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(54) **COPPER ALLOY AND METHOD FOR PRODUCTION THEREOF**

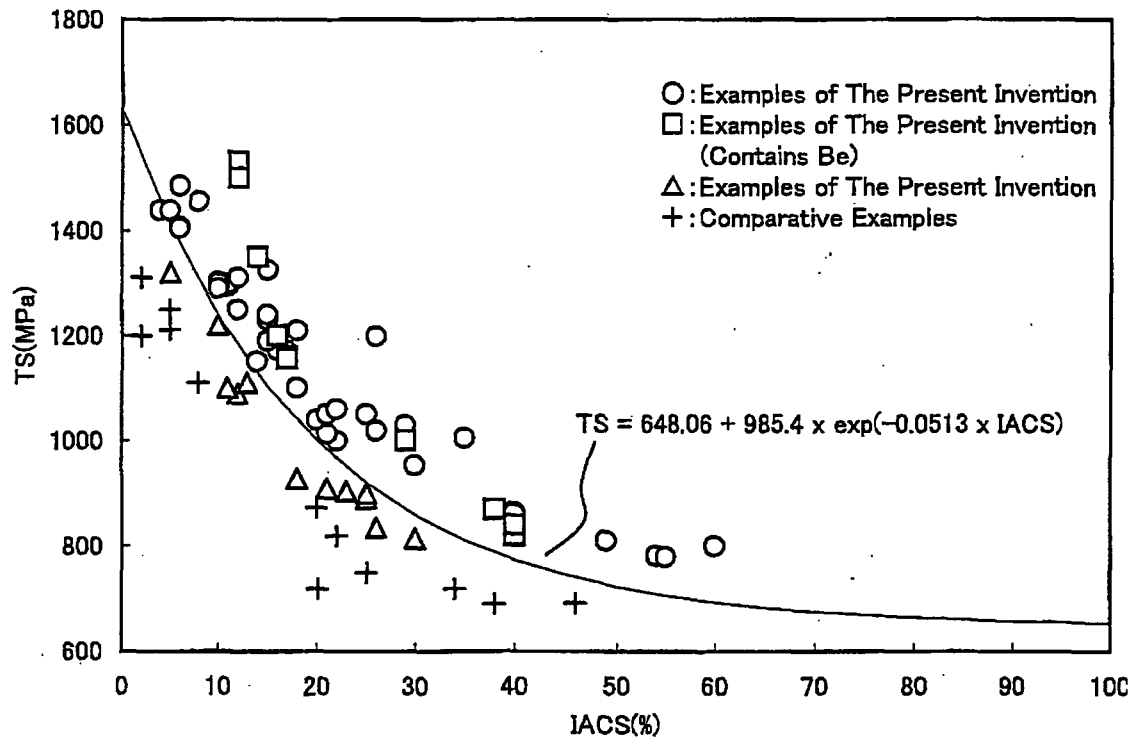
(57) A copper alloy that has a specific chemical composition, the balance being Cu and impurities, in which the relationship between the total number N and the diameter X satisfies the following formula (1). This copper alloy is obtained by cooling a bloom, a slab, a billet or an ingot in at least a temperature range from the temperature of the bloom, the slab, the billet or the ingot just after casting to 450°C, at a cooling rate of 0.5°C/s or more. After the cooling, working in a temperature range of 600°C or lower and further heat treatment of holding for 30 seconds or more in a temperature range of 150 to 750°C are desirably performed. The working and the heat treatment are most desirably performed for a plurality of times.

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 µm which are found in 1 mm² of the alloy; and X means the diameter in µm of the precipitates and the inclusions having a diameter of not smaller than 1 µm.

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[Figure 2]



Description

[Technical Field]

[0001] The present invention relates to a copper alloy, which can be produced at low cost and has excellent mechanical and electrical properties. This invention also relates to a process for producing the said copper alloy. This copper alloy is suitable for electrical and electronic parts, safety tools, and the like.

[0002] Examples of the electric and electronic parts include connectors for personal computers, semiconductor plugs, optical pickups, coaxial connectors, IC checker pins and the like in the electronics field; cellular phone parts (connector, battery terminal, antenna part), submarine relay casings, exchanger connectors and the like in the communication field; and various electric parts such as relays, various switches, micromotors, diaphragms, and various terminals in the automotive field; medical connectors, industrial connectors and the like in the medical and analytical instrument field; and air conditioners, home appliance relays, game machine optical pickups, card media connectors and the like in the electric home appliance field.

[0003] Examples of the safety tools include excavating rods and tools such as spanner, chain block, hammer, driver, cutting pliers, and nippers, which are used where a possible spark explosion hazard may take place, for example, in an ammunition chamber, a coal mine, or the like.

[Background Art]

[0004] A Cu-Be alloy has been known as a copper alloy that is used for the above-mentioned electric and electronic parts. This alloy is strengthened by age precipitation of the Be, and contains a substantial amount of Be. This alloy has been extensively used as a spring material or the like because it is excellent in both tensile strength and electric conductivity. However, Be oxide is generated in the production process of Cu-Be alloy and also in the process of forming to various parts.

[0005] Be is an environmentally harmful material as is Pb and Cd. Particularly, the substantial amount of Be in the conventional Cu-Be alloy necessitates a treatment process for the Be oxide in the production and working of the copper alloy. The treatment process leads to an increase in the production cost. It also causes a problem in the recycling process of the electric and electronic parts. Thus the Cu-Be alloy is a problematic material from the environmental point of view. Therefore, a material, which is excellent in both tensile strength and electric conductivity and in which the content of environmentally harmful elements such as Be is as low as possible, is desired.

[0006] A copper alloy called Corson alloy, in which Ni_2Si is precipitated, is proposed in Patent Document 1. This alloy has a relatively good balance of tensile strength and electric conductivity among alloys free from environmentally harmful elements such as Be, and has a electric conductivity of about 40% at a tensile strength of 750 to 820 MPa.

[0007] However, this alloy has limitations in enhancing strength and electric conductivity, and this still leaves a problem from the point of product variations as described below. This alloy has age hardenability due to the precipitation of Ni_2Si . If the electric conductivity is enhanced by reducing the contents of Ni and Si, the tensile strength is significantly reduced. On the other hand, even if the contents of Ni and Si are increased in order to raise the precipitation quantity of Ni_2Si , the electric conductivity is seriously reduced, although the rise of tensile strength is limited. Therefore, the balance between tensile strength and electric conductivity of the Corson alloys is disrupted in an area with high tensile strength and in an area with high electric conductivity, consequently narrowing the product variations. This is explained as follows.

[0008] The electric resistance (or electric conductivity that is the inverse thereof) of an alloy is determined by electron scattering, and fluctuates depending on the kinds of elements dissolved in the alloy. Since the Ni dissolved in the alloy noticeably raises the electric resistance (noticeably reduces the electric conductivity), the electric conductivity reduces in the above-mentioned Corson alloy if Ni is increased. On the other hand, the tensile strength of the copper alloy is obtained due to an age hardening effect. The tensile strength is improved more as the quantity of precipitates grows larger, or as the precipitates are dispersed more finely. The Corson alloy has limitations in enhancing the strength from the point of the precipitation quantity and from the point of the dispersing state, since the precipitated particle is made up of Ni_2Si only.

[0009] Patent Document 2 discloses a copper alloy with a satisfactory wire bonding property, which contains elements such as Cr and Zr and has a regulated surface hardness and surface roughness. As described in an embodiment thereof, this alloy is produced based on hot rolling and solution treatment.

[0010] However, the hot rolling needs a surface treatment for preventing hot cracking or removing scales, which result in a reduction in yield. Further, frequent heating in the atmosphere facilitates oxidation of active additive elements such as Si, Mg and Al. Therefore, the generated coarse internal oxides problematically cause deterioration of characteristics of the final product. Further, the hot rolling and solution treatment need an enormous amount of energy. The copper alloy described in Patent Document 2 thus has problems in view of an addition in production cost and energy saving because this alloy is based on the hot working and solution treatment. Furthermore, deterioration of product characteristics

(bending workability, fatigue characteristic and the like besides tensile strength and electric conductivity), which is result of generation of coarse oxides and the like.

[0011] On the other hand, the safety tool materials have required mechanical properties, for example, strength and wear resistance matching those of tool steel. It is also required to avoid generating sparks which could cause an explosion. In other words, excellent spark generation resistance is necessary for the safety tool materials. Therefore, a copper alloy with high thermal conductivity, particularly, a Cu-Be alloy aimed at strengthening by age precipitation of Be has been extensively used. Although the Cu-Be alloy is an environmentally problematic material, as described above, it has been heavily used as the safety tool material based on the following.

[0012] Fig.1 is a graph showing the relationship between electric conductivity [IACS (%)] and thermal conductivity [TC (W/m.K)] of a copper alloy. As shown in Fig.1, both are almost in a 1:1-relation. Enhancing of the electric conductivity [IACS (%)] means enhancing of the thermal conductivity [TC (W/m.K)], in other words, enhancing of the electric conductivity improves the spark generation resistance. Sparks are generated by the application of a sudden force by an impact blow or the like during the use of a tool due to a specified component in the alloy being burnt by the heat generated by an impact or the like. As described in Non-Patent Document 1, steel tends to cause a local temperature rise due to its thermal conductivity which can be as low as 1/5 or less of that of Cu. Since the steel contains C, a reaction " $C+O_2 \rightarrow CO_2$ " takes place, generating sparks. In fact, it is known that pure iron containing no C generates no sparks. Other metals which tend to generate sparks are Ti and Ti alloy. The thermal conductivity of Ti is as extremely low, as low as 1/20 of that of Cu, and therefore the reaction " $Ti+O_2 \rightarrow TiO_2$ " takes place. Data shown in Non-Patent Document 2 are summarized in Fig. 1.

[0013] However, the electric conductivity [IACS (%)] and the tensile strength [TS (MPa)] are in a trade-off relation, and it is extremely difficult to enhance both simultaneously. Therefore, the Cu-Be alloy was the only copper alloy that had sufficiently high thermal conductivity TC while retaining a tool steel-level high tensile strength in the past.

[0014]

[Patent Document 1]

Japanese Patent No.2,572,042

[Patent Document 2]

Japanese Patent No.2,714,561

[Non-Patent Document 1]

Industrial Heating, Vol. 36, No. 3 (1999), Japan Industrial Furnace Manufacturers Association, p. 59

[Non-Patent Document 2]

Copper and Copper Alloy Product Data Book, August 1, 1997, issued by Japan Copper and Brass Association, pp. 328-355

[Disclosure of the Invention]

[Subject to be solved by the Invention]

[0015] It is the primary objective of the present invention to provide a copper alloy, which is excellent in ductility and workability with a wide production variations and, further, excellent in performances required for safety tool materials, such as thermal conductivity, wear resistance and spark generation resistance. It is the second objective of the present invention to provide a method for producing the above-mentioned copper alloy.

[0016] The "wide production variations" mean that the balance between electric conductivity and tensile strength can be adjusted from a high level equal to or higher than that of the Cu-Be alloy to a low level equal to that of a conventionally known copper alloy, by minutely adjusting addition quantities and/or a production condition.

[0017] The "balance between electric conductivity and tensile strength can be adjusted from a high level equal to or higher than that of the Cu-Be alloy" specifically means a state satisfying the following formula (a). This state is hereinafter referred to as a "state with an extremely satisfactory balance of tensile strength and electric conductivity".

$$TS \geq 648.06 + 985.48 \times \exp(-0.0513 \times IACS) \quad \cdot \cdot \cdot (a)$$

wherein TS represents tensile strength (MPa) and IACS represents electric conductivity (%).

[0018] For the bending workability, it is also desirable to ensure a level equal to that of a conventional alloy such as Cu-Be alloy. Specifically, the bending workability can be evaluated by performing a 90°-bending test to a specimen at various curvature radiuses, measuring a minimum curvature radius R, never causing cracking, and determining the ratio $B (=R/t)$ of this radius to the plate thickness t. A satisfactory range of bending workability satisfies $B \leq 2.0$ in a plate material

with a tensile strength TS of 800 MPa or less, which satisfies the following formula (b) in a plate material having a tensile strength TS exceeding 800 MPa.

$$B \leq 41.2686 - 39.4583 \times \exp[-\{(TS - 615.675)/2358.08\}^2] \quad \cdot \cdot \cdot (b)$$

[0019] For a copper alloy as safety tool, wear resistance is also required in addition to other characteristics such as tensile strength TS and electric conductivity IACS as described above. Therefore, it is necessary to ensure that wear resistance is equal to that of tool steel. Specifically, a hardness at room temperature of 250 or more in the Vickers hardness is regarded as excellent wear resistance.

[Means to solve the Problems]

[0020] The present invention involves copper alloys shown in the following (A) to (C), and a method for producing a copper alloy shown in the following (D).

[0021]

(A) A copper alloy characterized in that the alloy consists of, by mass %, one or more elements selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se of 0.1 to 20 % respectively or in total, and the balance Cu and impurities; and the alloy satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having diameter of not smaller than 1 μm .

[0022]

(B) A copper alloy characterized in that the alloy consists of, by mass %, an element selected from Ti of 0.01 to 5 %, Zr of 0.01 to 5 % and Hf of 0.01 to 5 %, and one or more elements selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se of 0.01 to 20 % respectively or in total, and the balance Cu and impurities; and the alloy satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having diameter of not smaller than 1 μm .

[0023]

(C) A copper alloy characterized in that the alloy consists of, by mass %, Cr of 0.01 to 5 %, and one or more elements selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se of 0.01 to 20 % respectively or in total, and the balance Cu and impurities; and the alloy satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having diameter of not smaller than 1 μm .

[0024] The copper alloy shown in above (A), (B) or (C) may, instead of a part of Cu, contain one or more elements selected from Mg, Li, Ca and rare earth elements of 0.001 to 2 mass % respectively or in total, and/or one or more elements selected from P, B, Bi, Ti, Rb, Cs, Sr, Ba, Tc, Re, Os, Rh, In, Pd, Po, Sb, Au, Ga, S, Cd, As and Pb of 0.001 to 3 mass % respectively or in total. Further the alloy may contain 0.1 to 5 mass % of Be. In these alloys, it is desirable that the ratio of the "maximum value of the average content" and the "minimum value of the average content" of at least one alloy element in a micro area is not less than 1.5. The grain size of the alloy is desirably 0.01 to 35 μm .

[0025] (D) A method for producing a copper alloy, which satisfies the following formula (1), comprising cooling a bloom, a slab, a billet or an ingot obtained by melting a copper alloy, having a chemical composition described in the above (A), (B) or (C) followed by cooling in at least a temperature range from the temperature of the bloom, the slab, the billet or the ingot just after casting to 450°C, at a cooling rate of 0.5°C/s or more,

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \dots \quad (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

[0026] After the cooling, working in a temperature range of 600°C or lower, and a further heat treatment holding for 30 seconds or more in a temperature range of 150 to 750°C are desirably performed. The working in a temperature range of 600°C or lower and the heat treatment of holding in a temperature range of 150 to 750°C for 30 seconds or more may be performed for a plurality of times. After the final heat treatment, the working in a temperature range of 600°C or lower may be performed.

[0027] The precipitates in the present invention mean metals or compounds of copper and additive elements and between additive elements, for example, Cu_4Ti in the alloy containing Ti, Cu_9Zr_2 in the alloy containing Zr, metal Cr in the alloy containing Cr. The inclusions mean, for example, metal oxides, metal carbides, metal nitrides and the like.

[Best Mode for Carrying out the Invention]

[0028] An embodiment of the present invention will be described in detail. In the following description, "%" for content of each element represents "% by mass".

1. Copper Alloy of the Present Invention

(a) Chemical Composition

[0029] One of the copper alloy according to the present invention has a chemical composition consisting of 0.1 to 20 % respectively or in total of at least one element selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se (referred to as "the first group elements" hereinafter) and the balance Cu and impurities.

[0030] Each of these elements has an effect of improving corrosion resistance and heat resistance while keeping a balance between strength and electric conductivity. This effect is exhibited when 0.1% or more respectively or in total of these elements is contained. However, when their contents are excessive, the electric conductivity is reduced. Accordingly, these elements should be contained at 0.1 to 20% respectively or in total. Particularly, since Ag and Sn contribute to the increase in strength of the alloy by forming fine precipitates, active use of them is preferred. In the alloy that contains the following second group elements, the lower limit of the first group elements may be 0.01 % because the strength can be maintained the second group elements.

[0031] The copper alloy of the present invention may contain an element selected from 0.01 to 5 % of Ti, 0.01 to 5 % of Zr and 0.01 to 5 % of Hf, and also may contain 0.01 to 5.0 % Cr, instead of a part of Cu. Hereinafter, these elements are referred to as the second group elements.

An element selected from Ti: 0.01 to 5 %, Zr: 0.01 to 5 % and Hf: 0.01 to 5 %

[0032] Since Ti, Zr and Hf increase high-temperature strength of the alloy, an element selected from them can be contained in the alloy of the invention. The effect appears remarkably when the content of the elements is 0.01 % or more respectively. However, if the content exceeds 5%, the electric conductivity is deteriorated although the strength is enhanced. Further, segregation of these elements caused in casting makes it difficult to obtain a homogeneous dispersion of the precipitates, and cracking or chipping tends to occur in the subsequent working. Therefore, it is desirable to make the content of these elements 0.01 to 5.0 % respectively when they are added to the alloy. In order to obtain

an extremely satisfactorily balanced state of tensile strength and electric conductivity, it is desirable to make the alloy contain 0.1% or more of these elements.

Cr: 0.01 to 5%

[0033] Cr is an element that increases strength without making electric conductivity higher. In order to obtain the effect, the Cr content is preferably 0.01% or more. Particularly, in order to obtain an extremely satisfactorily balanced state of tensile strength and electric conductivity equal to or more than that of the Cu-Be alloy, a content of 0.1% or more is desirable. On the other hand, if the Cr content exceeds 5%, coarse metal Cr is formed so as to adversely affect the bending characteristic, fatigue characteristic and the like. Therefore, the preferable Cr content is 0.01 to 5% when it is added.

[0034] For the purpose of increasing high-temperature strength, the copper alloy of the present invention desirably contains, instead of a part of Cu, one or more elements selected from Mg, Li, Ca and rare earth elements of 0.001 to 2% respectively or in total. Hereinafter these elements are referred to as the third group elements.

[0035] Mg, Li, Ca and rare earth elements are easily bonded with an oxygen atom in the Cu matrix, leading to fine dispersion of the oxides, which enhance the high-temperature strength. This effect is noticeable when the total content of these elements is 0.001% or more. However, a content exceeding 2% could result in saturation, and causes problems such as reduction in electric conductivity and deterioration of bending workability. Therefore, when one or more element selected from Mg, Li, Ca and rare earth elements are included, the respective or total content thereof is desirably set to 0.001 to 2%. The rare earth elements mean Sc, Y and lanthanide, may be added separately or in a form of misch metal.

[0036] For the purpose of extending the width (ΔT) between liquidus and solidus in the casting, the copper alloy of the present invention desirably includes 0.001 to 0.3% respectively or in total of one or more elements selected from P, B, Bi, Tl, Rb, Cs, Sr, Ba, Tc, Re, Os, Rh, In, Pd, Po, Sb, Au, Ga, S, Cd, As and Pb instead of a part of Cu. However, it is recommendable not to use As, Pd and Cd because they are detrimental elements. Hereinafter these elements from P to Pb are referred to as the fourth group elements. Although ΔT is increased by a so-called supercooling phenomenon in rapid solidification, ΔT in a thermally equilibrated state is considered herein as a standard.

[0037] The above-mentioned elements are effective for lowering the solidus to extend ΔT . If this width ΔT is extended, casting is facilitated since a fixed time can be ensured up to solidification after casting. However, an excessively large ΔT causes reduction in proof stress in a low-temperature area, causing cracking at the end of solidification, or so-called solder brittleness. Therefore, ΔT is preferably set within the range of 50 to 200°C.

[0038] C, N and O are generally included as impurities. These elements form carbides, nitrides and oxides with metal elements in the alloy. These elements may be actively added since the precipitates or inclusions thereof are effective, if fine, for strengthening the alloy, particularly, for enhancing high-temperature strength similarly to the precipitates of metal, compounds of copper and additive elements or between additive elements and the like, which are described later. For example, O has an effect of forming oxides in order to enhance the high-temperature strength. This effect is easily obtained in an alloy containing elements which easily form oxides, such as Mg, Li, Ca and rare earth elements, Al, Si and the like. However, in this case, a condition in which the solid solution O never remains must be selected. Care should be taken with residual solid solution oxygen, since it may cause, in heat treatment under hydrogen atmosphere, a so-called hydrogen disease of causing a phreatic explosion as H₂O gas and generate blister or the like, which deteriorates the quality of the product.

[0039] When the content of each of these elements exceeds 1%, the precipitates or inclusions thereof are coarse, deteriorating the ductility. Therefore, each content is preferably limited to 1% or less, and further preferably to 0.1% or less. content of H is desirably as small as possible, since H included as an impurity in the alloy, remains in the state of H₂ gas, which causes rolling flaw or the like.

[0040] Be is an element that contributes to precipitation-strengthening without deteriorating electric conductivity remarkably. In order to obtain the effect, it is preferable that the content of Be is 0.1 mass % or more. However, a content exceeding 5% causes not only reduction in electric conductivity but also reduction of ductility, which deteriorates workability for rolling or bending and the like. Therefore, the preferable content of Be is 0.1 to 5 % when it is added.

(b) The total number of precipitates and inclusions

[0041] In the copper alloy of the present invention, the relationship between the total number N and the diameter X of precipitates and inclusions that have a diameter of not smaller than 1 μm satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having diameter of not smaller than 1 μm . In the formula (1), $X=1$ is substituted when the measured value of the grain size of the precipitates and the inclusions are 1.0 μm or more and less than 1.5 μm , and $X=\alpha$ (α is an integer of 2 or more) is substituted when the measured value is " $\alpha-0.5$ " μm or more and less than " $\alpha+0.5$ " μm .

[0042] In the copper alloy of the present invention, fine precipitates of metal, compounds of copper and additive elements and between additive elements can improve the strength without reducing the electric conductivity. They enhance the strength by precipitation hardening. The dissolved Cr, Ti, and Zr are reduced by precipitation, and the electric conductivity of the copper matrix comes close to that of pure copper.

[0043] However, when these precipitates and inclusions such as metal oxides, metal carbides and metal nitrides become coarse with a diameter of 20 μm or more, the ductility deteriorates, easily causing cracking or chipping, for example, at the time of bending or punching for making a connector. It might adversely affect fatigue characteristic and impact resistance characteristic in use. Particularly, when a coarse Ti-Cr compound is formed at the time of cooling after solidification, cracking or chipping tends to occur in the subsequent working process. Since the hardness is excessively increased in an aging treatment process, fine precipitation of said precipitates and inclusions is inhibited, so that the copper alloy cannot be strengthened. Such a problem is noticeable when the relationship between the total number of N and the diameter X does not satisfy the above formula (1).

[0044] In the present invention, therefore, an essential requirement is regulated so that the relationship between the total number of N and the diameter X satisfies the above formula (1). The total number of the precipitates and the inclusions desirably satisfies the following formula (2), and further preferably satisfies the following formula (3). The diameter and the total number of the precipitates and the inclusions can be determined by using a method shown in Examples.

$$\log N \leq 0.4742 + 7.9749 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (2)$$

$$\log N \leq 0.4742 + 6.3579 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (3)$$

wherein N means the total number of precipitates and inclusions, having a diameter not smaller than 1 μm which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having diameter not smaller than 1 μm .

(c) Ratio of the "average content maximum value" to the "average content minimum value" in micro-area of at least one alloy element

[0045] The presence of a structure, in which areas with different concentrations of alloy elements are finely mingled, in the copper alloy, or the occurrence of a periodic concentration change has an effect of facilitating acquisition of the micro-crystal grain structure, since it inhibits minute diffusion of each element and the grain boundary migration. Consequently, the strength and ductility of the copper alloy are improved according to the so-called Hall-Petch law. The micro-area means an area of 0.1 to 1 μm diameter, which substantially corresponds to an irradiation area in X-ray analysis.

[0046] The areas with different alloy element concentrations in the present invention are the following two types.

(1) A state basically having the same fcc structure as Cu, but having different alloy element concentrations. The lattice constant is generally differed in spite of the same fcc structure due to the different alloy element concentrations, and also the degree of work hardening is of course differed.

(2) A state where fine precipitates are dispersed in the fcc matrix. The dispersed state of precipitates after working and heat treatment is of course differed due to the different alloy element concentrations.

[0047] The average content in the micro-area means the value in an analysis area when narrowing to a fixed beam diameter of 1 μm or less in the X-ray analysis. The value is the average content in this area. In case of the X-ray analysis, an analyzer having a field emission type electron gun is desirably used. A desirable analyzing means are such that have a resolution of 1/5 or less of the concentration period, and 1/10 is further desirable. If the analysis area is too large during the concentration period, the whole is averaged to make the concentration difference difficult to emerge. Generally, the measurement can be performed by an X-ray analysis method with a probe diameter of about 1 μm .

[0048] It is the alloy element concentration and fine precipitates in the matrix that determines the material character-

istics. Therefore, the concentration difference in micro-area including fine precipitates is questioned in the present invention. Accordingly, signals from coarse precipitates or coarse inclusions of 1 μm or more are disturbance factors. However, it is difficult to perfectly remove the coarse precipitates or coarse inclusions from an industrial material, and therefore it is necessary to remove these disturbing factors from the coarse precipitates and inclusions at the time of analysis. The following procedure is therefore taken.

[0049] A line analysis is performed using of an X-ray analyzer with a probe diameter of about 1 μm in order to grasp the periodic structure of concentration, although it is varied depending on the materials. An analysis method is determined so that the probe diameter is about 1/5 of the concentration period or less as described above. Then a sufficient line analysis length, where the period emerges about three times or more is determined. The line analysis is performed m-times (desirably 10 times or more) under this condition, and the maximum value and the minimum value of concentration are determined for each of the line analysis results.

[0050] M pieces each of the resulting maximum values and minimum values are cut by 20% from the larger value side and averaged. By the above-mentioned procedure, the disturbing factors due to the signals from the coarse precipitates and inclusions can be removed.

[0051] The concentration ratio is determined by the ratio of the maximum value compared to the minimum value from which the disturbance factors have been removed. The concentration ratio can be determined for an alloy element, having a periodic concentration change of about 1 μm or more, without taking a concentration change of an atomic level of about 10 nm or less, such as spinodal decomposition or micro-precipitates, into consideration.

[0052] The reason that the ductility is improved by finely distributing alloy elements will now be described in detail. When a concentration change of an alloy element takes place, the mechanical properties are differed between the high-concentration part and the low-concentration part, since the degree of solid-solution hardening of materials and the dispersed state of precipitates between them are different. During deformation of such material, the relatively soft part, i.e., low-concentration part is work-hardened first, and then the deformation of the relatively hard part, i.e., high-concentration part is started. In other words, since the work hardening is caused for a plurality of times as the whole material, high elongation is shown, for example, in tensile deformation, and also ductility improvement is seen. Thus, in an alloy where a periodic concentration change of alloy elements takes place, high ductility advantages for bending work or the like can be exhibited while keeping the balance between electric conductivity and tensile strength.

[0053] Since the electric resistance (the inverse of electric conductivity) mainly responds to a phenomenon in which the electron transition is reduced due to the scattering of dissolved elements, and is hardly affected by a macro defect such as grain boundary, the electric conductivity is never reduced by the above-mentioned fine grain structure.

[0054] This effect is noticeable when the ratio of the "average content maximum value" to the "average content minimum value" in the micro-area of at least one alloy element in the matrix (hereinafter simply referred to as "concentration ratio") is 1.5 or more. The upper limit of the concentration ratio is not particularly determined. However, an excessively high concentration ratio might cause adverse effects, such that an excessively increased difference of the electrochemical characteristics which facilitates local corrosion, and in addition to that the fcc structure possessed by the Cu alloy cannot be kept. Therefore, the concentration ratio is set preferably to 20 or less, and more preferably to 10 or less.

(d) Grain size

[0055] A finer grain size of the copper alloy is advantageous for enhancing the strength, and also leads to an improvement in ductility which improves bending workability and the like. However, when the grain size is below 0.01 μm , high-temperature strength may be reduced, and if it exceeds 35 μm , the ductility is reduced. Therefore, the grain size is desirably set at 0.01 to 35 μm , and further desirably to 0.05 to 30 μm , and most desirably to 0.1 to 25 μm .

2. Method for producing a copper alloy of the present invention

[0056] In the copper alloy of the present invention, inclusions such as metal oxides, metal carbides and metal nitrides, which inhibit the fine precipitation of metals, compounds of copper and additive elements and between additive elements, tend to formed just after the solidification from the melt. It is difficult to dissolve such inclusions even if the solution treatment at a higher temperature is performed after casting. The solution treatment at a high temperature only causes coagulation and the coarsening of the precipitates and inclusions.

[0057] Therefore, in the method for producing the copper alloy of the present invention, a bloom, a slab, a billet or an ingot, obtained by melting the copper alloy having the above chemical composition by casting, is cooled to at least a temperature range from the bloom, the slab, the billet or the ingot temperature just after casting to 450°C, at a cooling rate of 0.5°C/s or more, whereby the relationship between the total number N and the diameter X of the precipitates and the inclusions having diameter of not smaller than 1 μm satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, which are found in 1 mm² of the alloy; and X means the diameter in μm of the precipitates and the inclusions having diameter of not smaller than 1 μm .

[0058] After the cooling, working in a temperature range of 600°C or lower, and a holding heat treatment for 30 seconds or more in a temperature range of 150 to 750°C after this working are desirably performed. The working in a temperature range of 600°C or lower and the holding heat treatment for 30 seconds or more in a temperature range of 150 to 750°C are further desirably performed for a plurality of times. After the final heat treatment, the working may be further performed.

(a) A cooling rate at least in a temperature range from the bloom, the slab, the billet or the ingot temperature just after casting to 450°C: 0.5°C/s or more

[0059] The precipitates such as metals, compounds of copper and added elements and between added compounds are formed in a temperature range of 280°C or higher. Particularly, when the cooling rate in a temperature range, from the bloom, the slab, the billet or the ingot temperature just after casting to 450°C is low, inclusions such as metal oxides, metal carbides and metal nitrides are coarsely formed, and the diameter thereof may reach 20 μm or more, and further hundreds μm . Further, the said precipitates are also coarsened to 20 μm or more. In a state where such coarse precipitates and inclusions are formed, not only cracking or chipping may take place in the subsequent working, but also a precipitation hardening effect of the precipitates in an aging process is impaired, so that the alloy cannot be strengthened. Accordingly, it is needed to cool the bloom, the slab, the billet or the ingot at a cooling rate of 0.5°C/s or more at least in the said temperature range. A higher cooling rate is more preferable. The cooling rate is preferably 2°C/s or more, and more preferably 10°C/s or more.

(b) Working temperature after cooling: A temperature range of 600°C or lower

[0060] In the method for producing a copper alloy of the present invention, the bloom, the slab, the billet or the ingot obtained by casting is made into a final product, after cooling under a predetermined condition, only by a combination of working and aging heat treatment without passing through a hot process, such as hot rolling or solution treatment.

[0061] A working such as rolling or drawing may be performed at 600°C or lower. For example, when continuous casting is adapted, such a working can be performed in the cooling process after solidification. When the working is performed in a temperature range exceeding 600°C, precipitates such as metals, compounds of copper and additive elements and between additive elements are coarsely formed at the time of working, deteriorating the ductility, impact resistance, and fatigue property of the final product. When the above-mentioned precipitates are coarsened at the time of working, fine precipitates cannot be formed in the aging treatment, resulting in an insufficient strengthening of the copper alloy.

[0062] Since the dislocation density in working is raised more as the working temperature is lower, precipitates such as metals, compounds of copper and additive elements and between additive elements can become finer in the subsequent aging treatment. Therefore, further high strength can be given to the copper alloy. The working temperature is preferably 450°C or lower, more preferably 250°C or lower, and most preferably 200°C or lower. The temperature may also be 25°C or lower.

[0063] The working in the above temperature range is desirably performed at a working rate (section reduction rate) of 20% or more, and more desirably 50% or more. If the working is performed at such a working rate, the dislocation introduced thereby can act as precipitation nuclei at the time of aging treatment, which leads to fine dispersion of the precipitates and also shortens of the time required for the precipitation, and therefore the reduction of dissolved elements harmful to electric conductivity can be early realized.

(c) Aging treatment condition: Holding for 30 seconds or more in a temperature range of 150 to 750°C

[0064] The aging treatment is effective for precipitating metals, compounds of copper and additive elements and between additive elements in order to strengthen the copper alloy, and also reduce dissolved elements (Cr, Ti, etc.) harmful to electric conductivity in order to improve the electric conductivity. However, at a treatment temperature below 150°C, an excessive amount of time is required for the diffusion of the precipitated elements, which reduces the productivity. On the other hand, at a treatment temperature exceeding 750°C, not only the precipitates are too coarsened to attain the strengthening by the precipitation hardening effect, but also the ductility, impact resistance and fatigue characteristic deteriorates. Therefore, the aging treatment is desirably performed in a temperature range of 150 to 750°C. The aging treatment temperature is desirably 200 to 750°C, further desirably 250 to 650°C, and most desirably 280 to

550°C.

[0065] When the aging treatment time is less than 30 seconds, a desired precipitation quantity cannot be ensured even if the aging treatment temperature is high. When the time is longer than 72 hours, production cost becomes higher. Therefore, the aging treatment in a temperature range of 150 to 750°C is desirably performed for 30 seconds or more.

The treatment time is desirably 5 minutes or more, further desirably 10 minutes or more, and most desirably 15 minutes or more. The upper limit of the treatment time is not particularly limited. However, 72 hours or less is desirable from the point of the treatment cost. When the aging treatment temperature is high, the aging processing time can be shortened.

[0066] The aging treatment is preferably performed in a reducing atmosphere, in an inert gas atmosphere, or in a vacuum of 20 Pa or less in order to prevent the generation of scales due to oxidation on the surface. Excellent plating property can also be ensured by the treatment in such an atmosphere.

[0067] The above-mentioned working and aging treatment may be performed repeatedly as the occasion demands. When the working and aging treatment are repeatedly performed, a desired precipitation quantity can be obtained in a shorter time than in the case of one set treatment (working and aging treatment), and precipitates such as metals, compounds of copper and additive elements and between additive elements can be more finely precipitated. For example, when the treatment is repeated twice, the second aging treatment temperature is preferably set slightly lower than the first aging treatment temperature (by 20 to 70°C). If the second aging treatment temperature is higher, the precipitates formed in the first aging treatment are coarsened. On and after the third aging treatment, the temperature is desirably set lower than the previous aging treatment temperature. The working in a temperature range of 600°C or lower may be performed after the final heat treatment.

(d) Others

[0068] In the method for producing the copper alloy of the present invention, conditions other than the above production conditions, for example, conditions for melting, casting and the like are not particularly limited. These treatments may be performed as follows.

[0069] Melting is preferably performed in a non-oxidative or reducing atmosphere. If the dissolved oxygen in a molten copper is increased, the so-called hydrogen-induced blistering due to generation of steam is caused in the subsequent process. Further, coarse oxides of easily-oxidizable dissolved elements such as Ti and Cr are formed, and if they are left in the final product, the ductility and fatigue characteristic are seriously reduced.

[0070] In order to obtain the bloom, the slab, the billet or the ingot, continuous casting is preferably adapted from the point of productivity and solidification rate. However, any other methods, which satisfy the above-mentioned conditions, for example, an ingot method, can be used. The casting temperature is preferably 1250°C or higher, and further preferably 1350°C or higher. At this temperature, Cr, Ti and Zr can be sufficiently dissolved, and formation of inclusions such as metal oxides, metal carbide and metal nitrides, precipitates such as metals, compounds of copper and additive elements and between additive elements can be prevented.

[0071] When the bloom, the slab or the billet is obtained by the continuous casting, a method using graphite mold, which is generally adapted for a copper alloy is recommended from the viewpoint of lubricating property. As a mold material, a refractory material, which is hardly reactive with Ti, Cr or Zr that is an essential alloy element, for example, zirconia may be used.

[Example 1]

[0072] Copper alloys, having chemical compositions shown in Tables 1 to 3 were melted by a vacuum induction furnace, and cast in a zirconia-made mold, whereby slabs 12mm thick were obtained. Each of rare earth elements was added alone or in a form of misch metal.

[Table 1]

[0073]

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Table 1

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements 3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
1	15Fe, 1.0Si, 0.2Sn, 1.2Al	17.4	0.05	-	-	-	0.5Y, 0.01Nd, 0.02Ca	0.53	0.001B	0.001	-
2	10Fe, 2.5Ni, 1.0Si, 0.4Zn	13.9	0.49	-	-	-	-	-	-	-	-
3	1.01Fe, 0.1Zn	1.11	1.02	-	-	-	0.02Mg	0.02	-	-	-
4	0.99Fe, 0.5Ag	1.49	1.51	-	-	-	-	-	0.01P, 0.1Bi	0.11	-
5	0.01Sn	0.01	1.93	-	-	-	0.001La	0.001	0.15Sr, 0.5Pd, 0.1Os	0.75	-
6*	5.0Zn, 15Fe, 5Co, 2.0Si	27.0*	5.80*	-	-	-	0.5Nd, 0.5Gd, 2.0Ca	3.0*	0.5B, 0.6Tc	1.1	-
7	0.2Ta, 12Co, 1.5Si	13.7	-	0.07	-	-	0.2Sc, 0.2Ce	0.4	0.1Ti, 0.5Cs, 0.1Po	0.7	-
8	2.5Fe, 15.5Nb, 0.1Ge	18.1	-	0.51	-	-	-	-	-	-	-
9	0.97Fe, 0.5V, 0.3Mo	1.77	-	1.02	-	-	0.01Mg, 0.1Gd	0.11	-	-	-
10	0.5Fe, 0.6Ta	1.0	-	1.48	-	-	0.01Mg	0.01	0.011P, 1.0Ba, 0.1Sb	1.111	-
11	1.01Fe, 0.1W, 0.1Ag	1.21	-	2.01	-	-	-	-	0.012B, 0.1Re, 0.1Tc	0.212	-
12*	1.5W, 0.5Al, 0.6Ag	2.5	-	6.10*	-	-	0.1La, 0.01Ca	0.11	0.2Sb	0.2	-
13	0.4Mo, 1.0Co, 15Fe, 0.4Se	16.8	-	-	0.01	-	0.1La, 0.01Mg, 0.001Li	0.111	0.1In, 0.5Pd, 0.1Ga	0.7	-
14	1.0Fe, 0.5Si, 1.0Nb	2.5	-	-	0.52	-	-	-	-	-	-
15	0.98Fe, 0.2Mo, 0.4Zn	1.58	-	-	0.99	-	0.01Li	0.01	-	-	-

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(continued)

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements 3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
16	0.99Fe	0.99	-	-	1.48	-	0.01Ca	0.01	0.010P, 0.028	0.03	-
17	0.4Si, 0.3Sn, 1.2V	1.9	-	-	2.01	-	-	-	0.1Sr, 0.2Re	0.3	-
18*	0.5Fe, 1.0Co, 0.4Sn	1.9	-	-	6.20*	-	0.01Sc, 0.1Mg	0.11	0.9Bi, 0.1P	1.0	-
19	10V, 2.2Co, 0.4Ta, 0.4Mn, 1.0Sn	14.0	-	-	-	0.05	0.01La	0.01	0.1Rh, 0.01P	0.11	-
20	2.01Fe, 0.2Mo, 0.5Nb	2.71	-	-	-	0.50	-	-	-	-	-
21	1.0Ni, 0.6Si, 0.4Sn	1.9	-	-	-	0.99	0.02Ca	0.02	-	-	-
22	0.99Fe	0.99	-	-	-	1.49	0.01Li, 0.03Ca	0.04	0.011P, 1.0Bi	1.011	-
23	1.0Fe, 0.5Sn	1.5	-	-	-	1.99	-	-	0.01B, 0.6Ha, 0.5Sb	1.01	-
24	12V, 15Fe, 0.5Mo, 1.0Si, 1.0Sn	29.5*	-	-	-	6.50*	0.1Sc, 0.01Mg	0.11	0.1Au, 0.01Po, 0.1Cs	0.21	-
25*	0.99Co, 1.02Fe, 0.4Sn	2.41	1.45	-	-	-	0.5Ca, 0.8Li, 1.5Mg	2.8*	0.001B	0.001	-
*: Out of the range regulated by the present invention.											

[Table 2]

[0074]

Table 2

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
26	1.01Nb	1.01	1.32	-	-	-	-	-	-	-	-
27	0.99Co	0.99	1.22	-	-	-	0.01Mg	0.01	-	-	-
28	0.98Fe	0.98	1.52	-	-	-	0.01Mg	0.01	0.008P, 0.01B	0.018	-

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(continued)

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
29	0.5V, 0.2Ag	0.7	1.98	-	-	-	-	-	0.009Bi	0.009	-
30*	12.5Ni, 5.1Si, 5.6Nb	23.2*	1.55	-	-	-	1.5Mg, 1.0La	2.5*	0.5In, 1.5Ba, 1.0Os	3.0*	-
31	0.95Co	0.95	-	1.11	-	-	-	-	0.001S	0.001	-
32	1.00Nb	1.00	-	1.48	-	-	0.1La, 1.5Ca	1.6	-	-	-
33	0.99Fe	0.99	-	1.49	-	-	0.1Mg, 0.5Nd, 0.8Li	1.4	0.01Cs, 0.03Bi	0.04	-
34	0.98Co	0.98	-	1.52	-	-	-	-	0.01P	0.01	-
35*	1.1V	1.1	-	1.32	-	-	0.1La, 1.5Rh, 2.0Ce	3.6*	1.0Ba, 1.3Po, 2.0Rh	4.3*	-
36	0.99V, 0.24Si	1.23	-	-	1.52	-	-	-	0.01Bi, 0.02Ba, 0.001P	0.031	-
37	1.01Co, 2.3Fe, 0.4Sn	3.71	-	-	1.48	-	-	-	-	-	-
38	1.1Nb, 0.3Sn, 1.2Ni	2.6	-	-	1.22	-	0.01Li, 0.03Gd	0.04	-	-	-
39*	10.0Co, 10.2Fe, 0.5Si, 4.3W, 1.0Mo	26.0*	-	-	1.38	-	0.01Ca, 0.1Sc	0.11	0.009P	0.009	-
40	0.99Co, 0.1Si	1.01	-	-	-	1.32	-	-	-	-	-
41*	0.99Nb, 0.10e	1.01	-	-	-	1.42	0.1Ce, 0.01Y	0.11	0.5Sb, 1.5Ba, 1.0Bi	3.0*	-
42*	1.01V, 0.1Al, 0.2Ni	1.31	-	-	-	1.48	0.01Mg	0.01	1.5Rb, 1.0Pd	2.5*	-
43	1.00Mo, 0.4Zn	1.40	-	-	-	1.36	-	-	0.012P	0.012	-
44	1.54Co, 0.8Al	2.34	-	-	-	-	0.01Nd, 0.05Sc	0.06	-	-	-
45	0.99Nb, 0.4Mn	1.39	-	-	-	-	-	-	0.01B	0.01	-
46	1.52Fe, 0.4Te	1.92	-	-	-	-	0.01Mg, 0.06Y, 0.001Li	0.061	0.011Pd, 0.1Re	0.11	-
47	2.01Fe, 0.4Zn	2.41	-	-	-	-	-	-	-	-	-

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(continued)

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
48*	8.0Nb, 4.0Si, 5.2Ta	17.2	-	-	-	-	0.7La, 0.5Ca, 1.2Sc	2.4*	-	-	-
49	14Ni, 4Si, 1Ag	19	-	-	-	-	0.01Nd, 0.05Y	0.06	-	-	-
50	5.2Mo, 3.1V	8.3	-	-	-	-	-	-	0.01P, 0.1Ba	0.11	-
*: Out of the range regulated by the present invention.											

[Table 3]

[0075]

Table 3

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements 3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
51	10.1W, 4.2Ge	14.3	-	-	-	-	0.1Ce, 0.01La	0.11	0.1Sr, 0.1Os	0.2	-
52	2.5Co	2.5	-	-	-	-	0.01Mg	0.01	-	-	-
53	1.54Fe	1.54	-	-	-	-	-	-	0.001B	0.001	-
54	1.24V	1.24	-	-	-	-	0.001Li	0.001	0.01Bi	0.01	-
55*	10.2Fe, 7.8Co, 3.4Zn, 3.2Al, 3.8W	28.4*	-	-	-	-	-	-	-	-	-
56	0.5Fe, 0.5Co, 0.5Ag	1.5	3.00	-	-	-	-	-	0.1Ba, 0.01Os	0.11	-
57	0.4Sn, 1.0Fe	1.4	4.00	-	-	-	0.1Sc, 0.1Ca	0.2	-	-	-
58	0.25Ta, 0.3Nb	0.55	-	2.50	-	-	0.01Nd, 0.1La	0.11	0.1Pd, 0.05Bi	0.15	-
59	0.5Mo, 0.1Fe	0.6	-	4.00	-	-	-	-	0.01P, 0.1Re	0.11	-
60	0.5Fe, 0.1Si, 0.2Sn	0.8	1.50	-	-	-	0.2Ca	0.2	0.01P, 0.1S	0.11	-
61	0.6Ag, 4.0Co	4.6	-	-	-	-	-	-	-	-	0.4
62	1.0Zn, 1.0Ag, 3.0Nb	5.0	-	-	-	-	0.5Mg, 0.1Gd	0.6	-	-	2.1
63	2.0Fe, 0.5Ta	2.5	-	-	-	-	-	-	0.1P, 0.01B	0.11	0.5

(continued)

Alloy No.	Chemical Composition (mass%, Balance: Cu & Impurities)										
	1st group elements	Total	2nd group elements				3rd group elements 3rd group elements	Total	4th group elements	Total	Be
			Ti	Zr	Hf	Cr					
64	0.4Ag	0.4	-	-	-	2.50	-	-	-	-	2.1
65	1.0Sn, 2.5Fe, 3.0Se	6.5	-	-	-	-	0.01Nd	0.01	0.25B, 0.001T1	0.251	0.6
66	2.0Sn, 0.1Al, 0.1Si	2.2	-	0.01	-	2.50	0.1Y, 0.5Sc	0.6	0.5Sb	0.5	2.3
67	0.2Sn, 0.4Te	0.6	0.50	-	-	-	0.1Ca	0.1	0.01P, 0.1B, 0.001Ga	0.111	2.8
68	0.1Ag, 0.3Fe, 0.5Mo, 0.2Se	1.1	0.20	0.20	-	-	-	-	-	-	0.6
69	0.5Sn, 0.1Ag	0.6	1.00	2.00	-	-	-	-	0.3B, 0.1Re, 0.2Rh	0.6	2.8
70	0.5Ta	0.5	-	0.30	-	-	0.10d	0.1	-	-	2.6
*: Out of the range regulated by the present invention.											

[0076] Each of the resulting slabs was cooled from a temperature between 950°C and 450°C, which is the temperature just after casting (the temperature just after taken out of the mold), by water spray. The temperature change of the mold in a predetermined place was measured by a thermocouple buried in the mold, and the surface temperature of the slab, after leaving the mold, was measured in several areas by a contact type thermometer. The average cooling rate, in the temperature range to 450°C, of the slab surface was calculated by using the above measuring results and a thermal conduction analysis. In another small-scale experiment, the solidification starting point was determined by using 0.2g of a melt of each alloy, and thermally analyzing it during continuous cooling at a predetermined rate.

[0077] A plate for subsequent rolling with 10mm thickness × 80mm width × 150mm length was prepared from each resulting slab by cutting and machining. For comparison, a part of the plate was subjected to a solution heat treatment at 950°C. The plates were rolled to 2 mm thick sheets by a reduction of 80% at a room temperature (first rolling), and further subjected to aging treatment under a predetermined condition (first aging). A part of the specimens were further subjected to rolling by a reduction of 95% into 0.1 mm thickness at room temperature (second rolling), and then subjected to aging treatment under a predetermined condition (second aging). The production conditions thereof are shown in Tables 4 to 7.

[0078] For the thus-produced specimens, the diameter and the total number per unit area of the precipitates and the inclusions, tensile strength, electric conductivity and bending workability were measured by the following methods. These results are also shown in Tables 4 to 7.

<Total number of precipitates and inclusions>

[0079] A section parallel to the rolling plane and that perpendicular to the transverse direction of each specimen were polish-finished, and a visual field of 1 mm × 1 mm was observed by an optical microscope at 100-fold magnification after being etched with an ammonia aqueous solution. Thereafter, the long diameter (the length of a straight line which can be drawn longest within a grain without contacting the grain boundary halfway) of the precipitates and the inclusions was measured, and the resulting value is determined as grain diameter. When the measured value of the grain diameter of the precipitates and the inclusions is 1.0 μm or more and less than 1.5 μm, X=1 is substituted to the formula (1), and when the measured value is "α-0.5" μm or more and less than "α+0.5" μm, X=α (α is an integer of 2 or more) can be substituted. Further, the total number n₁ is calculated by taking one crossing of the frame line of a visual field of 1 mm × 1 mm as 1/2 and one located within the frame line as 1 for every grain diameter, and an average "N/10" of the number

of the precipitates and the inclusions $N (=n_1+n_2+\dots+n_{10})$ in an optionally selected 10 visual fields is defined as the total number of the precipitates and the inclusions for each grain diameter of the sample.

<Content Ratio>

[0080] A section of the alloy was polished and analyzed at random 10 times for a length of 50 μm by an X-ray analysis at 2000-fold magnification in order to determine the maximum values and minimum values of each alloy content in the respective line analyses. Averages of the maximum value and the minimum value were determined for eight values each after removing the two larger ones respectively from the determined maximum values and minimum values, and the ratio thereof was calculated as the content ratio.

<Tensile Strength>

[0081] A specimen 13B regulated in JIS Z 2201 was prepared from the above-mentioned specimen so that the tensile direction is parallel to the rolling direction, and according to the method regulated in JIS Z 2241, tensile strength [TS (MPa)] at room temperature (25°C) thereof was determined.

< Electric Conductivity>

[0082] A specimen of 10 mm width $\times$ 60 mm length was prepared from the above-mentioned specimen so that the longitudinal direction is parallel to the rolling direction, and the potential difference between both ends of the specimen was measured by applying current in the longitudinal direction of the specimen, and the electric resistance was determined therefrom by a 4-terminal method. Successively, the electric resistance (resistivity) per unit volume was calculated from the volume of the specimen measured by a micrometer, and the electric conductivity [IACS (%)] was determined from the ratio to resistivity $1.72 \mu\Omega \cdot \text{cm}$ of a standard sample obtained by annealing a polycrystalline pure copper.

<Bending workability>

[0083] A plurality of specimens of 10mm width $\times$ 60mm length were prepared from the above-mentioned specimen, and a 90° bending test was carried out while changing the curvature radius (inside diameter) of the bent part. After the test the bent parts of the specimens were observed from the outer diameter side by use of an optical microscope. A minimum curvature radius free from cracking was taken as R, and the ratio B ($=R/t$) of R to the thickness t of specimen was determined.

[Table 4]

[0084]

Table 4

Division	Alloy	Production Condition										①	②	Grain Size (μm)	Characteristics				
		Cooling		1st Rolling		1st Heat Treatment		2nd Rolling		2nd Heat Treatment					Tensile Strength (MPa)	Conductivity (%)	Bending Workability		
		Rate (°C/s)	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	B (Rd)						Evaluation		
Examples of The Present Invention	1	1	9	25	2.0	400	25	2h	25	0.1	350	10h	Δ	10.5(Fe)	30	905	23	2	○
	2	2	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	10(Fe), 1.5(Si)	14	1020	26	2	○
	3	3	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	3.2(Ti)	10	1169	17	2	○
	4	4	11	25	2.0	400	25	2h	25	0.1	350	10h	⊙	2.5(Ti)	8	1301	10	3	○
	5	5	11	25	2.0	400	25	3h	25	0.1	350	10h	○	3.1(Ti)	0.1	1409	6	5	○
	6	7	10	25	2.1	400	25	2h	25	0.1	350	10h	Δ	2.4(Si)	20	910	21	2	○
	7	8	10	25	1.9	400	25	2h	25	0.1	350	10h	⊙	12(Nb), 2.5(Fe)	25	1019	26	2	○
	8	9	11	25	2.0	400	25	2h	25	0.1	350	10h	⊙	1.8(Zr)	15	1173	16	3	○
	9	10	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	2.5(Zr)	8	1295	10	5	○
	10	11	10	25	2.0	400	25	3h	25	0.1	350	10h	○	5.6(Zr)	1	1439	4	5	○
	11	13	10	25	2.0	400	25	2h	25	0.1	350	10h	Δ	5.2(Fe)	30	890	25	2	○
	12	14	10	25	1.9	400	25	2h	25	0.1	350	10h	⊙	1.5(Nb), 1.2(Fe)	16	1050	25	2	○
	13	15	11	25	2.0	400	25	2h	25	0.1	350	10h	⊙	1.8(Fe), 1.5(Zn)	12	1172	17	3	○
	14	16	9	25	1.9	400	25	2h	25	0.1	350	10h	⊙	1.8(Hf)	5	1293	11	5	○
	15	17	9	25	1.9	400	25	3h	25	0.1	350	10h	○	2.8(Hf)	0.2	1439	5	5	○
	16	19	11	25	2.0	400	25	2h	25	0.1	350	10h	Δ	12.5(V)	16	900	25	1	○
	17	20	11	25	2.0	400	25	2h	25	0.1	350	10h	⊙	3.9(Ti)	33	782	54	1	○
	18	21	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	2.3(Ni), 1.5(Si)	35	780	55	1	○
	19	22	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	1.8(Fe)	28	865	40	2	○
	20	23	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	1.9(Fe)	19	954	30	2	○
	21	24	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	11.9(V)	12	1000	22	2	○
	22	26	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	5.9(Ti)	10	1230	15	2	○
	23	27	10	25	2.0	400	25	2h	25	0.1	350	10h	⊙	3.5(Ti), 1.5(Co)	9	1209	18	3	○
	24	28	9	25	2.0	400	25	2h	25	0.1	350	10h	⊙	3.8(Ti), 1.6(Fe)	10	1290	10	3	○
	25	29	11	25	2.0	400	25	2h	25	0.1	350	10h	○	5.2(Ti), 1.5(Ag)	0.5	1405	6	5	○

"h" in "Time" means hour.

"Δ", "○" and "⊙" in ① mean that formulas (1), (2) and (3) are satisfied, respectively.

⊙ means "content maximum value/content minimum value". Object element is shown in parentheses.

"○" in "Bending Workability" means that formula (b) is satisfied.

[Table 5]

[0085]

Table 5

Division	Alloy No.	Production Condition										①	②	Grain Size (μm)	Characteristics			
		Cooling		1st Rolling		1st Heat Treatment		2nd Rolling		2nd Heat Treatment					Tensile Strength (MPa)	Conductivity (%)	Bending Workability	
		Rate (°C/s)	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	B						Evaluation	
Examples of The Present Invention	26	31	9	25	2.0	400	2h	25	0.1	350	10h	⊙	1.7(Zr)	10	1240	15	2	○
	27	32	10	25	1.9	400	2h	25	0.1	350	10h	⊙	2.1(Zr)	2	1302	10	3	○
	28	33	10	25	2.0	400	2h	25	0.1	350	10h	⊙	2.2(Zr)	4	1298	11	2	○
	29	34	10	25	2.0	400	2h	25	0.1	350	10h	⊙	2.5(Zr)	2	1300	10	3	○
	30	36	11	25	2.0	400	2h	25	0.1	350	10h	⊙	2.0(Zr)	2	1290	10	3	○
	31	37	10	25	2.0	400	2h	25	0.1	350	10h	⊙	13.0(Hf)	5	1230	15	3	○
	32	38	9	25	1.9	400	2h	25	0.1	350	10h	⊙	2.9(Hf)	12	1190	15	2	○
	33	40	10	25	2.0	400	2h	25	0.1	350	10h	⊙	2.5(Hf)	28	800	60	1	○
	34	43	9	25	2.0	400	2h	25	0.1	350	10h	△	3.5(Cr)	27	815	30	1	○
	35	44	10	25	2.0	400	2h	25	0.1	350	10h	⊙	5.2(Co), 1.5(Al)	15	1005	35	1	○
	36	45	10	25	2.0	400	2h	25	0.1	350	10h	△	1.5(Nb)	25	836	26	1	○
	37	46	9	25	2.0	400	2h	25	0.1	350	10h	△	12.6(Fe)	24	928	18	1	○
	38	47	10	25	2.0	400	2h	25	0.1	350	10h	⊙	3.2(Fe)	12	1014	21	2	○
	39	49	10	25	2.0	400	2h	25	0.1	350	10h	△	5.2(Ni), 2.4(Si)	8	1220	10	3	○
	40	50	9	25	2.0	400	2h	25	0.1	350	10h	⊙	15.2(Mo), 7.8(V)	12	1198	26	2	○
	41	51	9	25	2.0	400	2h	25	0.1	350	10h	△	21(W), 1.8(Ge)	2	1320	5	4	○
	42	52	10	25	2.0	400	2h	25	0.1	350	10h	⊙	5.8(Co)	10	1030	29	3	○
	43	53	11	25	2.0	400	2h	25	0.1	350	10h	⊙	2.8(Fe)	20	862	40	1	○
	44	54	11	25	2.0	400	2h	25	0.1	350	10h	⊙	5.2(Co), 2.5(Al)	21	810	49	1	○
	45	56	9	25	2.0	400	2h	25	0.1	350	10h	⊙	5.2(Ti)	1	1310	12	4	○
	46	57	10	25	2.0	400	2h	25	0.1	350	10h	○	10.2(Ti)	0.5	1456	8	5	○
	47	58	9	25	2.0	400	2h	25	0.1	350	10h	○	5.2(Zr)	0.1	1325	15	4	○
	48	59	9	25	2.0	400	2h	25	0.1	350	10h	○	8.2(Zr)	0.3	1485	6	5	○
	49	60	10	25	2.0	400	2h	25	0.1	350	10h	○	3.0(Ti)	5	1100	23	2	○
	50	61	9	25	2.0	400	2h	25	0.1	350	8h	⊙	3.2(Cr)	20	820	40	1	○

"h" in "Time" means hour.

"Δ", "○" and "⊙" in ① and ② are satisfied, respectively.

⊙ means "content maximum value/content minimum value". Object element is shown in parentheses.

"○" in "Bending Workability" means that formula (b) is satisfied.

[Table 6]

[0086]

Table 6

Division	Alloy No.	Production Condition														①	②	Grain Size (μm)	Characteristics			
		Cooling Rate (°C/s)		1st Rolling		1st Heat Treatment		2nd Rolling		2nd Heat Treatment		3rd Rolling		3rd Heat Treatment					Tensile Strength (MPa)	Conduc-tivity (%)	Bending Workability	
		Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	B	Evalu-ation							
51	62	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	10.2(Nb),1.5(Zn)	15	1160	17	2	○	
52	63	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	2.5(Fe)	25	840	40	1	○	
53	64	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	5.9(Cr)	12	1156	17	3	○	
54	65	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	4.8(Fe)	22	870	38	1	○	
55	66	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	1.5(Sn)	3	1200	16	2	○	
56	67	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	1.5(Be)	0.5	1350	14	4	○	
57	68	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	⊙	1.5(Be),1.5(Fe)	14	1000	29	1	○	
58	69	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	○	1.8(Zr)	0.01	1530	12	5	○	
59	70	10	25	2.0	400	2h	25	0.1	350	8h	-	-	-	-	○	5.4(Be)	0.05	1500	12	5	○	
60	3	10	580	3.0	-	-	25	1.0	450	1.5h	25	0.1	350	5h	⊙	2.5(Ti)	15	1040	20	1	○	
61	3	10	250	3.0	700	0.5h	25	1.0	450	1.5h	25	0.1	350	5h	⊙	2.3(Ti)	7	1050	21	1	○	
62	3	10	580	3.0	600	1h	25	1.0	450	1.5h	25	0.1	350	5h	⊙	2.5(Ti)	6	1060	22	1	○	
63	3	10	250	3.0	-	-	25	1.0	450	1.5h	25	0.1	350	5h	⊙	3.0(Ti)	13	1100	18	1	○	
64	4	10	500	3.0	-	-	25	1.0	450	1.5h	25	0.1	350	5h	⊙	2.7(Ti)	12	1090	12	1	○	
65	4	10	200	3.0	700	0.5h	25	1.0	450	1.5h	25	0.1	350	5h	⊙	2.5(Ti)	6	1110	13	1	○	
66	4	10	500	3.0	600	1h	25	1.0	450	1.5h	25	0.1	350	5h	⊙	2.8(Ti)	5	1100	11	1	○	
67	4	10	250	3.0	-	-	25	1.0	450	1.5h	25	0.1	350	5h	⊙	3.2(Ti)	12	1150	14	1	○	

"h" in "Time" means hour.

"○" and "⊙" in ①, ② and ③ are satisfied, respectively.

⊙ means "content maximum value/content minimum value". Object element is shown in parentheses.

"○" in "Bending Workability" means that formula (b) is satisfied.

[Table 7]

[0087]

Table 7

Division	Alloy No.	Production Condition										①	②	Grain Size (μm)	Characteristics					
		Cooling Rate (°C/s)	1st Rolling		1st Heat Treatment		2nd Rolling		2nd Heat Treatment		Tensile Strength (MPa)				Conductivity (%)	Bending Workability				
			Temp. (°C)	Thickness (mm)	Temp. (°C)	Time	Temp. (°C)	Thickness (mm)	Temp. (°C)	Time										
																B (R/t)	Evaluation			
Comparative Examples	1	6*	25	2.0	-	-	-	-	-	-	-	-	-	-	-	-	-			
	2	12*	25	2.0	-	-	-	-	-	-	-	-	-	-	-	-	-			
	3	18*	25	1.9	-	-	-	-	-	-	-	-	-	-	-	-	-			
	4	25*	25	1.9	400	2h	25	0.1	350	10h	350	10h	x	-	9	1250	5	6	x	
	5	26	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	0.1(Ti)	25	750	25	6	x	
	6	30*	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	-	3	1310	2	7	x	
	7	33	0.3*	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	4	720	20	5	x	
	8	33	10	800*	2.0	400	2h	25	0.1	-	-	-	-	-	-	-	-	-	-	
	9	34	10	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	0.05(Zr)	32	720	34	5	x
	10	35*	10	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	8	1110	8	5	x	
	11	37	10	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	0.11(Hf)	28	690	38	4	x
	12	39*	10	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	-	10	1210	5	6	x
	13	41*	9	25	1.9	400	2h	25	0.1	350	10h	350	10h	x	-	26	820	22	4	x
	14	42*	9	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	-	26	873	20	4	x
	15	43	9	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	0.9(Mo)	35	692	46	5	x
	16	48*	10	25	2.0	400	2h	25	0.1	350	10h	350	10h	x	-	10	1200	2	6	x
	17	55*	10	25	2.0	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-

"h" in "Time" means hour.

"x" in ① means that formulae (1), (2) and (3) are not satisfied.

② means "content maximum value/content minimum value". Object element is shown in parentheses.

"x" in "Bending Workability" means that formula (b) is not satisfied.

[0088] In the "Evaluation" column of bending workability of the tables, "O" shows those satisfying $B \leq 2.0$ in plate materials having tensile strength TS of 800 MPa or less and those satisfying the following formula (b) in plate materials having tensile strength TS exceeding 800 MPa, and "x" shows those that are not satisfactory.

$$B \leq 41.2686 - 39.4583 \times \exp \left[- \left\{ (TS - 615.675) / 2358.08 \right\}^2 \right] \quad \cdot \cdot \cdot (b)$$

[0089] Fig.2 is a graph showing the relationship between tensile strength and electric conductivity in each example. As shown in Tables 4 to 7 and Fig.2, regarding the chemical composition, the content ratio and the total number of the precipitates and the inclusions are within the ranges regulated by the present invention in Inventive Examples 1 to 67 and the tensile strength and the electric conductivity satisfied the above-mentioned formula (a). Accordingly, it can be said that the balance between electric conductivity and tensile strength of these alloys are of a level equal to or higher than that of the Be-added copper alloy. Thus, the copper alloy of the present invention is found to be rich in variations of tensile strength and electric conductivity. In Inventive Examples 1, 6, 11, 16, 34, 36, 37, 39, 41, 64, 65 and 66, the addition quantity and/or manufacturing condition were minutely adjusted with the same component system. It can be said that these alloys have a relationship between tensile strength and electric conductivity as shown by "Δ" in Fig.2, and also have the characteristics of the conventionally known copper alloy. Further, the bending property was also satisfactory.

[0090] On the other hand, Comparative Examples 1 to 4, 6, 10, 12 to 14, 16 and 17 were inferior in bending workability and electric conductivity because the content of any one of alloying elements is out of the range regulated by the present invention. For Comparative Examples 1 to 3 and 17, the characteristics could not be evaluated since edge cracking in the second rolling was too serious to collect the samples. Comparative Examples 5, 9, 11 and 15, which were subjected to solution treatment at 950°C, were inferior in tensile strength and bending workability.

[Example 2]

[0091] In order to evaluate the application to the safety tools, samples were prepared by the following method, and evaluated for wear resistance (Vickers hardness) and spark resistance.

[0092] Alloys having chemical compositions shown in Table 8 were melted in a high frequency furnace in the atmosphere, and were cast by the Durville process. Each bloom was produced by holding a metallic mold 1 in a state as shown in Fig.3 (a), pouring a melt of about 1300°C into the metallic mold 1 while ensuring a reducing atmosphere by charcoal powder, then tilting the mold as shown in Fig.3 (b), and solidifying the melt in a state shown in Fig.3 (c). The metallic mold 1 is made of cast iron with a thickness of 50 mm, and has a pipe arrangement with a cooling hole bored in the inner part so that air cooling can be performed. The bloom was made to a wedge shape having a bottom section of 30 × 300mm, an upper section of 50 × 400 mm, and a height of 700 mm so as to facilitate the pouring of the melt.

[0093] A part up to 300 mm from the lower end of the resulting bloom was prepared followed by surface-polishing, and then subjected to cold rolling (30 → 10mm) and heat treatment (375°C × 16h), whereby a plate 10 mm thick was obtained. Such a plate was examined for the total number of the precipitates and the inclusions, tensile strength, electric conductivity, and bending workability by the above-mentioned method and, further, examined for wear resistance, thermal conductivity and spark generation resistance by the method described below. The results are shown in Table 8.

<Wear Resistance>

[0094] A specimen of 10 mm width × 10 mm length was prepared from each specimen, a section vertical to the rolled surface and parallel to the rolling direction was polish-finished, and the Vickers hardness at 25°C and load 9.8N thereof was measured by the method regulated in JIS Z 2244.

<Thermal Conductivity>

[0095] The thermal conductivity [TC (W/m · K)] was determined by the use of the electric conductivity [IACS(%)] from the formula described in Fig.1, i.e., "TC=14.804+3.8172×IACS".

<Spark Generation Resistance>

[0096] A spark test according to the method regulated in JIS G 0566 was performed by use of a table grinder having a rotating speed of 12,000 rpm, and the spark generation was visually confirmed.

[0097] The average cooling rate to 450°C based on the liquidus induced by the heat conduction calculation with the temperature measured by inserting a thermocouple to a position of 5 mm under the mold inner wall surface in a position 100 mm from the bottom, was determined to be 10°C/s.

[Table 8]

[0098]

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Table 8

Division	Chemical Composition (mass%, Balance: Cu & Impurities)						①	Grain Size (μm)	Tensile Strength (MPa)	Conduc-tivity (%)	Bending Workability		Wear Resistance (Hv)	Thermal Conductivity (W/m·K)	Spark Generation Resistance
	Hf	Ti	Zr	Sn	Mg	P					B (R/t)	Evaluation			
Examples of The Present Invention	68	-	1.0	0.5	0.01	0.01	⊙	25	1110	32	2	○	342	137	Non
	69	-	1.5	0.4	-	0.05	⊙	12	1058	29	2	○	327	126	Non
	70	2.0	-	1.2	0.1	-	⊙	20	998	35	2	○	310	148	Non
Comparative Examples	18	-	5.4*	-	0.001	0.1	×	2	1402	1	6	×	426	19	Generated
	19	-	-	1.5	0.1	-	×	1	1395	1	6	×	424	19	Generated
"⊙" in ① means that formula (3) are satisfied, "×" means that formulas (1), (2) and (3) are not satisfied, respectively. "○" in "Bending Workability" means that formula (b) is satisfied. "×" means that formula (b) is not satisfied.															

[0099] As shown in Table 8, no spark was observed with satisfactory wear resistance and high thermal conductivity in Inventive Examples 68 to 70. On the other hand, sparks were observed with low thermal conductivity in Comparative Examples 18 and 19, since they did not satisfy the chemical composition regulated by the present invention and the relationship shown by formula (1).

[Industrial Applicability]

[0100] According to the present invention, a copper alloy that has wide product variations, and is excellent in high-temperature strength and workability, and also excellent in the performances required for safety tool materials, or thermal conductivity, wear resistance and spark generation resistance, and a method for producing the same can be provided.

[Brief Description of the Drawings]

[0101]

[Fig. 1] A graph showing the relationship between the electric conductivity and thermal conductivity;

[Fig. 2] A graph showing the relationship between the tensile strength and the electric conductivity of each of examples.

[Fig. 3] A schematic view showing a casting method by the Durville process.

Explanation of Letters

[0102]

1: metallic mold

Claims

1. A copper alloy **characterized in that** the alloy consists of, by mass%, one or more elements selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se of 0.1 to 20 % respectively or in total, and the balance Cu and impurities; and the alloy satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

2. A copper alloy **characterized in that** the alloy consists of, by mass%, any one element selected from Ti of 0.01 to 5 %, Zr of 0.01 to 5 % and Hf of 0.01 to 5 %, and one or more elements selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se of 0.01 to 20 % respectively or in total, and the balance Cu and impurities; and the alloy satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

3. A copper alloy **characterized in that** the alloy consists of, in mass %, Cr of 0.01 to 5 %, and one or more elements selected from Zn, Sn, Ag, Mn, Fe, Co, Al, Ni, Si, Mo, V, Nb, Ta, W, Ge, Te and Se of 0.01 to 20 % respectively or in total, and the balance Cu and impurities; and the alloy satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm , which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

4. A copper alloy according to any one of claims 1 to 3

characterized in that the alloy contains, instead of a part of Cu, one or more elements selected from Mg, Li, Ca and rare earth elements of 0.001 to 2 mass % respectively or in total.

5. A copper alloy according to any one of claim 1 to 4, **characterized**

in that the alloy contains, instead of a part of Cu, one or more elements selected from P, B, Bi, Tl, Rb, Cs, Sr, Ba, Tc, Re, Os, Rh, In, Pd, Po, Sb, Au, Ga, S, Cd, As and Pb of 0.001 to 3 mass% respectively or in total.

6. A copper alloy according to any one of claims 1 to 5,

characterized in that the alloy contains, instead of a part of Cu, Be of 0.1 to 5 mass %.

7. A copper alloy according to any one of claims 1 to 6, wherein the ratio of the "maximum value of an average content" and the "minimum value of an average content" of at least one alloy element in a micro area is not smaller than 1.5.

8. A copper alloy according to any one of claims 1 to 7, wherein the grain diameter is 0.01 to 35 μm .

9. A method for producing a copper alloy, comprising cooling a bloom, a slab, a billet or an ingot obtained by melting a copper alloy having a chemical composition described in any one of claims 1 to 6 followed by cooling in at least a temperature range from the temperature of the bloom, the slab, the billet or the ingot just after casting to 450°C at a cooling rate of 0.5 °C/s or more, so that the relationship between the total number N and the diameter X satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

10. A method for producing a copper alloy, comprising cooling a bloom, a slab, a billet or an ingot obtained by melting a copper alloy having a chemical composition described in any one of claims 1 to 6 followed by cooling in at least a temperature range from the temperature of the bloom, the slab, the billet or the ingot just after casting to 450°C at a cooling rate of 0.5°C/s or more, and performing working in a temperature range of 600°C or lower, so that the relationship between the total number N and the diameter X satisfies the following formula (1):

$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

11. A method for producing a copper alloy, comprising cooling a bloom, a slab, a billet, or an ingot obtained by melting a copper alloy having a chemical composition described in any one of claims 1 to 6 followed by cooling in at least a temperature range from the temperature of the bloom, the slab, the billet or the ingot just after casting to 450°C at a cooling rate of 0.5°C/s or more, performing working in a temperature range of 600°C or lower, and then performing heat treatment of holding for 30 seconds or more in a temperature range of 150 to 750°C, so that the relationship between the total number N and the diameter X satisfies the following formula (1):

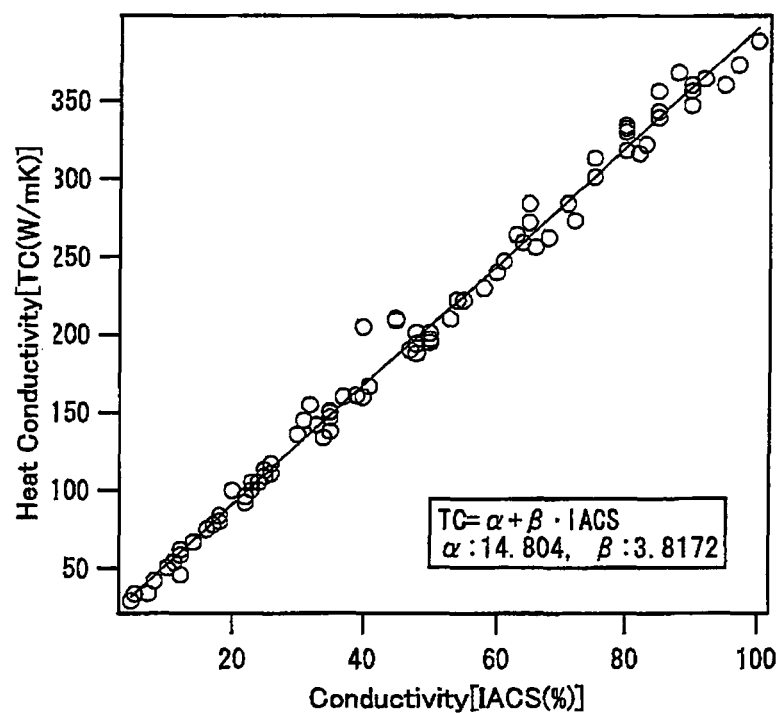
$$\log N \leq 0.4742 + 17.629 \times \exp(-0.1133 \times X) \quad \cdot \cdot \cdot (1)$$

wherein N means the total number of precipitates and inclusions, having a diameter of not smaller than 1 μm which are found in 1 mm^2 of the alloy; and X means the diameter in μm of the precipitates and the inclusions having a diameter of not smaller than 1 μm .

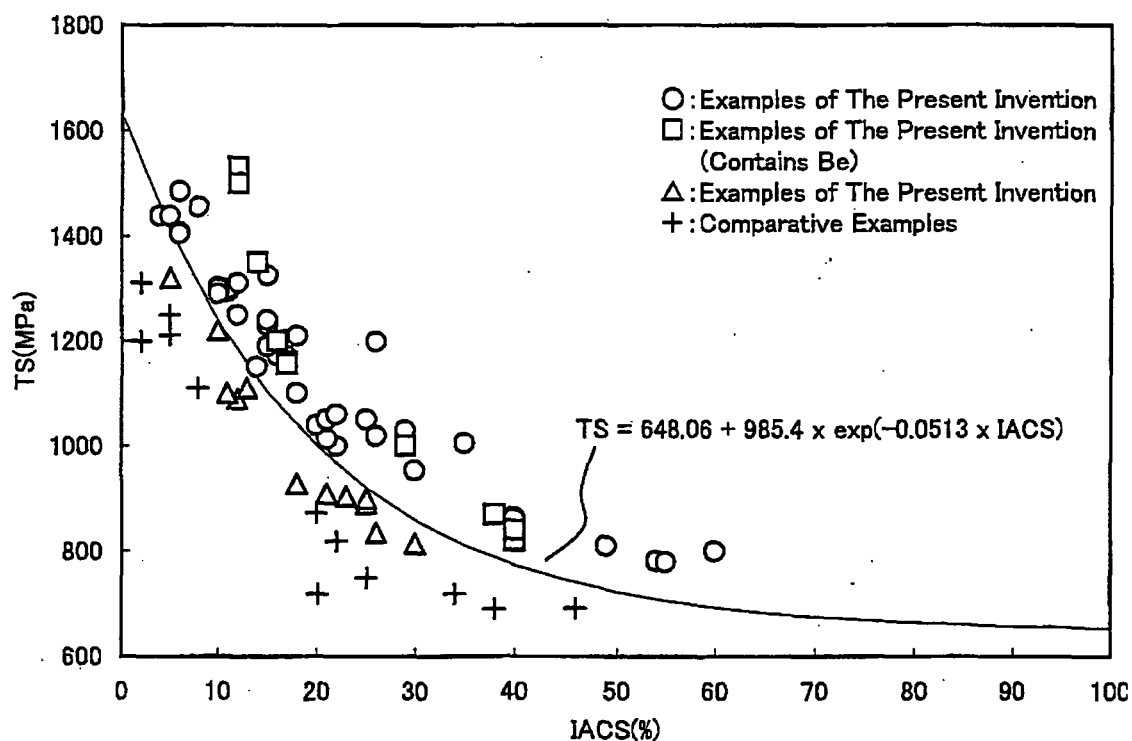
12. A method for producing a copper alloy according to claim 11, wherein the working in a temperature range of 600°C or lower and the heat treatment of holding for 30 seconds or more in a temperature range of 150 to 750°C are performed for a plurality of times.

13. The method for producing a copper alloy according to claim 11 or 13, wherein the working in a temperature range of 600°C or lower is performed after the final heat treatment.

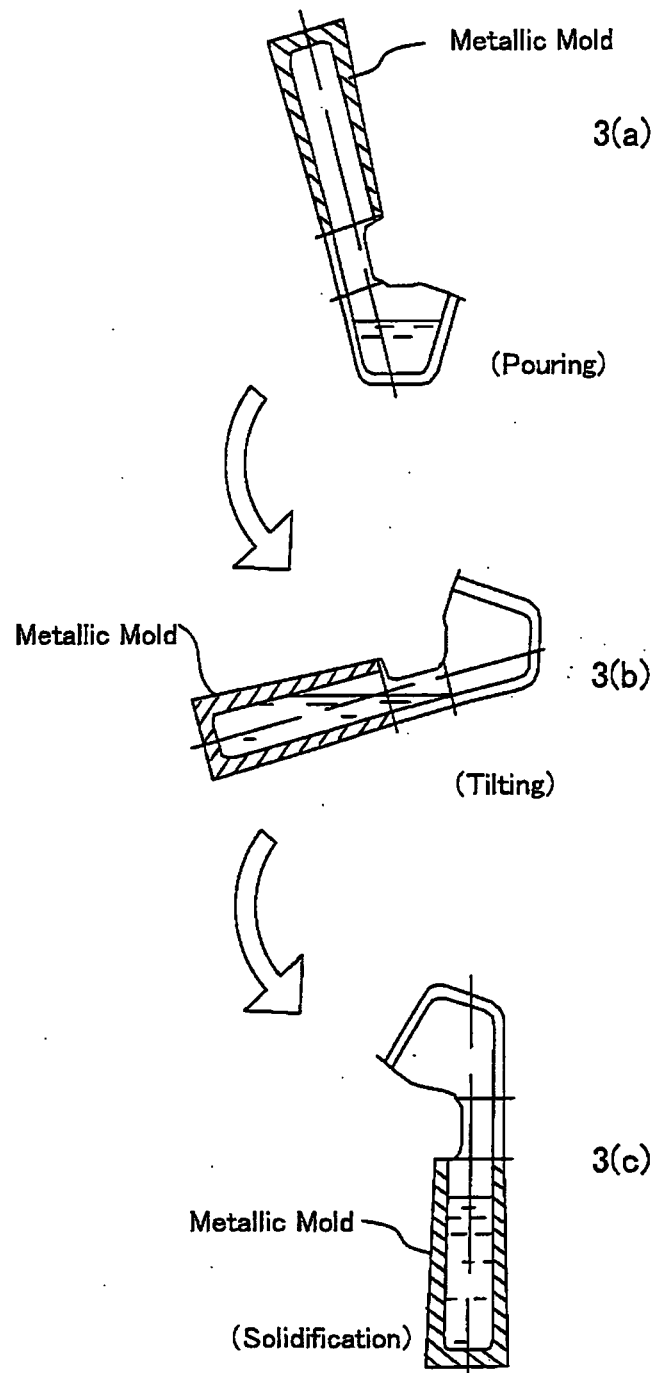
[Figure 1]



[Figure 2]



[Figure 3]



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2005/003502

A. CLASSIFICATION OF SUBJECT MATTER Int.Cl. ⁷ C22C9/00, C22F1/00 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) Int.Cl. ⁷ C22C9/00, C22F1/00 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2005 Kokai Jitsuyo Shinan Koho 1971-2005 Toroku Jitsuyo Shinan Koho 1994-2005 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 11-172350 A (Mitsubishi Materials Corp.), 29 June, 1999 (29.06.99), (Family: none)	1-13
A	JP 2002-285261 A (Kobe Steel, Ltd.), 03 October, 2002 (03.10.02), (Family: none)	1-13
☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.		
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Date of the actual completion of the international search 06 June, 2005 (06.06.05)		Date of mailing of the international search report 21 June, 2005 (21.06.05)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
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Patent documents cited in the description

- JP 2572042 B [0014]
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Non-patent literature cited in the description

- Industrial Heating. Japan Industrial Furnace Manufacturers Association, 1999, vol. 36, 59 [0014]
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