, Be, N, C, Si, Li, H, and the like. Since there is a possibility that the inevitable impurities lower a thermal conductivity, the total amount thereof is preferably 0.1 mass% or less.

(Average Crystal Grain Size A after Heat Treatment of Holding Copper Material at 800°C for 1 Hour: 200 μm or Less)

[0043] In the copper material according to the present embodiment, in a case in which the crystal grain size after the heat treatment of holding the copper material at 800°C for 1 hour is 200 μm or less, the coarsening of the crystal grains can be reliably suppressed even in a case in which the copper material is heated to 800°C or higher.

[0044] Note that the average crystal grain size after the heat treatment of holding the copper material at 800°C for 1 hour is preferably 180 μm or less, and more preferably 150 μm or less. Also, a lower limit of the average crystal grain size after the heat treatment of holding the copper material at 800°C for 1 hour is not particularly limited, but is substantially

50 μm or more.

(Area Ratio of Crystal Grains Having Grain Size in Range of 50 μm or More and 300 μm or Less after Heat Treatment of Holding Copper Material at 800°C for 1 Hour: 60% or More)

[0045] In the copper material according to the present embodiment, in a case in which an area ratio of the crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more after the heat treatment of holding the copper material at 800°C for 1 hour, the non-uniformity of the crystal grains can be reliably suppressed even in a case in which the copper material is heated to 800°C or higher.

[0046] Further, the minimum grain size in a range of the grain size of 60% or more of the area ratio of the crystal after the heat treatment of holding the copper material at 800°C for 1 hour is preferably 75 μm or more, and more preferably 100 μm or more.

(Ratio of Average Crystal Grain Size A after Heat Treatment of Holding Copper Material at 800°C for 1 Hour and Average Crystal Grain Size B after Heat Treatment of Holding Copper Material at 1000°C for 1 Hour: $B/A \leq 2$)

[0047] In the copper material according to the present embodiment, in a case in which the ratio B/A of the average crystal grain size A after the heat treatment of holding the copper material at 800°C for 1 hour and the average crystal grain size B after heat treatment of holding the copper material at 1000°C for 1 hour is 2 or less, the difference between the average crystal grain size B after the heat treatment of holding the copper material at 1000°C for 1 hour and the average crystal grain size A after the heat treatment of holding the copper material at 800°C for 1 hour is small, and even in a case in which the copper material is heated at a high temperature, the coarsening and the non-uniformity of the crystal grains can be sufficiently suppressed.

[0048] Note that the ratio B/A of the average crystal grain size A after the heat treatment of holding the copper material at 800°C for 1 hour and the average crystal grain size B after the heat treatment of holding the copper material at 1000°C for 1 hour is preferably 1.9 or less, and more preferably 1.5 or less. Further, a lower limit of B/A is not particularly limited, but is substantially 0.8 or more.

[0049] Next, a production method of the copper material according to the present embodiment will be described with reference to a flowchart shown in Fig. 1.

(Melt Casting Step S01)

[0050] First, a copper raw material is melted to produce molten copper. Note that as the copper raw material, for example, it is preferable to use oxygen-free copper having a purity of 99.99 mass% or more, and oxygen-free copper having a purity of 99.999 mass% or more.

[0051] Next, Ca is added to the obtained molten copper where composition adjustment is carried out such that a predetermined concentration is obtained. Note that in a case of adding Ca, solely Ca or Cu-Ca matrix alloy or the like can be used. Further, in a case of producing the Cu-Ca matrix alloy, it is preferable to use oxygen-free copper having a purity of 99.99 mass% or more and oxygen-free copper having a purity of 99.999 mass% or more.

[0052] Then, the molten copper in which the component is adjusted is poured into a mold to produce an ingot. Note that in a case in which mass production is considered, it is preferable to use a continuous casting method or a semi-continuous casting method.

[0053] In a process of the melt casting step S01, a part of added Ca reacts with S, Se, and Te contained as inevitable impurities to produce the Ca compound.

(Hot Working Step S02)

[0054] Next, hot working is carried out to uniform the structure. It is preferable that the heating in the hot working step is carried out in a non-oxidizing or reducing atmosphere.

[0055] The hot working temperature is not particularly limited, but is preferably carried out in a range of 500°C or higher and 1000°C or lower. In order to uniformly produce the Ca compound in the subsequent step, a hot working start temperature is preferably 700°C or higher in consideration of working heat generation. The hot working start temperature is more preferably 750°C or higher.

[0056] The total working rate of the hot working is preferably 40% or more, more preferably 60% or more, and still more preferably 70% or more.

[0057] The hot working end temperature is preferably lower than 700°C. The hot working end temperature is more preferably 650°C or lower.

[0058] Further, a cooling method after the hot working is not particularly limited, but it is preferable to carry out air

cooling or water cooling.

[0059] Further, a working method in the hot working step S02 is not particularly limited, and for example, rolling, extrusion, groove rolling, forging, pressing, or the like can be adopted. In a case in which a final shape is a plate or strip, it is preferable to adopt rolling, in a case in which the final shape is a wire or rod, it is preferable to adopt extrusion or groove rolling, and in a case in which the final shape is a bulk material, it is preferable to adopt forging or pressing.

(Cold Working Step S03)

[0060] Next, the copper material after the hot working step S02 is subjected to cold working to be worked into a predetermined shape. Note that a temperature condition in the cold working step S03 is not particularly limited, but the cold working is preferably carried out in a range of -200°C or higher and 200°C or lower. In addition, the working rate in the cold working step S03 is appropriately selected so as to approximate the final shape, but it is preferably 30% or more in order to improve the productivity.

[0061] Further, a working method in the cold working step S03 is not particularly limited, and for example, rolling, extrusion, groove rolling, forging, pressing, or the like can be adopted. In a case in which a final shape is a plate or strip, it is preferable to adopt rolling, in a case in which the final shape is a wire or rod, it is preferable to adopt extrusion or groove rolling, and in a case in which the final shape is a bulk material, it is preferable to adopt forging or pressing.

(Recrystallization Heat Treatment Step S04)

[0062] Next, the copper material after the cold working step S03 is subjected to the heat treatment for the objective of recrystallization. Here, in a case in which the recrystallization grains after a recrystallization heat treatment step S04 are fine, there is a possibility that the growth of the crystal grains and the non-uniformity of the structure are promoted in a case in which the recrystallization grains are subsequently heated to 800°C or higher. Therefore, the average crystal grain size of the recrystallization grains after the recrystallization heat treatment step S04 is preferably 10 μm or more. The average crystal grain size thereof is more preferably 15 μm or more, and still more preferably 20 μm or more. The upper limit of the grain size at the time of the recrystallization is not particularly specified, but is substantially 200 μm or less.

[0063] A heat treatment condition in the recrystallization heat treatment step S04 is not particularly limited, but it is preferable that the copper material be held at a heat treatment temperature in a range of 200°C or higher and 850°C or lower for time in a range of 1 second or longer and 24 hours or shorter. In this case, it is preferable that short-time heat treatment be carried out at a high temperature and prolong heat treatment be carried out at a low temperature such that the grain size after the recrystallization falls in the range described above. The cooling rate is not particularly specified, but in a case in which the heat treatment is carried out at a temperature of 800°C or higher, the cooling rate need only be 10°C/sec or less at a temperature of 500°C or higher and lower than 800°C, and is preferably 5°C/sec or less, and more preferably 1 °C/sec or less.

[0064] Further, for the uniformity of the recrystallization structure, the cold working step S03 and the recrystallization heat treatment step S04 may be repeated two times or more.

(Thermal Refining Step S05)

[0065] Next, in order to adjust the material strength, the copper material after the recrystallization heat treatment step S04 may be subjected to thermal refining. Note that in a case in which it is not necessary to increase the material strength, the thermal refining may not be carried out.

[0066] A working rate of the thermal refining is not particularly limited, but it is preferable that the thermal refining be carried out in a range of more than 0% and 50% or less in order to adjust the material strength. Also, if necessary, the heat treatment may further be carried out after the thermal refining in order to remove the residual strain.

[0067] As described above, the copper material according to the present embodiment is produced.

[0068] In the copper material according to the present embodiment, which has the configuration described above, since the amount of Ca is in a range of 3 mass ppm or more and 400 mass ppm or less, at the time of the casting or the hot working and the recrystallization heat treatment, Ca reacts with S, Se, and Te contained as inevitable impurities to produce the Ca compound. In a case in which the Ca compound is heated to 800°C or higher, the Ca compound decomposes into Ca, S, Se, and Te and dissolves, and the dissolved Ca, S, Se, and Te inhibit the growth of the crystal grains. Therefore, even in a case in which, for example, the copper material is heated to 800°C or higher, the secondary recrystallization can be sufficiently suppressed, and the coarsening and the non-uniformity of the crystal grains can be suppressed even after heating.

[0069] Further, in the copper material according to the present embodiment, since the ratio X/Y of the amount X (mass ppm) of Ca and the total amount Y (mass ppm) of O, S, Se, and Te contained as inevitable impurities is set to larger than 2, even in a case in which Ca preferentially reacts with oxygen and is consumed, the amount of residual Ca that

reacts with S, Se, and Te can be assured, and the Ca compound can be sufficiently produced.

[0070] Further, in the copper material according to the present embodiment, after the heat treatment of holding the copper material at 800°C for 1 hour, the average crystal grain size A is 200 μm or less. Therefore, even in a case in which the copper material is heated to 800°C or higher, the coarsening of the crystal grains can be reliably suppressed.

[0071] In addition, in the copper material according to the present embodiment, after the heat treatment of holding the copper material at 800°C for 1 hour, the area ratio of the crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more. Therefore, even in a case in which the copper material is heated to 800°C or higher, the non-uniformity of the crystal grains can be reliably suppressed.

[0072] Further, in the copper material according to the present embodiment, in a case in which a ratio B/A of the average crystal grain size A after the heat treatment of holding the copper material at 800°C for 1 hour and an average crystal grain size B after heat treatment of holding the copper material at 1000°C for 1 hour is 2 or less, the difference between the average crystal grain size B after the heat treatment of holding the copper material at 1000°C for 1 hour and the average crystal grain size A after the heat treatment of holding the copper material at 800°C for 1 hour is small, and even in a case in which the copper material is heated to a high temperature of 1000°C or higher, the coarsening and the non-uniformity of the crystal grains can be sufficiently suppressed.

[0073] The copper material according to the embodiment of the present invention have been described so far, but the present invention is not limited to this, and can be appropriately changed without departing from the technical idea of the present invention.

[0074] For example, in the embodiment described above, an example of the production method of the copper material has been described, but the production method of the copper material is not limited to the example described in the embodiment, and an existing production method may be appropriately selected for producing.

EXAMPLES

[0075] Hereinafter, the results of the confirmation experiment conducted to confirm the effects of the present invention will be described.

[0076] A copper raw material made of oxygen-free copper having a purity of 99.99 mass% or more was charged into a high-purity graphite crucible and then melted at high frequency in an atmosphere furnace having Ar gas atmosphere. A Cu-1mass% Ca matrix alloy was charged into the obtained molten copper to prepare a component composition as shown in Table 1.

[0077] The obtained molten copper was poured into a mold and an ingot was produced. Note that a size of the ingot was about 25 mm in thickness × about 70 mm in width × about 160 mm to 190 mm in length.

[0078] The obtained ingot was heated at 800°C for 1 hour in Ar gas atmosphere and subjected to hot rolling to obtain a thickness of 15 mm.

[0079] A copper material after the hot rolling was cut and surface grinding was carried out to remove oxide film on the surface. In this case, the thickness of the copper material to be subjected to cold rolling was adjusted such that a final thickness was 0.8 mm in consideration of rolling rates of the subsequent cold rolling and thermal refining rolling.

[0080] The copper material of which the thickness was adjusted as described above was subjected to the cold rolling under a condition of a working rate of 90%.

[0081] Next, the copper material after the cold rolling was subjected to recrystallization heat treatment under a condition of holding the copper material at 600°C to 850°C for 5 seconds.

[0082] Then, the copper material after the recrystallization heat treatment was subjected to the thermal refining rolling under a condition of a working rate of 5% to 50% to produce the copper material having a thickness of 0.8 mm and a width of 60 mm.

[0083] Further, the following items were evaluated. Table 2 shows the evaluation results.

(Composition Analysis of Copper Material)

[0084] A measurement sample was collected from the obtained copper material, and a composition analysis was carried out by an ICP-MS analyzer (7500CX manufactured by Agilent Technologies, Inc). As a result, the composition shown in Table 1 was confirmed.

(Average Crystal Grain Size A after Heat Treatment at 800°C for 1 hour)

[0085] The obtained copper material was subjected to the heat treatment of holding the copper material at 800°C for 1 hour. A 50 mm × 50 mm sample was cut out from a test piece, was subjected to mechanical polishing by using water-resistant abrasive paper and diamond abrasive grains, and then was subjected to finish polishing by using a colloidal silica solution.

[0086] A crystal grain boundary map was created with crystal grain boundaries between measurement points in which an orientation difference between adjacent measurement points was 15° or more in a measurement area of 1000 μm^2 in steps of measurement intervals of 5 μm by using an EBSD measurement device (QUANTA 450 EFG manufactured by Thermo Fisher Scientific and AMETEK 9424 manufactured by EDAX Inc/TSL solutions), and an analysis software (OIM Analysis 7 \times 64 manufactured by TSL solutions). For the crystal grain boundary map, the measurement points in which the CI value was 0.1 or less were excluded.

[0087] In accordance with the intercept method of JIS H 0501, 5 line segments of a predetermined length were drawn vertically and horizontally on the crystal grain boundary map described above, the number of the crystal grains completely intercepted by the line segments was counted, and an average value of the intercepted length was used as the average crystal grain size.

[0088] (Area Ratio of Crystal Grains Having Grain Size of 50 μm or More and 300 μm or Less after Heat Treatment at 800°C for 1 hour)

[0089] By using the analysis software (OIM Analysis 7 \times 64 manufactured by TSL solutions), the crystal grain size of each crystal grain was obtained from the grain boundary map created in which the crystal grain size A was measured as described above, and from the area fraction, the area ratio of the crystal grains having the grain size of 50 μm or more and 300 μm or less was calculated from the total area of all the crystal grains.

(Average Crystal Grain Size B after Heat Treatment at 1000°C for 1 hour)

[0090] A test piece was collected from the obtained copper material and was subjected to the heat treatment of holding the copper material at 1000°C for 1 hour. A 50 mm \times 50 mm sample was cut out from the test piece, and the average crystal grain size B after the heat treatment at 1000°C for 1 hour was calculated by the same procedure as the "average crystal grain size A after the heat treatment at 800°C for 1 hour" described above.

[Table 1]

		Component composition (mass ratio)						X/Y
		Ca (X) ppm	O ppm	S ppm	Se ppm	Te Ppm	Total of four elements (Y) ppm	
Present Invention Example	1	3	0.8	0.4	0.1	0.1	1.4	2.1
	2	5	0.8	1.0	0.3	0.1	2.2	2.3
	3	10	1.0	2.1	0.2	0.2	3.4	2.9
	4	20	2.0	5.0	0.4	0.1	7.5	2.7
	5	46	2.0	7.9	0.4	0.1	10.5	4.4
	6	54	5.0	12.0	0.2	0.1	17.3	3.1
	7	62	10.0	4.0	0.3	0.2	14.5	4.3
	8	77	1.0	7.0	0.2	0.1	8.3	9.3
	9	120	2.0	4.3	0.3	0.2	6.5	18.5
	10	157	2.0	4.0	0.3	0.2	6.5	24.2
	11	178	9.0	6.1	0.1	0.1	15.2	11.7
	12	192	2.0	3.0	0.1	0.1	5.2	36.9
	13	244	7.0	24.0	0.3	0.2	31.5	7.7
	14	265	3.0	5.2	0.1	0.1	8.2	32.3
	15	398	5.0	5.0	0.2	0.2	10.4	38.3
Comparative Example	1	-	1.0	5.0	0.2	0.1	6.3	-
	2	1	2.0	3.0	0.2	0.1	5.3	0.2
	3	10	0.8	5.5	0.1	0.1	6.5	1.5
	4	543	5.0	6.0	0.1	0.2	11.3	48.1

[Table 2]

		Temperature of recrystallization heat treatment step (°C)	Rolling rate of thermal refining step (%)	After heat treatment at 800°C for 1 hour				Average crystal grain size B after heat treatment at 1000°C for 1 hour (μm)	B/A
				Average crystal grain size A (μm)	Area ratio of 50 μm ≤ A ≤ 300 μm (%)	Area ratio of 75 μm ≤ A ≤ 300 μm (%)	Area ratio of 100 μm ≤ A ≤ 300 μm (%)		
Present Invention Example	1	650	25	144	69	67	64	152	1.1
	2	600	5	112	66	65	61	105	0.9
	3	650	25	135	81	79	75	136	1.0
	4	750	46	155	70	69	66	162	1.0
	5	800	9	121	68	66	64	103	0.9
	6	650	15	115	77	76	72	108	0.9
	7	850	13	122	70	69	66	174	1.4
	8	850	32	139	65	63	60	145	1.0
	9	700	40	144	73	71	69	151	1.0
	10	700	40	136	74	73	71	175	1.3
	11	700	30	134	65	63	61	155	1.2
	12	700	40	125	68	67	64	118	0.9
	13	700	12	126	83	82	78	134	1.1
	14	800	42	126	75	73	69	133	1.1
	15	800	46	132	69	68	65	183	1.4
Comparative Example	1	650	24	215	55	53	47	478	2.2
	2	700	32	204	49	47	42	506	2.5
	3	800	13	233	51	50	44	557	2.4
	4	800	7	-	-	-	-	-	-

[0091] In Comparative Example 1, Ca was not added, the average crystal grain size A after the heat treatment at 800°C for 1 hour was 215 μm, the average crystal grain size B after the heat treatment at 1000°C for 1 hour was 478 μm, and the crystal grains were coarsened after the heat treatment. Further, the area ratio of the crystal having a grain size of 50 μm or more and 300 μm or less after the heat treatment at 800°C for 1 hour was 55%, which is small, and the crystal grains after the heat treatment were non-uniform.

[0092] In Comparative Example 2, the ratio of the amount X (mass ppm) of Ca and the total amount Y (mass ppm) of O, S, Se, and Te contained as inevitable impurities was 0.2, the average crystal grain size A after the heat treatment at 800°C for 1 hour was 204 μm, the average crystal grain size B after the heat treatment at 1000°C for 1 hour was 506 μm, and the crystal grains were coarsened after the heat treatment. Further, the area ratio of the crystal having a grain size of 50 μm or more and 300 μm or less after the heat treatment at 800°C for 1 hour was 49%, which is small, and the crystal grains after the heat treatment were non-uniform.

[0093] In Comparative Example 3, the ratio of the amount X (mass ppm) of Ca and the total amount Y (mass ppm) of O, S, Se, and Te contained as inevitable impurities was 1.5, the average crystal grain size A after the heat treatment at 800°C for 1 hour was 233 μm, the average crystal grain size B after the heat treatment at 1000°C for 1 hour was 557 μm, and the crystal grains were coarsened after the heat treatment. Further, the area ratio of the crystal grains having

a grain size in a range of 50 μm or more and 300 μm or less after the heat treatment at 800°C for 1 hour was 51%, which is small, and the crystal grains after the heat treatment were non-uniform.

[0094] In Comparative Example 4, the amount of Ca was 543 mass ppm, and fracture occurred at the time of the working. Accordingly, the subsequent evaluation was canceled. It is presumed that a coarse Ca compound was produced at the time of the casting.

[0095] On the other hand, in Present Invention Examples 1 to 15 having the composition in which the amount of Ca was in a range of 3 mass ppm or more and 400 mass ppm or less with the remainder being Cu and inevitable impurities, in which the ratio X/Y of the amount X (mass ppm) of Ca and the total amount Y (mass ppm) of O, S, Se, and Te contained as inevitable impurities was larger than 2, the average crystal grain size A after the heat treatment at 800°C for 1 hour was 155 μm or less, the average crystal grain size B after the heat treatment at 1000°C for 1 hour was 183 μm or less, and the coarsening of the crystal grains after the heat treatment was suppressed. Further, the area ratio of the crystal having a grain size of 50 μm or more and 300 μm or less after the heat treatment at 800°C for 1 hour was 60% or more, and the crystal grains after the heat treatment were uniform.

[0096] From the above, according to Present Invention Examples, it was confirmed that the copper material capable of suppressing the coarsening and the non-uniformity of the crystal grains even after heating can be provided.

INDUSTRIAL APPLICABILITY

[0097] The copper material and heat-dissipating member according to the present invention can be used for a member in which it is preferable to suppress the coarsening of the crystal grains to prevent the changes in appearance, for example, the electric and electronic component including the heat sink or the thick copper circuit.

Claims

1. A copper material having:

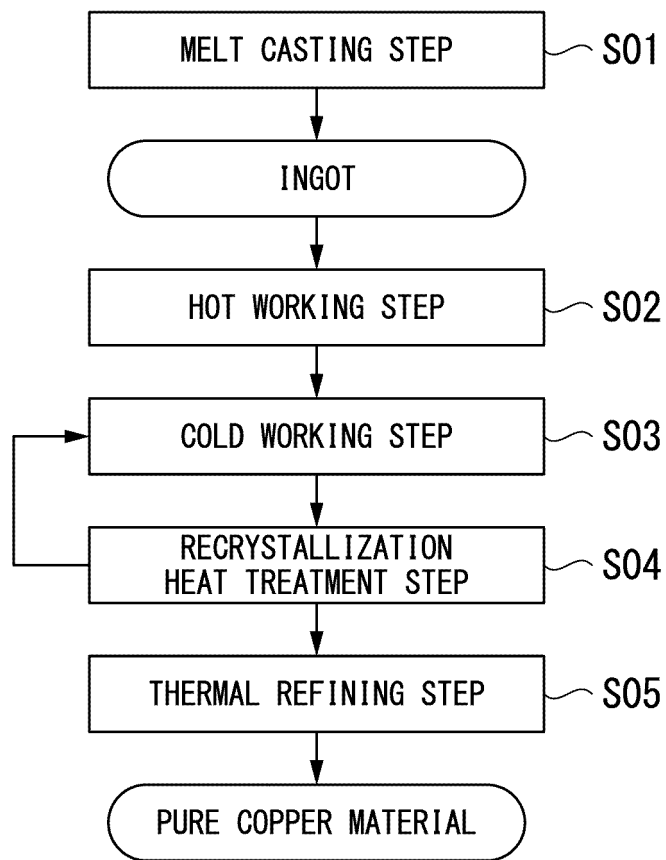
a composition in which an amount of Ca is in a range of 3 mass ppm or more and 400 mass ppm or less with the remainder being Cu and inevitable impurities,
wherein in a case in which the amount of Ca is defined as X (mass ppm) and a total amount of O, S, Se, and Te contained as inevitable impurities is defined as Y (mass ppm), $X/Y > 2$ is satisfied, and
after heat treatment of holding the copper material at 800°C for 1 hour, an average crystal grain size is 200 μm or less and an area ratio of crystal grains having a grain size in a range of 50 μm or more and 300 μm or less is 60% or more.

2. The copper material according to Claim 1,
wherein in a case in which the average crystal grain size after the heat treatment of holding the copper material at 800°C for 1 hour is defined as A and an average crystal grain size after heat treatment of holding the copper material at 1000°C for 1 hour is defined as B , $B/A \leq 2$ is satisfied.

3. The copper material according to Claim 1,
wherein a total amount of inevitable impurities excluding O, S, Se, and Te is 0.1 mass% or less.

4. A heat-dissipating member made of the copper material according to any one of Claims 1 to 3.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2020/010018

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. C22C9/00(2006.01)i, C22F1/00(2006.01)i, C22F1/08(2006.01)i
 Fi: C22C9/00, C22F1/08 A, C22F1/00 604, C22F1/00 623, C22F1/00 624, C22F1/00 625, C22F1/00 650F, C22F1/00 651A, C22F1/00 683, C22F1/00 694B, C22F1/00 694A, C22F1/00 691B, C22F1/00 691C, C22F1/00 685Z, C22F1/00 686A, C22F1/00 692A

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.
X	JP 2017-188339 A (MITSUBISHI MATERIALS CORP.) 12	1-3
Y	October 2017, claims, paragraphs [0034], [0054], tables 1, 2, examples 6, 7, 9	4
Y	JP 2014-189817 A (MITSUBISHI MATERIALS CORP.) 06 October 2014, claims, paragraph [0044]	4
A	JP 2000-212660 A (NIPPON MINING & METALS CO., LTD.) 02 August 2000	1-4
A	JP 2016-125115 A (MITSUBISHI MATERIALS CORP.) 11 July 2016	1-4



Further documents are listed in the continuation of Box C.



See patent family annex.

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"O" document referring to an oral disclosure, use, exhibition or other means

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

"I" 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

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

"&" document member of the same patent family

Date of the actual completion of the international search
27.05.2020Date of mailing of the international search report
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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.

PCT/JP2020/010018

Patent Documents referred to in the Report	Publication Date	Patent Family	Publication Date
JP 2017-188339 A	12.10.2017	(Family: none)	
JP 2014-189817 A	06.10.2014	(Family: none)	
JP 2000-212660 A	02.08.2000	US 6197433 B1	
		KR 10-2000-0052542 A	
		CN 1262335 A	
JP 2016-125115 A	11.07.2016	US 2018/0005731 A1	
		WO 2016/111159 A1	
		EP 3243916 A1	
		CN 107002179 A	
		KR 10-2017-0102224 A	

Form PCT/ISA/210 (patent family annex) (January 2015)

REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 2019068349 A [0002]
- JP H06002058 A [0010]