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# (54) WROUGHT COPPER ALLOY, COPPER ALLOY PART, AND PROCESS FOR PRODUCING WROUGHT COPPER ALLOY

(57) {Problem} To provide a copper alloy wrought material which is excellent in machinability and ductility and malleability, and which is optimal in applications in which at least one of high mechanical strength and high electrical conductivity is required, while attaining a reduced load to the environment.

{Means to solve} A copper alloy wrought material, containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, 0.02 to 1.0 mass% of S, and optionally at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%, with the balance being Cu and unavoidable impurities, wherein sulfide particles, which contribute to machinability, are dispersed therein, in which an average diameter of the sulfide particles is 0.1 to 10 μm, and in which an area ratio of the sulfide particles is 0.1 to 10%, and wherein the copper alloy wrought material has a tensile strength of 500 MPa or greater and an electrical conductivity of 25% IACS or higher.

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## Description

### TECHNICAL FIELD

**[0001]** The present invention relates to a metal part that can be used in electronic equipments, precision machines, automobiles, and the like, specifically to a copper alloy part produced by cutting. Further, the present invention relates to a copper alloy wrought material suitable for that copper alloy part, and to a method of producing the same.

### BACKGROUND ART

**[0002]** Examples of a method of producing a metal part include cutting, such as turning and punching. Cutting is a working method particularly effective for the production of a part which has a complicated shape or a part which requires a high dimensional accuracy. In the case of performing cutting, machinability often becomes a problem. Machinability is represented by items, such as cut chip treatment, tool service life, cutting resistance, and cut face roughness, and efforts have been made to improve the material in order to enhance those.

**[0003]** Copper alloys are used in many metal parts for the reasons, such as high in mechanical strength, excellent in electrical conductivity and heat conductivity, excellent in corrosion resistance, and excellent in color tone. Copper alloys are also frequently subjected to working by cutting, and are used in applications, such as, for example, faucets for tap water, valves, gears, and ornaments. In these applications, use is made of alloys prepared by adding lead to brass (Cu-Zn-based), bronze (Cu-Sn-based), aluminum-bronze (Cu-Al-based), and nickel silver (Cu-Zn-Ni-based), so as to enhance machinability. However, those applications are ones which do not require high mechanical strength or high electrical conductivity.

**[0004]** In the applications which require high mechanical strength or high electrical conductivity, for example, in an application, such as a pin material for coaxial connectors, use is made of any of free-cutting phosphor bronze (see Patent Literature 1) and free-cutting beryllium copper (see Patent Literature 2), which are obtained by adding lead to phosphor bronze and beryllium copper, respectively. These materials are subjected to cutting with a precision machine tool such, as an NC lathe, and are used in high-reliability parts for the applications of electronic equipments or the like.

**[0005]** As such, in order to enhance the machinability of copper alloys, generally lead is added. This is because, since lead does not form any solid solution in a copper alloy, lead is finely dispersed in the material, and cut chips are apt to be broken and separated off at the region in the cutting. However, since lead is considered to have adverse affection on the human body and the environment, use of lead has become restricted, and thus there is an increasing demand for a material which does not contain lead and has improved machinability. As an alternative material for copper alloys containing lead, there are known copper alloys obtained by adding bismuth to brass or bronze (see Patent Literatures 3 and 4). Further, it is also known that, in brass, the zinc concentration is increased to form a p phase or a y phase, which are each a copper-zinc-based compound, or alternatively silicon is added to form a κ phase, which is a copper-silicon-based compound, so that any of these compounds is made to serve as the starting point for the breakage and separation off of cut chips, and thereby machinability is enhanced (Patent Literatures 5 and 6). Further, there is a known method of adding sulfur to bronze to form a sulfide, and thereby making the sulfide to act as the starting point for the breakage and separation off of cut chips (Patent Literature 7). In addition to that, in connection with making the sulfide as the starting point for the breakage and separation off of cut chips, there is also a known method related to age-precipitation-type alloys of a copper-zirconium-based and a copper-titanium-based (Patent Literature 8).

### CITATION LIST

### PATENT LITERATURES

**[0006]**

Patent Literature 1: JP-A-50-066423 ("JP-A" means unexamined published Japanese patent application)
Patent Literature 2: JP-A-52-117244
Patent Literature 3: JP-A-2001-059123
Patent Literature 4: JP-A-2000-336442
Patent Literature 5: JP-A-2000-319737
Patent Literature 6: JP-A-2004-183056
Patent Literature 7: JP-A-2006-152373
Patent Literature 8: JP-A-2001-240923
Patent Literature 9: JP-A-2008-75172
Patent Literature 10: JP-A-6-212374

Patent Literature 11: JP-A-7-90520

## DISCLOSURE OF INVENTION

## TECHNICAL PROBLEM

**[0007]** However, the techniques descried in the patent literatures have the following problems.
In the techniques described in Patent Literatures 1 and 2, lead is used as an additive element for enhancing machinability as described above, and there is a concern for a load to the environment. Particularly, in the technique described in Patent Literature 2, there is no substance which can replace lead as an additive element for enhancing the machinability of free-cutting beryllium copper, and beryllium itself is also considered as one of elements having adverse affection on the environment. Therefore, there is an increasing demand for not only an alternative material of copper alloys to which lead is added, but also an alternative material of beryllium copper.

**[0008]** Further, in the techniques described in Patent Literatures 3 and 4, when bismuth is added, machinability is improved; however, the alloy becomes to be apt to be broken in working, and particularly, it becomes difficult to perform hot working. That is, another means is necessary to improve hot workability. The compounds formed in the alloys described in Patent Literatures 5 and 6 are unique to a brass-system, and it is substantially difficult to apply the compounds to other alloy systems. Patent Literature 7 is a technique related to a casting, and the technique is preferable in the case of directly cutting a casting; however, there is no disclosure on a technique for obtaining a wrought material (plastically-worked material), such as a bar material or a sheet material. The material obtained by the technique described in Patent Literature 8 is generally low in mechanical strength, and for example, the material is insufficient for applications which require high mechanical strength, such as a pin material for coaxial connectors. Thus, there is a need to apply other techniques.

**[0009]** The materials disclosed in Patent Literatures 1 to 8 are not Corson alloys (Cu-Ni-Si-based copper alloys), and actually do not serve as materials to which reference can be made. JP-A-2008-75172 (Patent Literature 9) discloses a Cu-Ni-Si-based alloy provided for use as an electronic material, which has improved electrical conductivity, mechanical strength, bending property, and stress relaxation resistance in combination, with minimized addition of other alloying elements. However, there is no disclosure on the balance between ductility and malleability (drawability) and machinability standing together, and there is no mention on the adjustment of the sulfur concentration. JP-A-6-212374 (Patent Literature 10) and JP-A-7-90520 (Patent Literature 11) disclose Corson alloys with ductility and malleability taken into consideration, but in both of the alloys, the sulfur concentration is restricted to 20 ppm (0.002%) or less because of the ductility and malleability.

**[0010]** The present invention has been made in view of such problems, and is contemplated for providing a copper alloy wrought material which is excellent in machinability and ductility and malleability, and which is optimal in applications in which high mechanical strength or high electrical conductivity is required, while attaining a reduced load to the environment. Further, the present invention is contemplated for providing a copper alloy part, which is obtained by subjecting the above-mentioned copper alloy wrought material to cutting, and for providing a method of producing the wrought material.

## SOLUTION TO PROBLEM

**[0011]** The inventors of the present invention, having been studied keenly, found that, by controlling the size (average diameter) and the area ratio of sulfide particles in an age-precipitation-type copper alloy of a specific composition, a copper alloy wrought material can be obtained, which is excellent in ductility and malleability (drawability) (hot- and cold-workability) and machinability, and which is also excellent in mechanical strength and electrically conductivity. Further, the inventors found a composition and a casting method, each of which is to obtain the sulfide particles, and also found a composition, a microstructure, and a casting method, each of which exhibits excellent hot workability and cold workability.
Further, the inventors of the present invention, having been studied keenly, found that, by forming sulfide particles in the matrix of an age-precipitation-type copper alloy of a specific composition, and by making 40% or more of the sulfide particles exist in the grains of the matrix having a cross-section that is in parallel to the wrought direction, and by making the sulfide particles having an aspect ratio in the cross-section parallel to the wrought direction of 1:1 to 1:100 be dispersed in the matrix, a copper alloy wrought material can be obtained, which is excellent in ductility and malleability (drawability) (hot- and cold-workability) and machinability, and which is also excellent in mechanical strength and electrically conductivity. Further, the inventors found a composition and a production method, each of which is to obtain the sulfide particles, and also found a composition, a microstructure, and a production method, each of which exhibits excellent hot workability and cold workability.
The present invention is attained based on those findings.

**[0012]** That is, the present invention is to provide the following means:

(1) A copper alloy wrought material, containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, and 0.02 to 1.0 mass% of S, with the balance being Cu and unavoidable impurities, wherein sulfide particles are dispersed therein, in which a size (average diameter) of the sulfide particles is 0.1 to 10 μm, and in which an area ratio of the sulfide particles is 0.1 to 10%, and wherein the copper alloy wrought material has a tensile strength of 500 MPa or greater and an electrical conductivity of 25% IACS or higher.
(2) The copper alloy wrought material as described in (1), further containing at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%.
(3) The copper alloy wrought material as described in (1) or (2), wherein the sulfide particles are composed of at least one selected from the group consisting of Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S.
(4) A copper alloy part, formed by subjecting the copper alloy wrought material as described in any one of (1) to (3) to cutting.
(5) The copper alloy part as described in (4), which is used in an electronic equipment part, a structural part, or an element part.
(6) A method of producing the copper alloy wrought material as described in any one of (1) to (3), wherein a cooling speed at the time of casting is set to 0.1 to 50°C/second.
(7) A copper alloy wrought material, containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, and 0.02 to 1.0 mass% of S, with the balance being Cu and unavoidable impurities, wherein sulfide particles are present in crystals of the matrix at 40% or larger in an area ratio of the sulfide particles in a cross-section parallel to the wrought direction, wherein the sulfide particles having an aspect ratio in the cross-section parallel to the wrought direction of 1:1 to 1: 100 are dispersed in the matrix, and wherein the copper alloy wrought material has a tensile strength of 500 MPa or greater and an electrical conductivity of 25% IACS or higher.
(8) The copper alloy wrought material as described in (7), further containing at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%.
(9) The copper alloy wrought material as described in (7) or (8), wherein the sulfide particles are composed of at least one selected from sulfides of Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S.
(10) A copper alloy part, formed by subjecting the copper alloy wrought material as described in any one of (7) to (9) to cutting.
(11) The copper alloy part as described in (10), which is used in applications which require mechanical strength, electrically conductivity, heat conductivity, and wear resistance, such as an electronic equipment part, a structural part, and an element part.
(12) A method of producing the copper alloy wrought material as described in any one of (7) to (9), containing the steps of:

> conducting any one of steps (a) and (b), at the time of working a copper alloy composition containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, and 0.02 to 1.0 mass% of S, with the balance being Cu and unavoidable impurities;
> area-reduction working at 0% to 95%; and
> subjecting the resultant worked-product to aging, in which the sulfide particles are present in crystals of the matrix at 40% or larger in a total area of the sulfide particles dispersed in the matrix in a cross-section parallel to the wrought direction, and in which the sulfide particles having an aspect ratio in the cross-section parallel to the wrought direction of 1:1 to 1:100 are dispersed in the matrix:
>
> > (a) subjecting the copper alloy composition to hot working, and then to quenching;
> > (b) subjecting the copper alloy composition to hot working, then to cold working and a heat treatment at a temperature of 600°C to 1,000°C repeatedly for one or more times, and to a solution treatment before final cold-working.

(13) The method of producing the copper alloy wrought material as described in (12), wherein the copper alloy wrought material further contains at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%.

Herein, the phrase that "sulfide particles are present in crystals of the matrix at 40% or larger in an area ratio of the sulfide particles in a cross-section that is in parallel to the wrought direction" means that 40% or more of the sulfide particles dispersed in the matrix are present in grain boundaries. Further, the phrase that "sulfide particles having an aspect ratio in the cross-section that is in parallel to the wrought direction of 1:1 to 1:100 are dispersed (in the matrix)" means that the aspect ratio of all the sulfide particles dispersed in the matrix is within the range of 1:1 to 1:100. Herein, the matrix refers to individual regions, or a collection of the regions, surrounded by the grain boundaries in an alloy structure, and typically, the matrix exists in the form of islands each having an arbitrary shape, which are respectively surrounded by the grain boundaries and are adjacent to each other.

## ADVANTAGEOUS EFFECTS OF INVENTION

**[0013]** The copper alloy wrought material of the present invention is excellent in mechanical strength and electrically conductivity, and is also excellent in machinability and ductility and malleability (drawability), without utilizing an environmentally hazardous substance, such as lead or beryllium. For example, in order to prevent a decrease in the insertion and extraction force that is required in connector pin materials, the decrease in the insertion and extraction force can be suppressed by having a high tensile strength in the same level of that of beryllium copper. The present invention can suppress a decrease in the insertion and extraction force in the same level of that of beryllium copper at a tensile strength of 500 MPa or greater. Further, in a part of an electronic equipment or the like, in which tensile strength or/and electrically conductivity is desired, since the copper alloy wrought material of the present invention has an electrical conductivity of 25% IACS or higher, the alloy material is superior to beryllium copper due to its excellent electrically conductivity. Further, the copper alloy wrought material of the present invention is preferably suitable as a material for a part of electronic equipments or the like, which is produced by cutting. The copper alloy part of the present invention can be produced with high accuracy through cutting, and has sufficient characteristics that are necessary as a part of electronic equipments and the like.

**[0014]** Other and further features and advantages of the invention will appear more fully from the following description, appropriately referring to the accompanying drawings.

## BRIEF DESCRIPTION OF THE DRAWINGS

**[0015]**

{Fig. 1}
Fig. 1 is a diagram schematically showing a lateral side (a) and the cross-section (b) of a copper alloy bar viewed in parallel with the wrought direction.
{Fig. 2}
Fig. 2 is a diagram schematically showing the cross-sectional structure of a copper alloy bar viewed under an electron microscope (SEM) in parallel to the wrought direction, and the diagram is an overview image of the grain boundaries and sulfide particles.
{Fig. 3}
Fig. 3 is a diagram schematically showing the cross-sectional structure of the copper alloy bar viewed under an electron microscope (SEM) in parallel to the wrought direction, and the diagram shows Fig. 2, with the sulfide particles on the grain boundaries being excluded.
{Fig. 4}
Fig. 4 is a diagram explaining the aspect ratio of the sulfide particles, shown as a magnification of a part of Fig. 2.
{Fig. 5}
Fig. 5 is a lateral side view schematically showing one shape of the connector pins produced in Examples 1-3 and 2-3.
{Fig. 6}
Fig. 6 is a lateral side view schematically showing the other shape of the connector pins produced in Examples 1-3 and 2-3.

## MODE FOR CARRYING OUT THE INVENTION

**[0016]** Preferred embodiments of the copper alloy wrought material of the present invention will be roughly divided into a first embodiment and a second embodiment, and each described in detail. Herein, with respect to the second embodiment, descriptions that are common with the first embodiment may be omitted. These two embodiments are intended to have special technical features that are the same as or corresponding to each other, and to form a single inventive concept. In the present specification, the term "copper alloy" means that the material does not encompass the conception of shape, and the terms "copper alloy material" and "copper alloy wrought material" mean that the material encompasses the conception of shape.

[First embodiment]

<Ni and Si>

**[0017]** In a preferred embodiment of the copper alloy wrought material of this embodiment, nickel (Ni) and silicon (Si) are added to form a Ni-Si precipitate ($Ni_2Si$) in the metal matrix by controlling the content ratio of Ni and Si, to thereby achieve precipitation hardening, and to enhance the mechanical strength and electrically conductivity of the copper alloy wrought material. This Ni-Si precipitate ($Ni_2Si$: precipitate for precipitation hardening) does not contribute much to enhancement of machinability.

**[0018]** In a preferred embodiment of the copper alloy wrought material of this embodiment, addition of sulfur (S) leads to the formation of sulfide particles, in the matrix, which contribute to enhancement of machinability. As the sulfide particles serve as the starting points for the breakage and separation off of chips when cutting is carried out, the chips become to be apt to be finely broken and separated off, to enhance machinability. Further, by controlling the cooling speed at the time of casting, the size (average diameter) and the area ratio of the sulfide particles are controlled, and chip breakability and separability is enhanced, but hot workability and cold workability are not impaired. Thus, wrought working such as extrusion, rolling or drawing, is made possible.

**[0019]** The copper alloy in this embodiment is subjected to hot working or cold working while being in the state in which nickel (Ni) and silicon (Si) have formed a solid solution, or in the state in which a Ni-Si precipitate has been formed. In each of the states, the wrought workability is generally poor, and cracking, breakage and the like are apt to occur in the working. When sulfide particles are formed in this copper alloy, wrought workability is further deteriorated, and working is made difficult. Since wrought workability is affected by the size (average diameter) and the area ratio of the sulfide particles, the size (average diameter) and the area ratio of the sulfide particles are specifically defined in this embodiment. Based on those, wrought workability and machinability, which are not easily achieved at the same time in a well balance, can be enhanced simultaneously in the Cu-Ni-Si-based alloy.

**[0020]** The content of Ni is 1.5 to 7.0 mass%, and preferably 1.7 to 6.5 mass%. If the amount of Ni is too small, the degree of precipitation hardening by the Ni-Si precipitate is small and the mechanical strength is not sufficient. If the amount of Ni is too large, which means that the amount is excessive, it leads not only not to increase the amount of the Ni-Si precipitate that contributes to the strength enhancement, but also to deteriorate hot workability and cold workability (that is, ductility and malleability) by forming a large amount of Ni-Si crystallized product upon melt-casting, which are not preferable.

**[0021]** The content of Si is necessary in an amount of about 1/5 to 1/3 of the Ni content, on the basis of mass%, for the formation of the Ni-Si precipitate ($Ni_2Si$). Thus, in this embodiment, the content of Si is 0.3 to 2.3 mass%, and preferably 0.34 to 2.2 mass%.

<S>

**[0022]** In the copper alloy wrought material of this embodiment, it is necessary that the size (average diameter) of the sulfide particles be 0.1 to 10 $\mu$m, and the sulfide particles be present with an area ratio thereof in 0.1 to 10%. For this purpose, the content of S is 0.02 to 1.0 mass%, and preferably 0.03 to 0.8 mass%. If the content is too small, the area ratio of the sulfide particles is small, and sufficient chip breakability and separability may not be obtained. If the content of S is too large, hot workability and cold workability (that is, ductility and malleability) are deteriorated.

It is conventionally known that the amount of S is limited to a trace amount in Corson alloys (Patent Literatures 10 and 11). In this embodiment, this amount is daringly increased to a large extent, while the amounts of other additive elements are set to be within specific ranges, and the working is preferably carried out under specific conditions. Thus, a copper alloy wrought material in which sulfide particles have a predefined aspect ratio in the wrought direction was obtained, and a good balance between the machinability and the ductility and malleability is achieved.

**[0023]** Further, the copper alloy wrought material of this embodiment may also contain one kind or two or more kinds of tin (Sn), manganese (Mn), cobalt (Co), zirconium (Zr), titanium (Ti), iron (Fe), chromium (Cr), aluminum (Al), phosphorus (P), and zinc (Zn). These elements enhance the mechanical strength of the Cu-Ni-Si alloy by forming solid solutions or precipitates, or enhance machinability by forming sulfide particles. In the case of containing any of these elements, it is preferable to contain one kind or two or more kinds selected from Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P and Zn in a total amount of 0.05 to 2.0 mass%. If the content is smaller than 0.05 mass%, the alloy material containing any of these elements is not much different from an alloy material which does not contain these elements in terms the effect of strength enhancement or machinability improvement. Further, if the content is larger than 2.0 mass%, not only the effect of enhancing mechanical strength and improving machinability is saturated, but also the electrical conductivity is lowered, thus it is not advantageous. Examples of the sulfide components include Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S, and particularly, the Cu-S-based sulfide is effective. There are also sulfides composed of unavoidable impurities and S.

<Definition on sulfide>

**[0024]** Examples of the sulfide components include Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S. The sulfide is preferably at least one selected from the group consisting of Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S, and particularly, Cu-S is effective. There are also sulfides composed of unavoidable impurities and S. Herein, the term "Cu-S" means a generic term for sulfides composed of Cu and S, such as $Cu_2S$ and CuS, and the same is also applied to the term "Mn-S" or the like.

**[0025]** Next, descriptions will be made on the definitions on the size (average diameter) and area ratio of the sulfides, which are compounds that contribute to enhancement of machinability, and features thereof. Sulfide particles have an effect of finely breaking and separating off the chips occurred upon the cutting, and machinability is enhanced thereby. However, if the size (average diameter) of the sulfide particles is smaller than 0.1 μm, significant effects may not be obtained. Further, even if there are sulfide particles having a size (average diameter) of 0.1 μm or larger, if the total area ratio is small, chips are not finely broken and separated off. Specifically, if sulfide particles having a size (average diameter) of 0.1 μm or larger are not distributed at a density of 0.1 to 10% in terms of area ratio, chips are not sufficiently broken and separated off. In addition, since sulfides are soft, the sulfide particles may be extended longitudinally depending on the working ratio at hot working or cold working, but it is acceptable as long as the above-described ranges of the size (average diameter) and area ratio of the sulfide particles are satisfied in the cross-section perpendicular to the longitudinal direction of the wrought material (transverse cross-section). The size (average diameter) of the sulfide particles is defined as the value obtained, by observing the transverse cross-sections with an electron microscope, measuring the sizes of 100 or more sulfide particles to convert those into diameters of respective circles equivalent in areas, and averaging the diameters. The area ratio of the sulfide particles is defined as the value obtained, by counting the number of sulfide particles seen in one visual field that is observed with an electron microscope, determining the respective diameters of the individual sulfide particles by converting the sizes into diameters of respective circles equivalent in areas, averaging the diameters, determining the area from the average diameter, determining the total area of the sulfide particles per visual field by multiplying the area by the number of sulfide particles, and dividing the resultant total area of the sulfide particles by the total area of one visual field.

**[0026]** On the other hand, sulfide deteriorates hot workability and cold workability of a material. Since sulfide particles are apt to be formed at the grain boundaries, to lower the grain boundary strength, if the size (average diameter) of the sulfide particles is too large, or if the area ratio is too large, the sulfide particles cause cracking when the material is subjected to hot working or cold working, to lead that the resultant material cannot be used as a wrought material. Thus, it is necessary to limit the size (average diameter) of the sulfide particles to 10 μm or less, and the area ratio of the sulfide particles to 10% or less.

**[0027]** This size (average diameter) of the sulfide particles varies depending onto the cooling speed at casting. If the cooling speed is slow, the sulfide particles become larger, and on the contrary, if the cooling speed is high, the sulfide particles become smaller. The cooling speed is preferably 0.1 to 50°C/second, and more preferably 0.3 to 40°C/second.

<Mechanical properties and production conditions>

**[0028]** Next, description will be made on the mechanical properties of the copper alloy wrought material in a preferred embodiment of the first embodiment.

The copper alloy wrought material in this embodiment is intended to substitute lead-containing phosphor bronze or beryllium copper, that is, to substitute copper alloys containing environmentally hazardous substances, and therefore, the copper alloy wrought material needs to have a mechanical strength equivalent to that of the wrought materials of these alloys. Accordingly, the copper alloy wrought material is required to have a tensile strength of 500 MPa or greater and an electrical conductivity in terms of IACS (International Annealed Copper Standard) of 25% IACS or higher, as the mechanical strength and electrically conductivity that would not cause any problem in practical use. The copper alloy in this embodiment is of age-precipitation-type, and the mechanical strength and electrically conductivity of the copper alloy are enhanced by forming $Ni_2Si$ as described above. Thus, it is necessary that the copper alloy contain Ni in an amount of 1.5 to 7.0 mass%, and Si in an amount of 0.3 to 2.3 mass%. Further, the temperature at the time of the solution treatment in the course of the production process is preferably within the range of 750 to 1,000°C, and the temperature at the time of aging is preferably within the range of 350 to 600°C.

**[0029]** In this embodiment, there are no particular limitations on the method of producing the copper alloy wrought material, except that the size (average diameter) of the sulfide particles is controlled by setting the cooling speed at casting to the range described above. For example, it is enough if the area of the transverse cross-section of the ingot (cake or billet) is larger than the area of the cross-section of the wrought material to be produced. Since the copper alloy wrought material of this embodiment is a wrought material of an age-precipitation-type copper alloy, at least an aging heat treatment step is necessary after the melt-casting step of the copper alloy raw material, but the steps of hot working, annealing, and solution treatment, other than the step(s) to obtain the copper alloy wrought material, may be carried out optionally, if needed. For example, in regard to the hot working step, it is possible to produce the copper alloy wrought material of this embodiment through any one of the production methods, such as hot extrusion of a billet, hot forging of an ingot, and continuous casting. Further, there are no particular limitations on the shape of the product, and it is preferable to produce the product in a shape with which a copper alloy part of the final form can be easily obtained by the subsequent cutting step. That is, it is enough to produce a copper alloy wrought material having a predetermined shape, such as wire, rod, bar, sheet, or tube, in accordance with the application of the copper alloy part, and to use the formed material appropriately. For example, when the copper alloy part as the final form is a screw, a rivet or the like, the shape of the copper alloy wrought material is preferably a round rod shape.

**[0030]** Examples of the copper alloy part include parts, which currently use lead-containing phosphor bronze or beryllium copper, which require mechanical strength, electrically conductivity, heat conductivity, and wear resistance, and which are produced in complicated shapes mainly by cutting, for example, electronic equipment parts, such as male pins and female pins of coaxial connectors, barrel and plunger materials of the probes used in IC sockets or battery terminal connectors, and connector terminals for audio cables; structural parts, such as hinges of antennas, fasteners, bearings, guide rails, resistance welders, and timepieces; and element parts, such as cogwheels, bearings, and ejector pins of molds. The "copper alloy part" of this embodiment may also be a product which includes the copper alloy part produced by cutting, as a part thereof.

[Second embodiment]

<Ni and Si>

**[0031]** Also for the copper alloy wrought material of this embodiment, the content ratio of Ni and Si is controlled. The contents are the same as those in the first embodiment.

**[0032]** In a preferred embodiment of the copper alloy wrought material of this embodiment, addition of sulfur (S) leads to the formation of sulfide particles that contribute to enhancement of machinability, in the matrix. This embodiment has a common feature to the first embodiment, from the viewpoint that as these sulfide particles serve as the starting points for the breakage and separation off of chips when cutting is carried out, the chips become to be apt to be finely broken and separated off, to enhance machinability. Sulfide particles are formed upon casting, but when once formed, a large portion of the sulfide particles are present at the grain boundaries, to cause deterioration of hot workability and cold workability (that is, ductility and malleability). Thus, through wrought working and heat treatment, the sulfide particles formed in the ingot (cake or billet) are made to exist in the crystals of the matrix such that the area ratio of sulfide particles in a cross-section that is in parallel to the wrought direction would be 40% or higher, and sulfide particles having an aspect ratio, as viewed from the wrought direction, in the cross-section parallel to the wrought direction, of 1:1 to 1:100, preferably 1:1 to 1:50, are dispersed in the matrix, chip breakability and separability is enhanced, and hot workability and cold workability are not impaired, to thereby that wrought working, such as extrusion, rolling or drawing, is made possible. The copper alloy in this embodiment is subjected to hot working or cold working while being in the state in which nickel (Ni) and silicon (Si) have formed a solid solution, or in the state in which a Ni-Si precipitate has been formed. In each of the states, the wrought workability is generally poor, and cracking, breakage and the like are apt to occur in the working. When sulfide particles are formed in this copper alloy, wrought workability is further deteriorated, and working is made difficult. Since wrought workability is largely affected by the position where the sulfide particles exist, when a large amount of the sulfide particles are made to exist in the crystals, ductility and malleability are improved. In this embodiment, the area ratio of the sulfide particles that exist in the grains is defined.

**[0033]** The content of Ni is 1.5 to 7.0 mass%, and preferably 1.7 to 6.5 mass%. If the amount of Ni is too small, the degree of precipitation hardening by the Ni-Si precipitate is small and the mechanical strength is not sufficient. If the amount of Ni is too large, which means that the amount is excessive, it leads not only not to increase the amount of the Ni-Si precipitate that contributes to the strength enhancement, but also to deteriorate hot workability and cold workability (that is, ductility and malleability) by forming a large amount of Ni-Si crystallized product upon melt-casting, which are not preferable.

**[0034]** The content of Si is necessary in an amount of about 1/5 to 1/3 of the Ni content, on the basis of mass%, for the formation of the Ni-Si precipitate ($Ni_2Si$). Thus, in this embodiment, the content of Si is 0.3 to 2.3 mass%, and preferably 0.34 to 2.2 mass%.

<S>

**[0035]** In the copper alloy wrought material of this embodiment, it is necessary to make the sulfide particles thus formed to exist in the crystals of the matrix in the cross-section that is in parallel to the wrought direction, at an area ratio of 40% or larger, and to control the aspect ratio of the sulfide particles in the cross-section parallel to the wrought direction, to the ratio described above. In order to achieve those, the content of S is set to 0.02 to 1.0 mass%, and preferably 0.03

to 0.8 mass%. If this content is too small, sufficient chip breakability and separability is not obtained. If the content of S is too large, hot workability and cold workability (that is, ductility and malleability) becomes poor. It is preferable that the sulfide particles thus formed and dispersed be present in the crystals of the matrix at an area ratio of 50% or larger. This embodiment is also similar to the first embodiment, from the viewpoint that S is actively contained in the addition amount described above, which exceeds the general upper-limit amount defined conventionally.

<Other additive elements>

**[0036]** The copper alloy wrought material of this embodiment may also contain one kind or two or more kinds of tin (Sn), manganese (Mn), cobalt (Co), zirconium (Zr), titanium (Ti), iron (Fe), chromium (Cr), aluminum (Al), phosphorus (P), and zinc (Zn). The effects, the ranges of preferable contents and the like of the additive element are similar to those of the first embodiment.

<Definition on sulfide>

**[0037]** Next, description will be made on the definitions on the proportion of the sulfide particles, which are compounds to contribute to enhancement of machinability, existing in the crystals of the matrix in the cross-section parallel to the wrought direction, and the aspect ratio of the sulfide particles, and features thereof. The sulfide particles have an effect of finely breaking separating off the chips occurred upon cutting, and thereby machinability is enhanced. However, the position at which the sulfide particles are present largely affects the ductility and malleability (hot workability and cold workability). The proportion of the sulfide particles that are present in the grains of the matrix is the value obtained, by observing the cross-section parallel to the wrought direction with an electron microscope, counting the number of total sulfide particles observed in one visual field, measuring the sizes of each sulfide particles to convert those into diameters of the respective circles equivalent in area, averaging the diameters, determining the area from the average diameter, and multiplying the area by the number of sulfide particles, to thereby determine the total area of total sulfide particles seen in one visual field, subsequently counting only the number of sulfide particles that are in the grains and across the grain boundaries, measuring the sizes of each of said sulfide particles to convert those into diameters of the respective circles equivalent in area, averaging the diameters, determining the area from the average diameter, and multiplying the area by the number of said sulfide particles, to thereby determine the total area of the sulfide particles that are present in the grains and across the grain boundaries, and dividing the thus-determined total area by the total area of all the sulfide particles seen in one visual field. It is enough that this proportion of sulfide particles that are present in the grains and across the grain boundaries is 40% or higher. If the proportion is 40% or less, the ductility and malleability become poor. In this case, the area ratio of the sulfide particles is in the range of 0.1% to 20%, and preferably 0.1 to 10%. The area ratio of the sulfide particles is the value obtained by dividing the total area of the sulfide particles seen in one visual field, by the total area of one visual field.

**[0038]** Since sulfide particles are soft, the sulfide particles may be extended longitudinally depending on the working ratio of hot working or cold working, and are broken and separated, to be dispersed in the matrix. In regard to the aspect ratio of the dispersed sulfide particles, when the cross-section is observed with an electron microscope, and the length $t_1$ in the direction perpendicular to the wrought direction is defined to be 1, the aspect ratio is designated as the ratio $(t_2/t_1)$ of the length $t_2$ of the sulfide particles that are extended in parallel to the wrought direction. If the aspect ratio is greater than 1:100, there is a possibility that the defined content of S may not be satisfied, and thus chips may not be finely broken and separated upon cutting. Even in the case where the sulfide particles do not have a shape that is linear in the wrought direction, the definition does not change, and as shown in Fig. 4, the aspect ratio is evaluated by determining the length $t_2$ in the wrought direction of the area occupying the region, and the length $t_1$ in the direction perpendicular to the length in the wrought direction.

**[0039]** Measurement examples for sulfide particles

Fig. 1(a) is a front view in which a copper alloy rod 10 is viewed in parallel to the wrought direction R, and Fig. 1(b) is a cross-sectional view, while 10a represents the cross-section, illustrated schematically.

Fig. 2 is a schematic diagram of the electron microscopic observation of the cross-section viewed in parallel to the wrought direction, and shows grain boundaries 21 and the state of sulfide particles, observed in one visual field. In the figure, 21 represents the grain boundary, 22 represents sulfide particle present at the grain boundary, and 23 represents sulfide particle present in the grain. Herein, the total area of all the sulfide particles observed in one visual field is determined.

Next, Fig. 3 is a diagram schematically showing the cross-sectional microstructure of a copper alloy rod viewed, with an electron microscope (SEM), in parallel to the wrought direction, and shows sulfide particles that are present in the grains, with the grain boundaries, and the sulfide particles present at the grain boundaries of Fig. 2 being excluded. The total area of the sulfide particles that are present in the grains as shown in this diagram is determined, and the proportion of the sulfide particles that are present in the grains and the sulfide particles that are seen in one visual field is determined.

In this case, the area ratio of the sulfide particles that are present in the grains is 61 %.
The aspect ratio of a sulfide particle means, as shown in Fig. 4, when the length $t_1$ of the sulfide particle in the direction perpendicular to the wrought direction is defined to be 1, the ratio of the length $t_2$ of the sulfide particle that is extended in parallel to the wrought direction, to the length in the perpendicular direction (in the case of the lower example of the drawing, 13).

<Mechanical properties and production conditions>

**[0040]** Next, description will be made on the mechanical properties of the copper alloy wrought material in a preferred embodiment of this embodiment. The copper alloy in this embodiment is intended to substitute lead-containing phosphor bronze or beryllium copper, that is, to substitute copper alloys containing environmentally hazardous substances, and therefore, this embodiment is similar to the first embodiment from the viewpoint that the copper alloy needs to have a mechanical strength equivalent to that of these alloys. Accordingly, this embodiment is also similar to the first embodiment in terms of the preferable ranges of the properties (tensile strength, electrical conductivity) that are required for practical use.
**[0041]** The method of producing the copper alloy wrought material of this embodiment is primarily characterized in that the sulfide particles that are present in a large amount at the grain boundaries upon casting are made, through wrought working and heat treatment, to exist in the crystals of the matrix such that the area ratio of sulfide particles in the cross-section in parallel to the wrought direction would be 40% or greater, and to disperse the sulfide particles in the cross-section in parallel to the wrought direction such that the aspect ratio would be in the range of 1:1 to 1:100.
Preferable examples of the wrought working and heat treatment include the followings.

(a) The copper alloy is rapidly cooled after hot working, followed by subjecting to area-reduction working at 0% to 95% (more preferably 30 to 90%), and to a final aging treatment.
(b) After hot working, the copper alloy is subjected to cold working and a heat treatment at a temperature of 600°C to 1,000°C repeatedly for one or more times, followed by subjecting to a solution treatment before the final cold-working, to area-reduction working at 0% to 95% (more preferably, 30 to 90%), and to a final aging treatment.

Herein, in the case where the cold working and the heat treatment at a temperature of 600°C to 1,000°C are respectively carried out once, the cold working is carried out as the final cold-working, and the heat treatment at a temperature of 600°C to 1,000°C is carried out as a solution treatment.
Further, the area-reduction working is a cold working, and the phrase "area-reduction working at 0%" means that the area-reduction working is not carried out. The temperature of the final aging treatment is preferably 350°C to 600°C, and more preferably 400°C to 550°C.
The purpose of the heat treatment at a temperature of 600°C to 1,000°C is to enhance the workability of the wrought material. The temperature range is preferably 800°C to 1,000°C, and more preferably 900°C to 1,000°C. Further, the time period of the heat treatment is preferably from 1 hour to 3 hours. The cooling conditions are substantially arbitrary, and cooling may be carried out in the manner of slow cooling or rapid cooling. The cooling speed is sufficient if it is in the range of 0.1 to 1,000 C°second.
The step immediately before the area-reduction working is preferably a hot working or a solution treatment, from the viewpoint that the control of the shape and the dispersion state of the sulfide particles is appropriately conducted through the area-reduction working, while the aspect ratio of the sulfide particles in the cross-section in parallel to the wrought direction is brought close to 1:1. In this case, the temperature of the hot working or solution treatment is preferably 750°C to 1,000°C, more preferably 850°C to 1,000°C, and even more preferably 900°C to 1,000°C.
By conducting rapid cooling (water quenching or the like) immediately after the hot working (hot rolling, hot drawing, hot extrusion or the like), an effect equivalent to the solution treatment can be obtained.
Since the copper alloy wrought material of this embodiment is a wrought material of an age-precipitation-type copper alloy, it is essential that the aging treatment step is preferably employed at least after the step of melt-casting of the copper alloy raw material, and other steps than the step to obtain the copper alloy wrought material, such as the hot working step, an annealing step, the solution treatment step, and the heat treatment step at a temperature of 600°C to 1,000°C, are carried out optionally, if needed. For example, in regard to the hot working step, it is possible to produce the copper alloy wrought material of this embodiment through any one of the usual production methods, such as hot extrusion of a billet, hot forging of an ingot, and continuous casting.
In addition to the above, preferred examples of the shape of the product or the copper alloy part may be similar to those of the first embodiment described above.

EXAMPLES

**[0042]** The present invention will be described in more detail based on examples given below, but the invention is not meant to be limited by these.

(Example 1)

(Example 1-1)

**[0043]** Each of copper alloys of the respective composition having alloying elements as shown in Table 1-1 was melted in a high frequency melting furnace, followed by casting the respective billet at the cooling speed of 0.5 to 5°C/second. The diameter of the billet was set to 200 mm. The resultant billet was hot extruded at 950°C, immediately followed by water quenching, to obtain a round bar with diameter 20 mm. Then, the resultant round rod was subjected to cold drawing, to obtain a round rod with diameter 10 mm, followed by subjecting to an aging heat treatment at a temperature of 450°C for 2 hours.

**[0044]** With respect to the resultant samples of each of the thus-obtained copper alloy wrought materials (round rods), [1] tensile strength, [2] electrical conductivity, and [3] machinability were investigated by the following methods. Measurement methods of each evaluation item are described below.

[1] Tensile strength (TS)

**[0045]** The tensile strength of each of three samples was measured in accordance with JIS Z 2241, and its average value (MPa) was obtained and shown.

[2] Electrical conductivity (EC)

**[0046]** The electrical conductivity of each of two samples was measured in a thermostatic bath controlled at 20°C (±1°C) by using a four-terminal method, and its average value (%IACS) was obtained and shown.

[3] Machinability

**[0047]** Stepwise cutting was conducted to cut the outer diameter of the round rod using a general lathe, to produce a rivet with diameter 9.6 mm at the major diameter portion and diameter 8 mm at the minor diameter portion. The shapes of the respective chips thus occurred were observed. Chips that were broken and separated off at a length of 5 mm or less were judged to be "good"; chips that were broken and separated off but had a length of 5 mm or longer but 10 mm or shorter were judged to be "fair"; and chips that were connected in a helical shape were judged to be "poor". The grades that do not cause any problem in practical use are "good" and "fair". The cutting conditions were: the rotation speed at 1,010 rpm, the conveyance speed at 0.1 mm per rotation, and the notch margin at 0.2 mm. An ultra-hard bit was used, and no cutting oil was used.

**[0048]** Further, the size (average diameter) and the area ratio of the sulfide particles were determined, by observing the microstructure of the respective sample of the round rod with diameter 10 mm on any three transverse cross-sections, under a scanning electron microscope (SEM), in three visual fields, respectively. The size (average diameter) of the sulfide particles was determined, by measuring the sizes of 100 or more sulfide particles per visual field to convert those into diameters of respective circles equivalent in areas, and averaging the diameters. The area ratio of the sulfide particles was determined, by counting the number of sulfide particles seen in one visual field, determining the area of an individual sulfide particle from the average diameter converted from the size into a diameter of a circle equivalent in area, multiplying the area by the number to determine the total area of the sulfide particles per visual field, and dividing the total area by the area of one visual field. Further, the alloying elements of the sulfide particles were analyzed, by using an energy dispersive fluorescent X-ray analyzer (EDX) attached to the SEM.

**[0049]** The results are shown in Table 1-1. In Examples 1-1 to 1-25, the contents of the alloying elements were within the range according to the present invention, and all of the working examples satisfied the conditions of tensile strength 500 MPa or greater and electrical conductivity 25% IACS or higher. Further, the size (average diameter) of the sulfide particles was 0.1 to 10 μm, and the area ratio of the sulfide particles satisfied the range of 0.1 to 10%, while the working examples had no cracking upon material working and had satisfactory machinability.

**[0050]** Comparative examples 1-1 to 1-9 are comparative examples in which the contents of the alloying elements were outside of the range as defined in the present invention. Comparative examples 1-1 and 1-3 had a low Ni content and a low Si content, and was poor in the tensile strength. Comparative example 1-2 had a high Ni content and a high Si content, and was poor in the electrical conductivity. Comparative example 1-4 had a high Ni content and a high Si content, and cracking was occurred in the cold working. Comparative example 1-5 had a low S content and a small area ratio of sulfide particles, and was poor in the machinability. Comparative examples 1-6 and 1-7 had a high S content and a large area ratio of sulfide particles, and cracking was occurred in the hot working. Comparative examples 1-8 and 1-9 had the total amount of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P and Zn greater than 2.0 mass%, and was poor in the electrical conductivity.

Conventional examples 1-1 and 1-2 are free cutting phosphor bronze and free cutting beryllium copper. The copper alloy wrought materials of Examples can exhibit properties that are equivalent or superior to those of Conventional examples 1-1 and 1-2, without containing any environmentally hazardous substances which are contained in the materials of Conventional examples 1-1 and 1-2.

Table 1-1

| Name | Alloy composition (mass%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ni | Si | S | Sn | Mn | Co | Zr | Ti | Fe | Cr | Al | P | Zn | Total amount of Sn to Zn | Cu |
| Example 1-1 | 1.5 | 0.37 | 0.69 | | | | | | | | | | | 0.00 | Balance |
| Example 1-2 | 1.8 | 0.46 | 0.26 | | | | | | | | | | | 0.00 | Balance |
| Example 1-3 | 2.3 | 0.54 | 0.46 | | | | | | | | | | | 0.00 | Balance |
| Example 1-4 | 2.8 | 0.69 | 0.14 | 0.26 | | | | | | | | | | 0.26 | Balance |
| Example 1-5 | 3.3 | 0.84 | 0.21 | 0.08 | | | | | | | | | | 0.08 | Balance |
| Example 1-6 | 3.8 | 0.96 | 0.12 | 0.11 | | | | | | | | | | 0.11 | Balance |
| Example 1-7 | 4.2 | 1.12 | 0.29 | | 0.13 | | | | | | | | | 0.13 | Balance |
| Example 1-8 | 4.8 | 1.30 | 0.31 | | 0.11 | | | | | | | | | 0.11 | Balance |
| Example 1-9 | 5.5 | 1.36 | 0.18 | 0.13 | | 0.08 | | | | | | | | 0.21 | Balance |
| Example 1-10 | 6.3 | 1.53 | 0.22 | 0.24 | 0.09 | | | | | | | | | 0.33 | Balance |
| Example 1-11 | 7.0 | 1.96 | 0.27 | | 0.15 | 0.16 | | | | | | | | 0.31 | Balance |
| Example 1-12 | 2.2 | 0.55 | 0.28 | 0.08 | | | 0.11 | | | | | | | 0.19 | Balance |
| Example 1-13 | 2.7 | 0.73 | 0.25 | | | 0.07 | | 0.22 | | | | | | 0.29 | Balance |
| Example 1-14 | 3.2 | 0.83 | 0.03 | 0.15 | | | | 0.18 | | | | | | 0.33 | Balance |
| Example 1-15 | 3.7 | 0.93 | 0.11 | 0.09 | | | | | 0.13 | | | | | 0.22 | Balance |
| Example 1-16 | 1.6 | 0.34 | 0.98 | | 0.23 | | | | | | | | | 0.23 | Balance |
| Example 1-17 | 2.4 | 0.57 | 0.31 | | | | | | | 0.05 | 0.11 | | 0.63 | 0.79 | Balance |
| Example 1-18 | 2.7 | 0.75 | 0.18 | | | | | | | 0.08 | | 0.04 | | 0.12 | Balance |
| Example 1-19 | 3.3 | 0.82 | 0.23 | | | | | | 0.21 | | | | 0.35 | 0.56 | Balance |
| Example 1-20 | 3.7 | 0.95 | 0.09 | 0.16 | | | | | 0.10 | | | | | 0.26 | Balance |
| Example 1-21 | 5.8 | 1.28 | 0.08 | | 0.22 | | 0.18 | | | | 0.05 | 0.02 | | 0.47 | Balance |
| Example 1-22 | 6.5 | 1.77 | 0.11 | 0.10 | 0.14 | 0.21 | | | | | | | 0.38 | 0.83 | Balance |
| Example 1-23 | 2.3 | 0.55 | 0.08 | 0.22 | | | 0.08 | | 0.12 | 0.11 | | | 0.39 | 0.92 | Balance |
| Example 1-24 | 1.8 | 0.49 | 0.42 | | 0.12 | 0.18 | | 0.17 | 0.05 | | | | 0.72 | 1.24 | Balance |
| Example 1-25 | 3.1 | 0.79 | 0.26 | 0.12 | 0.19 | | 0.13 | | | 0.08 | 0.08 | 0.02 | 0.43 | 1.05 | Balance |

Table 1-1 (continued)

| Name | Alloy composition (mass%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ni | Si | S | Sn | Mn | Co | Zr | Ti | Fe | Cr | Al | P | Zn | Total amount of Sn to Zn | Cu |
| Comparative example 1-1 | *1.3* | *0.29* | 0.21 | | | | | | | | | | | 0.00 | Balance |
| Comparative example 1-2 | *7.5* | *2.31* | 0.25 | 0.08 | | | | | | | | | | 0.08 | Balance |
| Comparative example 1-3 | *1.4* | *0.29* | 0.31 | 0.18 | | | | | | | | | | 0.18 | Balance |
| Comparative example 1-4 | *7.8* | *2.45* | 0.19 | | 0.27 | | | | | | | | | 0.27 | Balance |
| Comparative example 1-5 | 3.2 | 0.82 | *0.01* | 0.24 | 0.17 | | | | | | | | | 0.41 | Balance |
| Comparative example 1-6 | 3.1 | 0.80 | *1.08* | 0.18 | | | | | | | | | | 0.18 | Balance |
| Comparative example 1-7 | 3.7 | 0.94 | *1.22* | | 0.24 | | 0.15 | | | | | | | 0.39 | Balance |
| Comparative example 1-8 | 3.3 | 0.80 | 0.25 | 0.53 | | 0.12 | 0.28 | 0.25 | 0.42 | | | | 0.64 | *2.24* | Balance |
| Comparative example 1-9 | 2.7 | 0.68 | 0.54 | | 0.86 | | | | | 0.21 | 0.18 | 0.08 | 0.71 | *2.04* | Balance |
| Conventional example 1-1 | Sn: 0.4, Zn: 0.4, Pb: 4.0, P: 0.1 (free-cutting phosphor bronze) | | | | | | | | | | | | | | Balance |
| Conventional example 1-2 | Be: 1.9, Pb:0.4, Ni+Co: 0.4 (free-cutting beryllium copper) | | | | | | | | | | | | | | Balance |

Table 1-1 (continued)

| Name | Component of sulfide | Size of sulfide particles (µm) | Area ratio of sulfide particles (%) | TS (MPa) | EC (%IACS) | Machinability |
|---|---|---|---|---|---|---|
| Example 1-1 | Cu-S | 4.6 | 5.5 | 515 | 39.3 | Good |
| Example 1-2 | Cu-S | 2.3 | 1.9 | 603 | 38.2 | Good |
| Example 1-3 | Cu-S | 2.9 | 3.8 | 712 | 39.5 | Good |
| Example 1-4 | Cu-S | 1.8 | 1.1 | 810 | 35.3 | Good |
| Example 1-5 | Cu-S | 1.6 | 1.5 | 864 | 35.9 | Good |
| Example 1-6 | Cu-S | 1.4 | 0.8 | 942 | 35.6 | Good |
| Example 1-7 | Cu-S, Mn-S | 3.1 | 2.4 | 961 | 31.0 | Good |
| Example 1-8 | Cu-S, Mn-S | 2.5 | 2.7 | 983 | 30.0 | Good |
| Example 1-9 | Cu-S | 1.7 | 1.3 | 996 | 35.7 | Good |
| Example 1-10 | Cu-S, Mn-S | 2.1 | 2.0 | 987 | 33.3 | Good |
| Example 1-11 | Cu-S, Mn-S | 2.6 | 2.3 | 1,011 | 25.3 | Good |
| Example 1-12 | Cu-S, Zr-S | 1.8 | 2.2 | 692 | 37.4 | Good |
| Example 1-13 | Cu-S, Ti-S | 2.0 | 2.0 | 781 | 35.2 | Good |
| Example 1-14 | Cu-S | 0.9 | 0.3 | 858 | 34.4 | Fair |
| Example 1-15 | Cu-S | 1.3 | 0.8 | 913 | 28.0 | Good |
| Example 1-16 | Cu-S, Mn-S | 5.1 | 7.7 | 559 | 32.5 | Good |
| Example 1-17 | Cu-S, Al-S, Zn-S | 2.6 | 2.8 | 726 | 36.2 | Good |
| Example 1-18 | Cu-S, Cr-S | 1.6 | 1.7 | 771 | 30.7 | Good |
| Example 1-19 | Cu-S, Fe-S, Zn-S | 1.9 | 2.0 | 856 | 25.2 | Good |
| Example 1-20 | Cu-S | 1.2 | 0.5 | 921 | 28.3 | Fair |
| Example 1-21 | Cu-S, Mn-S | 1.3 | 0.8 | 994 | 28.8 | Good |
| Example 1-22 | Cu-S, Mn-S | 1.7 | 1.1 | 1,018 | 26.2 | Good |
| Example 1-23 | Cu-S, Zr-S | 1.2 | 0.5 | 731 | 28.4 | Fair |
| Example 1-24 | Cu-S, Mn-S, Ti-S, Zn-S | 2.9 | 3.8 | 602 | 29.3 | Good |
| Example 1-25 | Cu-S, Mn-S, Zr-S, Al-S | 2.2 | 2.4 | 842 | 28.3 | Good |

Table 1-1 (continued)

| Name | Component of sulfide | Size of sulfide particles (µm) | Area ratio of sulfide particles (%) | TS (MPa) | EC (%IACS) | Machinability |
|---|---|---|---|---|---|---|
| Comparative example 1-1 | Cu-S | 1.8 | 1.9 | *441* | 39.0 | Good |
| Comparative example 1-2 | Cu-S | 2.5 | 2.0 | 971 | *21.4* | Good |
| Comparative example 1-3 | Cu-S | 2.7 | 2.7 | *469* | 35.7 | Good |
| Comparative example 1-4 | Cu-S, Mn-S | 1.9 | 1.5 | *Cracked in cold working* | | |
| Comparative example 1-5 | Cu-S | 0.9 | 0.08 | 867 | 30.4 | *Poor* |
| Comparative example 1-6 | Cu-S | 5.9 | 10.5 | *Cracked in hot working* | | |
| Comparative example 1-7 | Cu-S, Mn-S, Zr-S | 6.2 | 11.2 | *Cracked in hot working* | | |
| Comparative example 1-8 | Cu-S, Zr-S, Ti-S | 2.2 | 2.0 | 905 | *17.4* | Good |
| Comparative example 1-9 | Cu-S, Mn-S, Cr-S, Al-S | 3.6 | 4.3 | 776 | *18.7* | Good |
| Conventional example 1-1 | None (Pb particles) | Pb: 4.7 | 1.3 | 475 | 15.3 | Good |
| Conventional example 1-2 | None (Pb particles) | Pb: 2.8 | 0.1 | 1,130 | 23.4 | Good |

(Example 1-2)

**[0051]** Small-sized ingots were produced, with the alloying elements of Example 1-6 and Example 1-16 in Table 1-1, using a small-sized mold (25mm x 25mm x 300mm) for laboratory use, while the cooling speed at casting was changed, for example, by changing the preheating temperature of the mold. The ingots thus obtained were subjected to hot rolling at a temperature of 950°C, immediately followed by water quenching, to obtain round rods with diameter 20 mm, respectively. Then, the resultant round rods were subjected to cold drawing, to obtain round rods with diameter 10 mm, followed by subjecting to an aging heat treatment at a temperature of 450°C for 2 hours. With respect to the respective samples of the copper alloy wrought materials (round rods) obtained as above, [1] tensile strength, [2] electrical conductivity, and [3] machinability were examined in the same manner as in Example 1-1, and the size (average diameter) and the area ratio of the sulfide particles were also similarly determined by the methods described above. The results are shown in Table 1-2.

Table 1-2

| Name | Alloy composition (mass%) | | | | | |
|---|---|---|---|---|---|---|
| | Ni | Si | S | Sn | Mn | Cu |
| Example 1-26 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance |
| Example 1-27 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance |
| Example 1-28 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance |
| Example 1-29 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance |
| Example 1-30 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance |
| Example 1-31 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance |
| Example 1-32 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance |
| Example 1-33 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance |
| Comparative example 1-10 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance |
| Comparative example 1-11 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance |
| Comparative example 1-12 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance |
| Comparative example 1-13 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance |

Table 1-2 (continued)

| Name | Cooling speed (°C/sec.) | Component of sulfide | Size of sulfide particles (µm) | Area ratio of sulfide particles (%) | TS (MPa) | EC (%IACS) | Machinability |
|---|---|---|---|---|---|---|---|
| Example 1-26 | 0.1 | Cu-S | 9.6 | 0.9 | 948 | 36.1 | Fair |
| Example 1-27 | 2 | Cu-S | 1.4 | 0.8 | 952 | 35.7 | Good |
| Example 1-28 | 11 | Cu-S | 0.6 | 0.8 | 950 | 35.6 | Good |
| Example 1-29 | 45 | Cu-S | 0.1 | 0.7 | 936 | 35.3 | Fair |
| Example 1-30 | 0.2 | Cu-S, Mn-S | 9.2 | 7.8 | 572 | 32.1 | Good |
| Example 1-31 | 1 | Cu-S, Mn-S | 4.0 | 7.8 | 566 | 32.6 | Good |
| Example 1-32 | 10 | Cu-S, Mn-S | 1.2 | 7.6 | 562 | 31.7 | Good |
| Example 1-33 | 48 | Cu-S, Mn-S | 0.3 | 7.3 | 558 | 31.3 | Good |
| Comparative example 1-10 | 0.09 | Cu-S | *10.7* | 0.9 | *Cracked in cold working* | | |
| Comparative example 1-11 | 59 | Cu-S | *0.06* | 0.5 | 942 | 35.1 | *Poor* |
| Comparative example 1-12 | 0.08 | Cu-S, Mn-S | *15.3* | 8.0 | *Cracked in hot working* | | |
| Comparative example 1-13 | 65 | Cu-S, Mn-S | *0.08* | 7.2 | 574 | 31.7 | *Poor* |

**[0052]** In Table 1-2, Examples 1-26 to 1-29 are working examples produced with the same alloying elements as those in Example 1-6 and Examples 1-30 to 1-33 are working examples produced with the same alloying elements as those in Example 1-16, each by changing the cooling speed in the range according to the present invention. When the cooling speed is made fast, the size (average diameter) of the sulfide particles tends to be small, but all of the working examples satisfied the values within the range according to the present invention, to exhibit excellent machinability. In Table 1-2, Comparative examples 1-10 and 1-11 are comparative examples produced with the same alloying elements as those in Example 1-6 and Comparative examples 1-12 and 1-13 are comparative examples produced with the same alloying elements as those in Example 1-16, each by setting the cooling speed outside of the range defined in the present invention. When the cooling speed was slow (Comparative examples 1-10 and 1-12), the size (average diameter) of the sulfide particles become large, and cracking was occurred in the cold working or hot working. When the cooling speed was fast (Comparative examples 1-11 and 1-13), the size (average diameter) of the sulfide particles was less than 0.1 μm, and the machinability was poor.

(Example 1-3)

**[0053]** Round rods with diameter ϕ2 mm and ϕ7 mm, respectively, were obtained, from the round rods with diameter 10 mm which were obtained by the method in Example 1-1, using the alloying elements of Example 1-6 and Example 1-16 in Table 1-1, respectively. Using the thus-obtained round rods, 1,000 connector pins, as shown in Fig. 5 and Fig. 6, respectively, were obtained by using an NC lathe. As a result, working into the parts was able to carry out, without any twining of chips to the worked parts, and without any changes in the dimension due to tool abrasion. The outer diameter working conditions were: the rotation speed at 3,000 rpm, and the conveyance speed at 0.02 mm per rotation; and the drilling conditions were: the rotation speed at 2,500 rpm, and the conveyance speed at 0.03 mm per rotation, and a cutting oil was used. In Fig. 5, 50 represents a connector pin, and 51 represents a slit. In Fig. 6, 60 represents a connector pin of another form, 61 represents a slit, and 62 represents a tapering section.
With respect to the connector pin with the shape of Fig. 5, evaluation was made on the insertion/extraction property that is required as a characteristic of a pin material. The evaluation method was as follows: a pin gauge with diameter ϕ0.92 mm was inserted into the pin worked above, and the insertion/extraction force (initial value T0) was measured; then, the same pin was repeatedly subjected to inserting and extracting for 500 times, and the insertion/extraction force (T1) was measured again; and the ratio to the initial value, T1/T0, was determined. It can be said that the larger the value of T1/T0 is, the smaller the lowering in the insertion/extraction force is, which is satisfactory in the performance as a connector pin. The evaluation was made with five pins, and the average value was determined. For comparison, the same evaluation was carried out with respect to the materials of Conventional examples 1-1 and 1-2 in Table 1-1. The results are shown in Table 1-3.
It can be seen from Table 1-3 that Examples exhibit insertion/extraction property that are equivalent to that of free cutting beryllium copper of Conventional example 1-2, and that they are excellent connector pins. The insertion/extraction property of free cutting phosphor bronze of Conventional example 1-1 was inferior to that of Examples, with resulting in that there is a concern for contact failure upon a long-term use.
**[0054]**

Table 1-3

| Name | Evaluation of insertion/extraction property (T1/T0) |
|---|---|
| Example 1-6 | 0.86 |
| Example 1-16 | 0.80 |
| Conventional example 1-1 | 0.53 |
| Conventional example 1-2 | 0.85 |

(Example 2)

(Example 2-1)

**[0055]** Samples were obtained in the same manner as in Example 1-1, using copper alloys of the respective composition having alloying elements as shown in Table 2-1. The measurement methods and conditions for the properties were also the same as those in Example 1-1.
**[0056]** The area ratio of the sulfide particles that were present in the crystals of the matrix in the cross-section in parallel to the wrought direction, was determined, by observing the microstructure of the respective sample of round rod with diameter 10 mm on any three cross-sections each in parallel to the wrought direction, under a scanning electron microscope (SEM), in three visual fields, respectively. That is, the area ratio was determined, by counting the number of total sulfide particles observed in one visual field, measuring the sizes of each sulfide particles to convert those into diameters of the respective circles equivalent in area, averaging the diameters, determining the area from the average diameter, and multiplying the area by the number of sulfide particles, to thereby determine the total area of total sulfide particles seen in one visual field, subsequently counting only the number of sulfide particles that were in the grains and across the grain boundaries, measuring the sizes of each of said sulfide particles to convert those into diameters of the respective circles equivalent in area, averaging the diameters, determining the area from the average diameter, and

multiplying the area by the number of said sulfide particles, to thereby determine the total area of the sulfide particles that were present in the grains and across the grain boundaries, and dividing the thus-determined total area by the total area of all the sulfide particles seen in one visual field. Further, the alloying elements of the sulfide particles were analyzed, by using an energy dispersive fluorescent X-ray analyzer (EDX) attached to the SEM. Please note, although not shown in the table, that the wrought materials of Examples each had the aspect ratio in the cross-section that was in parallel to the wrought direction, within the range of 1:1 to 1:100, and that the area ratio of the sulfide particles in the transverse cross-section of the wrought materials satisfied the requirement of 0.1 to 10%.

**[0057]** The results are shown in Table 2-1. In Examples 2-1 to 2-25, the contents of the alloying elements were within the range according to the present invention, and all of the working examples satisfied the conditions of tensile strength 500 MPa or greater and electrical conductivity 25% IACS or higher. Further, 40% or more of sulfide particles in the cross-section in parallel to the wrought direction were present in the crystals of the matrix, while the working examples had no cracking upon material working and had satisfactory machinability.

**[0058]** Comparative examples 2-1 to 2-9 are comparative examples in which the respective alloy composition was outside of the range as defined in the present invention. Comparative examples 2-1 and 2-3 was too low in the Ni content and Si content, resulted in an insufficient tensile strength. Comparative example 2-2 was too high in the Ni content and the Si content, and was poor in the electrical conductivity. Comparative example 2-4 was too high in the Ni content and the Si content, and cracking was occurred in the cold working. Comparative example 2-5 had a low S content, and 40% or more of the sulfide particles in the cross-section in parallel to the wrought direction were present in the crystals of the matrix, but the machinability was poor. Comparative examples 2-6 and 2-7 had a high S content, and 40% or more of the sulfide particles in the cross-section in parallel to the wrought direction were not present in the crystals of the matrix, and cracking was occurred in the hot working. Comparative examples 2-8 and 2-9 had the total amount of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P and Zn greater than 2.0 mass%, and was poor in the electrical conductivity.
Conventional examples 2-1 and 2-2 are free cutting phosphor bronze and free cutting beryllium copper. The copper alloy wrought materials of Examples can exhibit properties that are equivalent or superior to those of Conventional examples 2-1 and 2-2, without containing any environmentally hazardous substances which are contained in the materials of Conventional examples 2-1 and 2-2.

Table 2-1

| Name | Alloy composition (mass%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ni | Si | S | Sn | Mn | Co | Zr | Ti | Fe | Cr | Al | P | Zn | Total amount of Sn to Zn | Cu |
| Example 2-1 | 1.5 | 0.37 | 0.69 | | | | | | | | | | | 0.00 | Balance |
| Example 2-2 | 1.8 | 0.46 | 0.26 | | | | | | | | | | | 0.00 | Balance |
| Example 2-3 | 2.3 | 0.54 | 0.46 | | | | | | | | | | | 0.00 | Balance |
| Example 2-4 | 2.8 | 0.69 | 0.14 | 0.26 | | | | | | | | | | 0.26 | Balance |
| Example 2-5 | 3.3 | 0.84 | 0.21 | 0.08 | | | | | | | | | | 0.08 | Balance |
| Example 2-6 | 3.8 | 0.96 | 0.12 | 0.11 | | | | | | | | | | 0.11 | Balance |
| Example 2-7 | 4.2 | 1.12 | 0.29 | | 0.13 | | | | | | | | | 0.13 | Balance |
| Example 2-8 | 4.8 | 1.30 | 0.31 | | 0.11 | | | | | | | | | 0.11 | Balance |
| Example 2-9 | 5.5 | 1.36 | 0.18 | 0.13 | | 0.08 | | | | | | | | 0.21 | Balance |
| Example 2-10 | 6.3 | 1.53 | 0.22 | 0.24 | 0.09 | | | | | | | | | 0.33 | Balance |
| Example 2-11 | 7.0 | 1.96 | 0.27 | | 0.15 | 0.16 | | | | | | | | 0.31 | Balance |
| Example 2-12 | 2.2 | 0.55 | 0.28 | 0.08 | | | 0.11 | | | | | | | 0.19 | Balance |
| Example 2-13 | 2.7 | 0.73 | 0.25 | | | 0.07 | | 0.22 | | | | | | 0.29 | Balance |
| Example 2-14 | 3.2 | 0.83 | 0.03 | 0.15 | | | | 0.18 | | | | | | 0.33 | Balance |
| Example 2-15 | 3.7 | 0.93 | 0.11 | 0.09 | | | | | 0.13 | | | | | 0.22 | Balance |
| Example 2-16 | 1.6 | 0.34 | 0.98 | | 0.23 | | | | | | | | | 0.23 | Balance |
| Example 2-17 | 2.4 | 0.57 | 0.31 | | | | | | | 0.05 | 0.11 | | 0.63 | 0.79 | Balance |
| Example 2-18 | 2.7 | 0.75 | 0.18 | | | | | | | 0.08 | | 0.04 | | 0.12 | Balance |
| Example 2-19 | 3.3 | 0.82 | 0.23 | | | | | | 0.21 | | | | 0.35 | 0.56 | Balance |
| Example 2-20 | 3.7 | 0.95 | 0.09 | 0.16 | | | | | 0.10 | | | | | 0.26 | Balance |
| Example 2-21 | 5.8 | 1.28 | 0.08 | | 0.22 | | 0.18 | | | | 0.05 | 0.02 | | 0.47 | Balance |
| Example 2-22 | 6.5 | 1.77 | 0.11 | 0.10 | 0.14 | 0.21 | | | | | | | 0.38 | 0.83 | Balance |
| Example 2-23 | 2.3 | 0.55 | 0.08 | 0.22 | | | 0.08 | | 0.12 | 0.11 | | | 0.39 | 0.92 | Balance |
| Example 2-24 | 1.8 | 0.49 | 0.42 | | 0.12 | 0.18 | | 0.17 | 0.05 | | | | 0.72 | 1.24 | Balance |
| Example 2-25 | 3.1 | 0.79 | 0.26 | 0.12 | 0.19 | | 0.13 | | | 0.08 | 0.08 | 0.02 | 0.43 | 1.05 | Balance |

Table 2-1 (continued)

| Name | Alloy composition (mass%) | | | | | | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Ni | Si | S | Sn | Mn | Co | Zr | Ti | Fe | Cr | Al | P | Zn | Total amount of Sn to Zn | Cu |
| Comparative example 2-1 | *1.3* | *0.29* | 0.21 | | | | | | | | | | | 0.00 | Balance |
| Comparative example 2-2 | *7.5* | *2.31* | 0.25 | 0.08 | | | | | | | | | | 0.08 | Balance |
| Comparative example 2-3 | *1.4* | 0.29 | 0.31 | 0.18 | | | | | | | | | | 0.18 | Balance |
| Comparative example 2-4 | *7.8* | *2.45* | 0.19 | | 0.27 | | | | | | | | | 0.27 | Balance |
| Comparative example 2-5 | 3.2 | 0.82 | *0.01* | 0.24 | 0.17 | | | | | | | | | 0.41 | Balance |
| Comparative example 2-6 | 3.1 | 0.80 | *1.08* | 0.18 | | | | | | | | | | 0.18 | Balance |
| Comparative example 2-7 | 3.7 | 0.94 | *1.22* | | 0.24 | | 0.15 | | | | | | | 0.39 | Balance |
| Comparative example 2-8 | 3.3 | 0.80 | 0.25 | 0.53 | | 0.12 | 0.28 | 0.25 | 0.42 | | | | 0.64 | *2.24* | Balance |
| Comparative example 2-9 | 2.7 | 0.68 | 0.54 | | 0.86 | | | | | 0.21 | 0.18 | 0.08 | 0.71 | *2.04* | Balance |
| Conventional example 2-1 | Sn: 0.4, Zn: 0.4, Pb: 4.0, P: 0.1 (free-cutting phosphor bronze) | | | | | | | | | | | | | | Balance |
| Conventional example 2-2 | Be: 1.9, Pb: 0.4, Ni+Co: 0.4 (free-cutting beryllium copper) | | | | | | | | | | | | | | Balance |

Table 2-1 (continued)

| Name | Component of sulfide | Area ratio of sulfide particles in gains (%) | TS (MPa) | EC (%IACS) | Machinability |
|---|---|---|---|---|---|
| Example 2-1 | Cu-S | 61 | 515 | 39.3 | Good |
| Example 2-2 | Cu-S | 55 | 603 | 38.2 | Good |
| Example 2-3 | Cu-S | 53 | 712 | 39.5 | Good |
| Example 2-4 | Cu-S | 50 | 810 | 35.3 | Good |
| Example 2-5 | Cu-S | 62 | 864 | 35.9 | Good |
| Example 2-6 | Cu-S | 58 | 942 | 35.6 | Good |
| Example 2-7 | Cu-S, Mn-S | 57 | 961 | 31.0 | Good |
| Example 2-8 | Cu-S, Mn-S | 54 | 983 | 30.0 | Good |
| Example 2-9 | Cu-S | 58 | 996 | 35.7 | Good |
| Example 2-10 | Cu-S, Mn-S | 55 | 987 | 33.3 | Good |
| Example 2-11 | Cu-S, Mn-S | 60 | 1,011 | 25.3 | Good |
| Example 2-12 | Cu-S, Zr-S | 50 | 692 | 37.4 | Good |
| Example 2-13 | Cu-S, Ti-S | 62 | 781 | 35.2 | Good |
| Example 2-14 | Cu-S | 48 | 858 | 34.4 | Fair |
| Example 2-15 | Cu-S | 58 | 913 | 28.0 | Good |
| Example 2-16 | Cu-S, Mn-S | 55 | 559 | 32.5 | Good |
| Example 2-17 | Cu-S, Al-S, Zn-S | 63 | 726 | 36.2 | Good |
| Example 2-18 | Cu-S, Cr-S | 50 | 771 | 30.7 | Good |
| Example 2-19 | Cu-S, Fe-S, Zn-S | 55 | 856 | 25.2 | Good |
| Example 2-20 | Cu-S | 44 | 921 | 28.3 | Fair |
| Example 2-21 | Cu-S, Mn-S | 61 | 994 | 28.8 | Good |
| Example 2-22 | Cu-S, Mn-S | 53 | 1,018 | 26.2 | Good |
| Example 2-23 | Cu-S, Zr-S | 52 | 731 | 28.4 | Fair |
| Example 2-24 | Cu-S, Mn-S, Ti-S, Zn-S | 52 | 602 | 29.3 | Good |
| Example 2-25 | Cu-S, Mn-S, Zr-S, Al-S | 61 | 842 | 28.3 | Good |

Table 2-1 (continued)

| Name | Component of sulfide | Area ratio of sulfide particles in grains (%) | TS (MPa) | EC (%IACS) | Machinability |
|---|---|---|---|---|---|
| Comparative example 2-1 | Cu-S | 62 | *441* | 39.0 | Good |
| Comparative example 2-2 | Cu-S | 54 | 971 | *21.4* | Good |
| Comparative example 2-3 | Cu-S | 59 | *469* | 35.7 | Good |
| Comparative example 2-4 | Cu-S, Mn-S | 55 * | Cracked in cold working | | |
| Comparative example 2-5 | Cu-S | 63 | 867 | 30.4 | Poor |
| Comparative example 2-6 | Cu-S | 35 * | Cracked in hot working | | |
| Comparative example 2-7 | Cu-S, Mn-S, Zr-S | 33 * | Cracked in hot working | | |
| Comparative example 2-8 | Cu-S, Zr-S, Ti-S | 57 | 905 | *17.4* | Good |
| Comparative example 2-9 | Cu-S, Mn-S, Cr-S, Al-S | 50 | 776 | *18.7* | Good |
| Conventional example 2-1 | Pb particles | | *475* | *15.3* | Good |
| Conventional example 2-2 | Pb particles | | 1,130 | *23.4* | Good |

* The area ratio of sulfide particles in grains, in the samples cracked

(Example 2-2)

**[0059]** Copper alloys having the compositions of Examples 2-1, 2-6 and 2-16 and Comparative example 2-5 in Table 2-1 were melted in a high frequency melting furnace, respectively, and billets with diameter 300 mm were obtained by casting at a cooling speed of 1°C/second, respectively. The respective billet was hot extruded at a temperature of 950°C, immediately followed by water quenching, to obtain a round rod with diameter 30 mm. Then, the resultant round rod was worked to diameter 20 mm by cold drawing, followed by subjecting to a solution treatment at a temperature of 950°C, to obtain a round rod with diameter 20 mm.

The thus-obtained round rod was subjected to area-reduction working, to obtain a round rod with diameter 20 mm (an area-reduction working 0%), a round rod with diameter 16 mm (an area-reduction working 36.0%), a round rod with diameter 10 mm (an area-reduction working 75.0%), a round rod with diameter 4.5 mm (an area-reduction working 94.9%), and a round rod with diameter 3.5 mm (an area-reduction working 96.9%), respectively. Further, the resultant round rods were subjected to an aging treatment as follows: the round rod with diameter 20 mm was treated at 500°C for 2 hours; the round rod with diameter 16 mm was treated at 480°C for 2 hours; the round rod with diameter 10 mm was treated at 450°C for 2 hours; and the round rods with diameter 4.5 mm and 3.6 mm were treated at 430°C for 2 hours. With respect to the thus-obtained samples of the copper alloy wrought materials (round rods), [1] tensile strength and [2] electrical conductivity were examined in the same manner as in Example 1, and [3] machinability was examined by the following method.

[3] Machinability

**[0060]** The materials with the respective diameters were subjected to external cutting, using a general lathe, to obtain round rods with diameter 3 mm, followed by stepwise cutting to cut the outer diameter of the round rods. The shapes of the respective chips thus occurred were observed. Chips that were broken and separated off at a length of 5 mm or less were judged to be "good"; chips that were broken and separated off but had a length of 5 mm or longer but 10 mm or shorter were judged to be "fair"; and chips that were connected in a helical shape were judged to be "poor". The grades that do not cause any problem in practical use are "good" and "fair". The cutting conditions were: the rotation speed at 1,010 rpm, the conveyance speed at 0.1 mm per rotation, and the notch margin at 0.2 mm. An ultra-hard bit was used, and no cutting oil was used.

**[0061]** The area ratio of the sulfide particles in the cross-section in parallel to the wrought direction and present in the crystals of the matrix, was determined, by the method described above, by observing the microstructure of the respective sample of round rod with diameter of 20, 16, 10, 4.5, or 3.5 mm on any three cross-sections each in parallel to the wrought direction, under a scanning electron microscope (SEM), in three visual fields, respectively. Further, the aspect ratio of the sulfide particles was determined from the ratio of the length of the sulfide particles that were extended in parallel to the wrought direction, while the length in the direction perpendicular to the wrought direction of the sulfide particles observed with the electron microscope was defined to be 1.

**[0062]**

Table 2-2

| Name | Alloy composition (mass%) | | | | | | Working ratio in area-reduction (%) |
|---|---|---|---|---|---|---|---|
| | Ni | Si | S | Sn | Mn | Cu | |
| Example 2-26 | 1.5 | 0.37 | 0.69 | | | Balance | 0.0 |
| Example 2-27 | 1.5 | 0.37 | 0.69 | | | Balance | 36.0 |
| Example 2-28 | 1.5 | 0.37 | 0.69 | | | Balance | 75.0 |
| Example 2-29 | 1.5 | 0.37 | 0.69 | | | Balance | 94.9 |
| Example 2-30 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance | 0.0 |
| Example 2-31 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance | 36.0 |
| Example 2-32 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance | 75.0 |
| Example 2-33 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance | 94.9 |
| Example 2-34 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance | 0.0 |
| Example 2-35 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance | 36.0 |
| Example 2-36 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance | 75.0 |
| Example 2-37 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance | 94.9 |
| Reference comparative example 2-1 | 1.5 | 0.37 | 0.69 | | | Balance | 97.0 |
| Reference comparative example 2-2 | 3.8 | 0.96 | 0.12 | 0.11 | | Balance | 97.0 |
| Reference comparative example 2-3 | 1.6 | 0.34 | 0.98 | | 0.23 | Balance | 97.0 |
| Reference comparative example 2-4 | 3.2 | 0.82 | 0.01 | 0.24 | 0.17 | Balance | 0.0 |
| Reference comparative example 2-5 | 3.2 | 0.82 | 0.01 | 0.24 | 0.17 | Balance | 36.0 |
| Reference comparative example 2-6 | 3.2 | 0.82 | 0.01 | 0.24 | 0.17 | Balance | 75.0 |
| Reference comparative example 2-7 | 3.2 | 0.82 | 0.01 | 0.24 | 0.17 | Balance | 97.0 |

Table 2-2 (continued)

| Name | Area ratio of sulfide particles in grains (%) | Aspect ratio | TS (MPa) | EC (%IACS) | Machinability |
|---|---|---|---|---|---|
| Example 2-26 | 55 | 1:1 to 1:3 | 504 | 37.5 | Good |
| Example 2-27 | 62 | 1:1 to 1:9 | 522 | 34.5 | Good |
| Example 2-28 | 61 | 1:1 to 1:60 | 515 | 39.3 | Good |
| Example 2-29 | 53 | 1:1 to 1:72 | 580 | 33.0 | Good |
| Example 2-30 | 57 | 1:1 to 1:4 | 890 | 34.5 | Good |
| Example 2-31 | 60 | 1:1 to 1:15 | 896 | 33.4 | Good |
| Example 2-32 | 58 | 1:1 to 1:78 | 942 | 35.6 | Good |
| Example 2-33 | 59 | 1:1 to 1:80 | 954 | 35.0 | Good |
| Example 2-34 | 60 | 1:1 to 1:5 | 526 | 30.3 | Good |
| Example 2-35 | 55 | 1:1 to 1:20 | 550 | 30.8 | Good |
| Example 2-36 | 55 | 1:1 to 1:71 | 559 | 32.5 | Good |
| Example 2-37 | 49 | 1:1 to 1:95 | 606 | 32.4 | Good |
| Reference comparative example 2-1 | Cracked in cold working | | | | |
| Reference comparative example 2-2 | Cracked in cold working | | | | |
| Reference comparative example 2-3 | Cracked in cold working | | | | |
| Reference comparative example 2-4 | 52 | 1:1 to 1:3 | 808 | 31 | Poor |
| Reference comparative example 2-5 | 42 | 1:1 to 1:5 | 854 | 32.2 | Poor |
| Reference comparative example 2-6 | 57 | 1:1 to 1:76 | 867 | 30.4 | Poor |
| Reference comparative example 2-7 | 45 | 1:1 to 1:131 | 958 | 31.5 | Poor |

**[0063]** In Table 2-2, Examples 2-26 to 2-37 are working examples, in which use was made of the same alloying elements as those in Examples 2-1, 2-6 and 2-16, respectively, each by conducting the area-reduction working within the range according to the present invention. Each of those working examples satisfied the requirements of tensile strength of 500 MPa or greater and electrical conductivity of 25% IACS or higher. Further, 40% or more of the sulfide particles in the cross-section in parallel to the wrought direction were present in the crystals of the matrix, and the sulfide particles having an aspect ratio of 1:1 to 1:100 were dispersed in the cross-section in parallel to the wrought direction, and no cracking occurred in the material working, and the machinability was also satisfactory.

Comparative examples 2-10 to 2-12 each had alloy compositions defined in the present invention, but the working ratio in the area-reduction working was outside of the range according to the present invention, and cracking was occurred in the cold working. Comparative examples 2-13 to 2-16 had the same alloying elements as in Comparative example 2-5. Comparative examples 2-13 to 2-15 were subjected to the area-reduction working to an extent according to the present invention; however, since the S content was low, although 40% or more of the sulfide particles in the cross-section in parallel to the wrought direction were present in the crystals of the matrix, the machinability was poor. Comparative example 2-16 was subjected to the area-reduction working to an extent that was outside of the range according to the present invention, although 40% or more of the sulfide particles in the cross-section in parallel to the wrought direction were present in the crystals of the matrix and no cracking was occurred, sulfide particles with an aspect ratio exceeding 1:100 were dispersed in the cross-section in parallel to the wrought direction, and the machinability was poor.

(Example 2-3)

**[0064]** Samples having the alloy compositions of Example 2-6 and Example 2-16 in Table 2-1, respectively, were evaluated on the insertion/extraction property of connectors in the same manner as in Example 1-3. The results are shown in Table 2-3, and it can be seen that Examples exhibit the insertion/extraction property equivalent to free cutting beryllium copper of Conventional example 2-2, and that the samples of the working examples are excellent connector pins. The insertion/extraction property of free cutting phosphor bronze of Conventional example 2-1 was inferior to Examples.

**[0065]**

Table 2-3

| Name | Ratio of insertion/extraction force to initial value |
|---|---|
| Example 2-6 | 0.86 |
| Example 2-16 | 0.80 |
| Conventional example 2-1 | 0.53 |
| Conventional example 2-2 | 0.85 |

**[0066]** Having described our invention as related to the present embodiments, it is our intention that the invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.

This application claims priority on Patent Application No. 2010-280946 filed in Japan on December 16, 2010, Patent Application No. 2010-210201 filed in Japan on September 17, 2010, Patent Application No. 2010-143420 filed in Japan on June 24, 2010, and Patent Application No. 2010-88228 filed in Japan on April 7, 2010, each of which is entirely herein incorporated by reference.

REFERENCE SIGNS LIST

**[0067]**

10 Copper alloy rod
10’ Copper alloy rod cut along the wrought direction
10a Cross-section in parallel to the wrought direction
R Wrought direction
21 Grain boundary

22 Sulfide particle present at a grain boundary
23 Sulfide particle present in a grain
24 Length of a sulfide particle in the direction perpendicular to the wrought direction
25 Length of the sulfide particle in the direction parallel to the wrought direction
50, 60 Connector pins
51, 61 Slits
62 Tapering section

## Claims

1. A copper alloy wrought material, containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, and 0.02 to 1.0 mass% of S, with the balance being Cu and unavoidable impurities, wherein sulfide particles are dispersed therein, in which an average diameter of the sulfide particles is 0.1 to 10 μm, and in which an area ratio of the sulfide particles is 0.1 to 10%, and wherein the copper alloy wrought material has a tensile strength of 500 MPa or greater and an electrical conductivity of 25% IACS or higher.

2. The copper alloy wrought material according to claim 1, containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, 0.02 to 1.0 mass% of S, and at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%, with the balance being Cu and unavoidable impurities, wherein sulfide particles are dispersed therein, in which an average diameter of the sulfide particles is 0.1 to 10 μm, and in which an area ratio of the sulfide particles is 0.1 to 10%, and wherein the copper alloy wrought material has a tensile strength of 500 MPa or greater and an electrical conductivity of 25% IACS or higher.

3. The copper alloy wrought material according to claim 1 or 2, wherein the sulfide particles are composed of at least one selected from the group consisting of Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S.

4. A copper alloy part, formed by subjecting the copper alloy wrought material according to any one of claims 1 to 3 to cutting.

**5.** The copper alloy part according to claim 4, which is used in an electronic equipment part, a structural part, or an element part.

**6.** A method of producing the copper alloy wrought material according to any one of claims 1 to 3, wherein a cooling speed at the time of casting is set to 0.1 to 50°C/second.

**7.** A copper alloy wrought material, containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, and 0.02 to 1.0 mass% of S, with the balance being Cu and unavoidable impurities, wherein sulfide particles are present in crystals of the matrix at 40% or larger in an area ratio of the sulfide particles in a cross-section parallel to the wrought direction, wherein the sulfide particles having an aspect ratio in the cross-section parallel to the wrought direction of 1:1 to 1: 100 are dispersed in the matrix, and wherein the copper alloy wrought material has a tensile strength of 500 MPa or greater and an electrical conductivity of 25% IACS or higher.

**8.** The copper alloy wrought material according to claim 7, further containing at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%.

**9.** The copper alloy wrought material according to claim 7 or 8, wherein the sulfide particles are composed of at least one selected from sulfides of Cu-S, Mn-S, Zr-S, Ti-S, Fe-S, Al-S, Cr-S, and Zn-S.

**10.** A copper alloy part, formed by subjecting the copper alloy wrought material according to any one of claims 7 to 9 to cutting.

**11.** The copper alloy part according to claim 10, which is used in applications which require mechanical strength, electrically conductivity, heat conductivity, and wear resistance, such as an electronic equipment part, a structural part, and an element part.

**12.** A method of producing the copper alloy wrought material according to any one of claims 7 to 9, containing the steps of:

conducting any one of steps (a) and (b), at the time of working a copper alloy composition containing 1.5 to 7.0 mass% of Ni, 0.3 to 2.3 mass% of Si, and 0.02 to 1.0 mass% of S, with the balance being Cu and unavoidable impurities;
area-reduction working at 0% to 95%; and
subjecting the resultant worked-product to aging, in which the sulfide particles are present in crystals of the matrix at 40% or larger in a total area of the sulfide particles dispersed in the matrix in a cross-section parallel to the wrought direction, and in which the sulfide particles having an aspect ratio in the cross-section parallel to the wrought direction of 1:1 to 1:100 are dispersed in the matrix:

(a) subjecting the copper alloy composition to hot working, and then to quenching;
(b) subjecting the copper alloy composition to hot working, then to cold working and a heat treatment at a temperature of 600°C to 1,000°C repeatedly for one or more times, and to a solution treatment before final cold-working.

**13.** The method of producing the copper alloy wrought material according to claim 12, wherein the copper alloy wrought material further contains at least one selected from the group consisting of Sn, Mn, Co, Zr, Ti, Fe, Cr, Al, P, and Zn in a total amount of 0.05 to 2.0 mass%.

Fig. 1

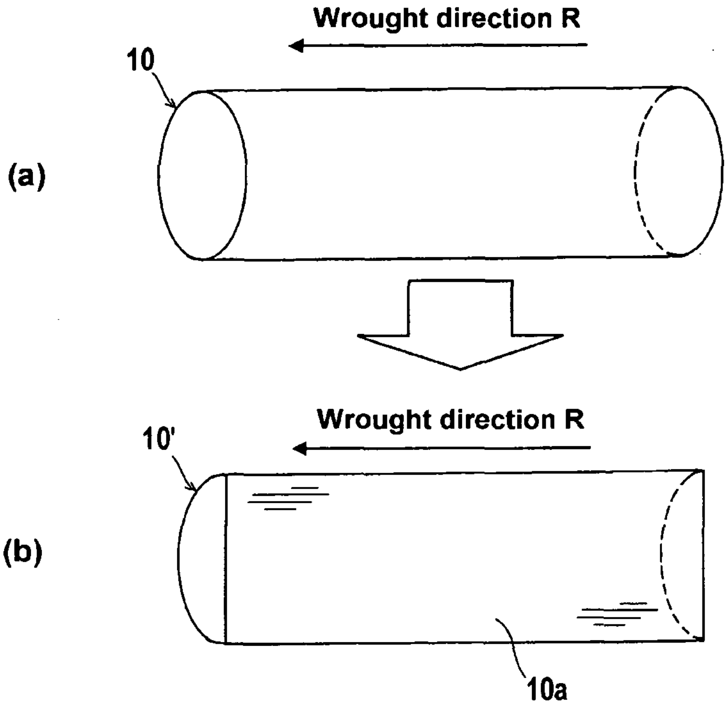


Fig. 2

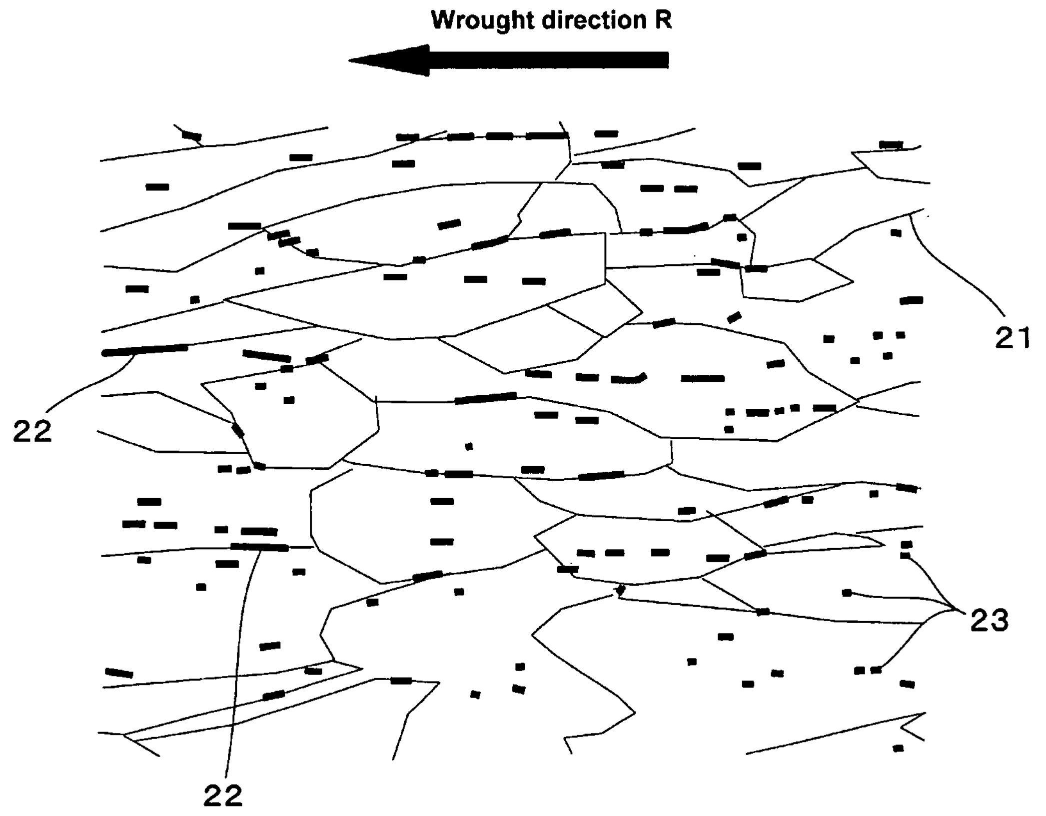


Fig. 3

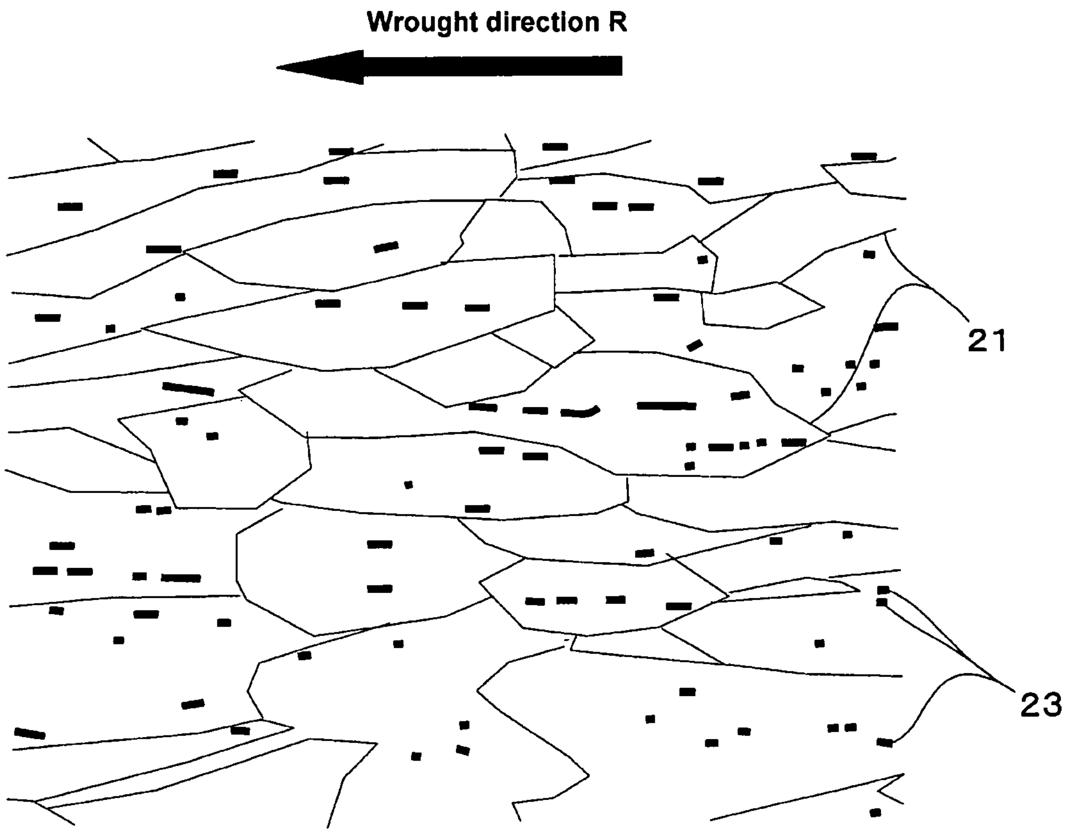


Fig. 4

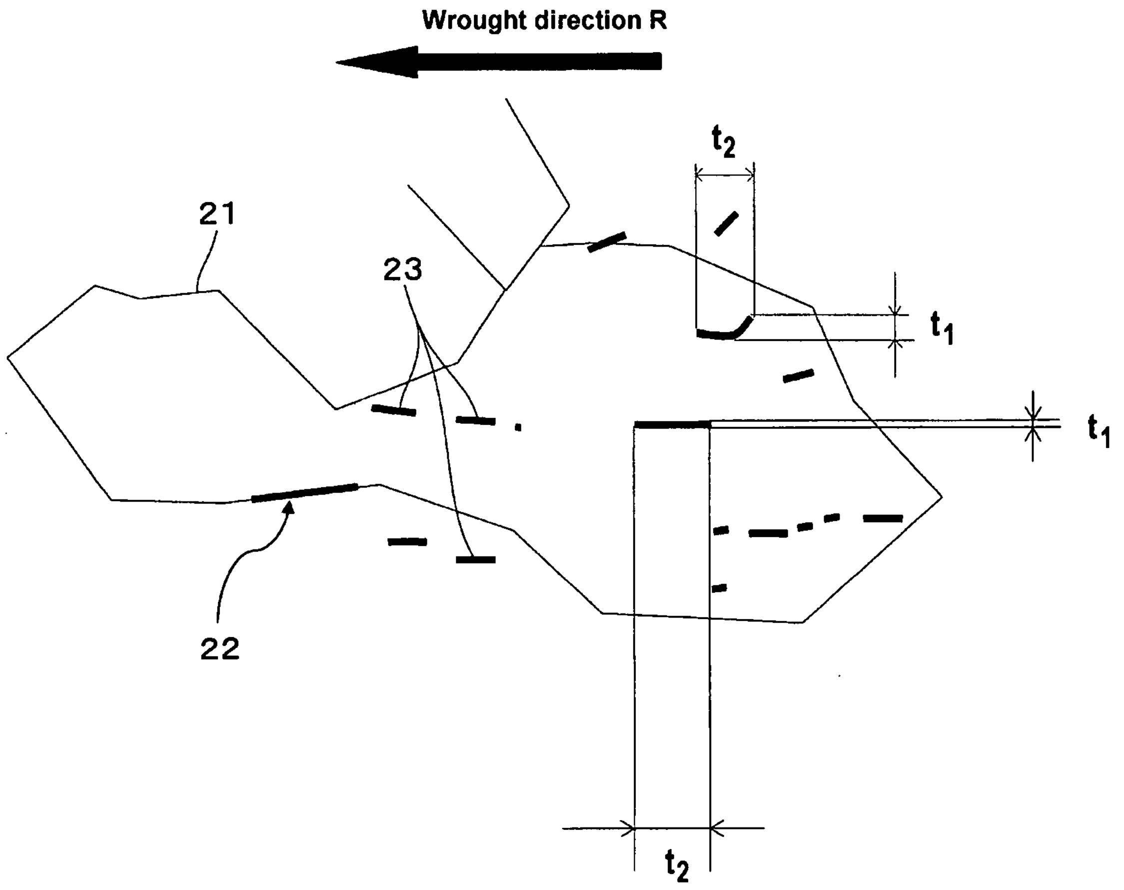


Fig. 5

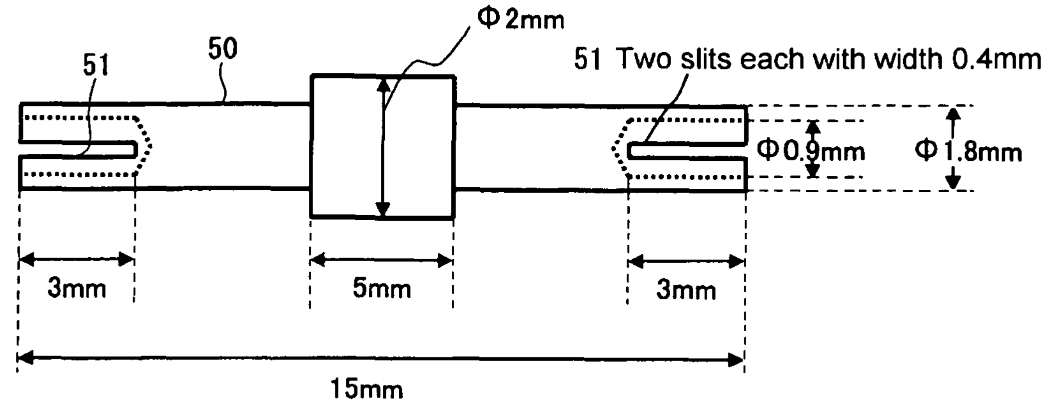
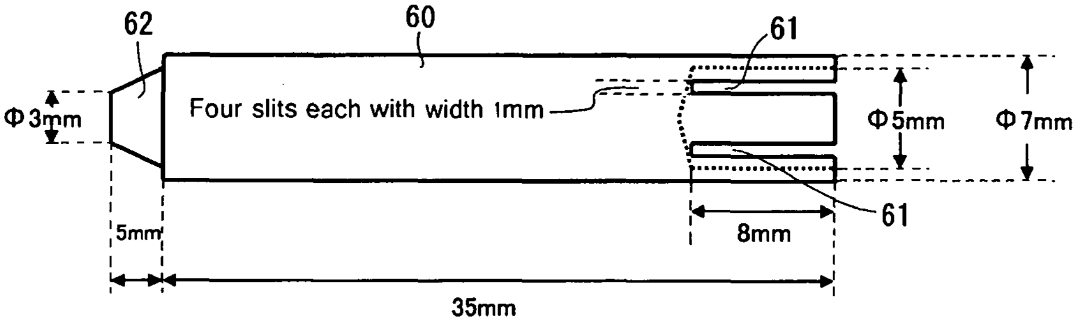

Φ2mm
51
50
51 Two slits each with width 0.4mm
Φ0.9mm
Φ1.8mm
3mm
5mm
3mm
15mm

Fig. 6


62
60
61
Φ3mm
Four slits each with width 1mm
Φ5mm
Φ7mm
61
5mm
8mm
35mm

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2010/073451

A. CLASSIFICATION OF SUBJECT MATTER
*C22C9/06*(2006.01)i, *C22C9/00*(2006.01)i, *C22C9/01*(2006.01)i, *C22C9/02*(2006.01)i, *C22C9/04*(2006.01)i, *C22C9/05*(2006.01)i, *C22C9/10*(2006.01)i, *C22F1/08*(2006.01)i, *C22F1/00*(2006.01)n
According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C9/00-9/10, C22F1/08, C22F1/00

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

| | | | |
|---|---|---|---|
| Jitsuyo Shinan Koho | 1922-1996 | Jitsuyo Shinan Toroku Koho | 1996-2011 |
| Kokai Jitsuyo Shinan Koho | 1971-2011 | Toroku Jitsuyo Shinan Koho | 1994-2011 |

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | WO 2007/126006 A1 (Kaibara Corp.),<br>08 November 2007 (08.11.2007),<br>entire text; all drawings<br>(Family: none) | 1-13 |

☒ 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
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“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<br>23 March, 2011 (23.03.11) | Date of mailing of the international search report<br>05 April, 2011 (05.04.11) |
| Name and mailing address of the ISA/<br>Japanese Patent Office<br>Facsimile No. | Authorized officer<br>Telephone No. |

Form PCT/ISA/210 (second sheet) (July 2009)

**INTERNATIONAL SEARCH REPORT**

International application No.
PCT/JP2010/073451

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages | Relevant to claim No. |
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| A | JP 2009-52097 A (Keiichi ARAKI, Tohoku University),<br>12 March 2009 (12.03.2009),<br>entire text; all drawings<br>(Family: none) | 1-13 |
| A | JP 2006-152373 A (Shiga Valve Kyodo Kumiai, Shiga-Ken),<br>15 June 2006 (15.06.2006),<br>entire text; all drawings<br>(Family: none) | 1-13 |

Form PCT/ISA/210 (continuation of second sheet) (July 2009)

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- JP 2006152373 A **[0006]**
- JP 2001240923 A **[0006]**
- JP 2008075172 A **[0006] [0009]**
- JP 6212374 A **[0006] [0009]**
- JP 7090520 A **[0006] [0009]**
- JP 2010280946 A **[0066]**
- JP 2010210201 A **[0066]**
- JP 2010143420 A **[0066]**
- JP 2010088228 A **[0066]**