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(54) **COPPER ALLOY AND METHOD FOR PRODUCING COPPER ALLOY**

(57) To provide a copper alloy of the FCC structure containing Ni: 3.0 to 29. mass%, Al: 0.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass%, with the remainder consisting of Cu and incidental impurities, wherein the copper alloy is of the high strength, but is excellent in workability, and

has high electrical conductivity, and can control property thereof, by precipitating a γ' phase of the L1₂ structure including Si at an average particle diameter of 100 nm or less in a parent phase of the copper alloy.

Description

Technical Field

5 **[0001]** The present invention relates to a copper alloy having the high strength and high electrical conductivity which is applied to a lead frame, a connector, a terminal material and the like for electric and electronic instruments and a process for producing a copper alloy, which produces this copper alloy.

Background Art

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[0002] Conventionally, in materials requiring electrical conductivity and spring property such as various terminals such as a lead frame and the like, a connector, a relay or a switch and the like of electronic instruments, inexpensive brass has been applied to utilities setting a high value on the manufacturing cost. On the other hand, in utilities setting a high value on a mechanical nature such as spring property and the like, phosphorus bronze has been applied thereto. Further,

- *15* in addition to spring property, nickel silver has been applied to utilities setting a high value on corrosion resistance. However, with weight saving, thinning and miniaturization of electronic instruments and parts thereof in recent years, if these materials are used, the necessary strength cannot be sufficiently satisfied under the current circumstances. In recent years, in materials requiring electrical conductivity and spring property of various terminals and the like of electronic instruments, in place of the conventional solid- solution strengthening alloy, a representative of which is
- *20* phosphorus bronze, brass and the like, a use amount of an aging hardening- type copper alloy is increasing, from a view point of the high strength and high electrical conductivity. An aging hardening- type copper alloy is a copper alloy which, by aging- treating a supersaturated solid solution which has been solution- treated, contributes to improvement in strength property such as a proof stress or a spring limit value by uniform precipitation of fine particles, and improvement in electrical conductivity by decrease in a solid solution element
- *25* amount.

Therefore, as a material satisfying demand of weight saving of electronic instruments and parts thereof, and high strengthening of materials, which are becoming severe increasingly, for example, an aging hardening- type copper alloy such as a Cu- Ni- Si alloy (Colson) and beryllium copper is used.

- *30* **[0003]** Additionally, as weight saving, and high strengthening of materials, improvement by a manufacturing process using a Cu- Ni- Si alloy (Colson) as a copper alloy responding to electronic instruments has been also tried. For example, Patent Literature 1 discloses a copper alloy material containing 1.0 to 5.0 mass% of Ni, 0.2 to 1.0 mass% of Si, 1.0 to 5.0 mass% of Zn, 0.1 to 0.5 mass% of Sn, and 0.003 to 0.3 mass% of P, with the remainder consisting of Cu and incidental impurities, which is obtained by a first cold rolling step of cold rolling to a thickness which is 1.3 to 1.7- fold of an objective final plate thickness, a first heat- treating step of heating a material after the first cold rolling to 700 to 900°C
- *35 40* and, thereafter, cooling the material to 300°C or lower at a temperature lowering rate of 25°C or more per minute, a second cold rolling step of cold- rolling a material after the first heat treatment to a final plate thickness, a second heattreating step of heating a material after the second cold rolling to 400 to 500°C, and holding it for 30 minutes to 10 hours, and a step of heating and holding a material after the second heat treatment at 400 to 550°C for 10 seconds to 3 minutes while a tensile force is applied in a longitudinal direction. However, a manufacturing step becomes complicated, and it
- is difficult to realize reduction in the manufacturing cost. **[0004]** Improvement by addition of other metal elements utilizing this Cu-Ni-Si (Colson) alloy is disclosed (see Patent Literatures 2 to 4). For example, Patent Literature 2 describes a copper alloy for electronic materials containing Ni: 1.0 to 4.5 mass%, Si: 0.50 to 1.2 mass%, and Cr: 0.0030 to 0.3 mass% (provided that a weight ratio of Ni and Si is 3 ≤ Ni/Si ≤ 5.5), with the remainder being composed of Cu and incidental impurities, in which a Cr-Si compound having a size of
- *45* 0.1 μ m or more and 5 μ m or less, which is dispersed in a material is such that an atomic concentration ratio of Cr relative to Si in the dispersed particle is 1 to 5, and a dispersion density thereof is 1×10^6 /mm² or less. However, this alloy improves the strength of a Ni-Si intermetallic compound, and there is a limit regarding the high strength and high electrical conductivity.
- *50* **[0005]** Further, a copper alloy in which a Cr- Si, Ni- P- Fe obtained by adding Fe to Ni- P, or Ni- Ti intermetallic compound, being an intermetallic compound different from a Ni- Si intermetallic is precipitated, is disclosed (see Patent Literatures 5 to 7) . For example, Patent Literature 7 describes a copper alloy for electric and electronic instruments containing 1 to 3 mass% of Ni and 0.2 to 1.4 mass% of Ti, in which a ratio (Ni/Ti) of a mass percentage of the Ni and the Ti is 2.2 to 4.7, containing 0.02 to 0.3 mass % of one or both of Mg and Zr, and 0.1 to 5 mass% of Zn, with the remainder consisting of Cu and incidental impurities, in which the copper alloy contains at least one of an intermetallic
- *55* compound consisting of Ni, Ti and Mg, an intermetallic compound consisting of Ni, Ti and Zr, or an intermetallic compound consisting of Ni, Ti, Mg, and Zr, a distribution density of the intermetallic compounds is 1×10^9 to 1×10^13 /mm², the tensile strength is 650 MPa or more, electrical conductivity is 55 IACS% or more, and a stress relaxation ratio when held at 150°C for 1000 hours is 20% or less.

Citation List

Patent Literatures

5 **[0006]**

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Patent Literature 1: JP- A- 2007- 070651 Patent Literature 2: JP- A- 2009- 242921 Patent Literature 3: JP- A- 2010- 090408 Patent Literature 4: JP- A- 2008- 266787 Patent Literature 5: JP- A- 2007- 126739 Patent Literature 6: JP- A- 2001- 335864 Patent Literature 7: JP- A- 2006- 336068

15 Summary of Invention

Technical Problem

[0007] However, in any copper alloy, the high strength and high electrical conductivity which are possessed together are insufficient for a recent demand.

Then, the present invention was done in view of the aforementioned problems, and an object thereof is to provide a copper alloy which is excellent in workability in spite of the high strength, and is of high electrical conductivity, and a process for producing such the copper alloy.

Another object of the present invention is to provide a copper alloy which is excellent in workability in spite of the high

25 strength, and has high electrical conductivity, and which can control physical property, and a process for producing such the copper alloy.

Solution to Problem

- *30* **[0008]** As the characteristic of the present invention which is the means to solve the aforementioned problems, the present inventors studied in order to obtain a high strength copper alloy and, as a result, found out that it is effective to finely precipitate a γ phase of the L1₂ structure with Ni₃Al in a parent phase of the FCC structure, in a Cu-Ni-Al alloy. Further, it was found out that the copper alloy is further highly strengthened by adding Si.
- *35* Therefore, the copper alloy of the present invention is a copper alloy of the FCC structure containing Ni: 3.0 to 29.5 mass%, Al : 0.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass%, with the remainder consisting of Cu and incidental impurities, in which a γ' phase of the L1₂ structure is precipitated at an average particle diameter of 100 nm or less with Ni₃Al including Si, in a parent phase of the copper alloy. Further, the copper alloy of the present invention is further characterized in that the copper alloy contains Ni: 3.0 to 14.0

mass%, Al: 0.5 to 4. mass%, and Si: 0.1 to 1.5 mass%, and electrical conductivity is 8.5 IACS% or more.

- *40* Further, the copper alloy of the present invention is further characterized in that cold workability is 10 to 95%. Further, the copper alloy of the present invention is further characterized in that the copper alloy is in a region A surrounded by four points of (Al: 2.0 mass%, Ni: 3.0 mass%, (Al: 4.0 mass%, Ni: 9.5mass%), (Al: 1.5 mass%, Ni: 14.0mass%), and $(AI: 0.5 \text{ mass}\%$, Ni: 5.0 mass%), as a range shown by Al equivalent (mass%) = (Al mass% + 1.19Si mass%) and Ni mass%. Further, the copper alloy of the present invention is further characterized in that the copper alloy contains Ni: 9.5 to 29.5
- *45* mass%, Al: 1.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass%, and a Vickers hardness is 220 Hv or more. Further, the copper alloy of the present invention is further characterized in that the copper alloy is in a region B surrounded by four points of (Al: 4.0 mass%, Ni: 9.5 mass%), (Al: 7. 0 mass%, Ni: 16.0 mass%), (Al: 2.5 mass%, Ni: 29. 5 mass%), and (Al: 1.5 mass%, Ni: 14.0 mass%), as a range shown by Al equivalent (mass%) = (Al mass% +1.19Si mass%) and Ni mass%.
- *50* Further, the copper alloy of the present invention is further characterized in that the copper alloy contains, as an addition element, a total amount of 0.01 to 5.0 mass% of one or two or more elements selected from the group consisting of Co, Ti, Sn, Cr, Fe, Zr, Mg and Zn.

Further, the copper alloy of the present invention is further characterized in that the copper alloy contains, as an addition element, a total amount of 0.001 to 0.5 mass% of one or two or more elements selected from the group consisting of C, P and B.

[0009] The process for producing a high strength copper alloy of the present invention is characterized in that raw materials are integrated, melted and mixed, and hot-worked and cold-worked and, thereafter, the mixture is heat-treated in a range of 700 to 1020°C for 0.1 to 10 hours and, thereafter, this is aging-treated in a range of 400 to 650°C and 0.1

to 48 hours.

Further, the process for producing a high strength copper alloy of the present invention is further characterized in that, before or after the aging treatment, cold working at a working rate of 10 to 95% is performed.

5 Advantageous Effects of Invention

> **[0010]** High electrical conductivity was studied by the copper alloy of the present invention which is the means to solve the problems and, as a result, it was found out that both of the strength and electrical conductivity are satisfied in a region A and a region B. In the region A, a high strength copper alloy having, particularly, high electrical conductivity and excellent workability can be obtained and, in the region B, particularly, a high strength copper alloy having the high

strength can be obtained.

Further, high electrical conductivity was studied by the process for producing a copper alloy of the present invention and, as a result, in the region A and the region B, a copper alloy satisfying both of the strength and electrical conductivity can be produced.

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Brief Description of Drawings

[0011] Fig. 1 is a photograph of a transmission electron microscope in which an upper side shows a crystal structure $L1₂$ of a precipitate according to electron beam diffraction, and a lower shows the state of a precipitate.

Description of Embodiments

[0012] A best mode for carrying out the present invention will be explained below based on the drawing. In addition, a so-called person skilled in the art easily changes or modifies the present invention within the patent claims to create

25 other embodiment. These change and modification are included in the patent claims, and the following explanation is an example of a best mode of the present invention, and does not limit the patent claims. The copper alloy of the present invention is a copper alloy of the FCC structure containing Ni: 3.0 to 29.5 mass%, Al: 0.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass%, with the remainder consisting of Cu and incidental impurities, in which a γ phase of the L1₂ structure is precipitated at an average particle diameter of 100 nm or less with Ni₃AI including Si, in a

30 parent phase of the copper alloy. The $L1₂$ structure can be confirmed, for example, by an arrangement structure of an electron beam diffraction image.

Fig. 1 is a photograph of a transmission electron microscope in which an upper side shows a crystal structure L1₂ of a precipitate by electron beam diffraction, and a lower side shows the state of a precipitate.

35 In addition, the present photograph is a composition of Ni: 12.3 mass%-Al: 1.0 mass%-Si: 0.3 mass%-Cu, and the composition has been subjected to solution treatment: 900°C 10 minutes-cold working 30%-aging treatment 500°C 6 hours.

As in Fig. 1, electron beam diffraction is directed to a regular phase having a diffraction plane 110. That is, the γ phase is an intermetallic compound, and has a regularized FCC structure in which an atom positioning at a corner is Al and Si, and an atom positioning at a face center is Ni.

40 Further, as described later, in a lower photograph of Fig. 1, it is seen that the γ phase of the L1₂ structure is finely precipitated.

Since these copper of a parent phase having the FCC structure and γ' phase having the L1₂ structure are both of the FCC structure, they are good in integrity, they contribute to improvement in the strength and, at the same time, a solute element concentration of a parent phase is decreased by precipitating the γ' phase, and they also contribute to improvement in electrical conductivity.

The copper alloy of the present invention is a copper alloy while it has the FCC structure. The FCC structure is a structure in which metal elements are laminated most closely, and is suitable as a parent phase alloy of the high strength and high electrical conductivity. Therefore, copper having the FCC structure is excellent in workability, and an objective shape can be easily made.

- *50* In the copper alloy of the present invention, inclusion of Ni: 3.0 to 29.5 mass%, Al: 0.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass% is necessary for satisfying the high intensity and high electrical conductivity. Ni and Al precipitate an intermetallic compound of Ni₃Al to form a y' phase in Cu of a parent phase. Further, since Al and Si together with Ni form a Ni₃ (Al, Si) intermetallic compound, Al and Si together are required at an amount adapted for this system, and form not a system of Ni₃Al or Ni₃Si alone, but one Ni₃ (Al, Si) intermetallic compound while it resides
- *55* in mixture at a corner of the FCC structure in the $L1₂$ type. The y' phase having the L1₂ structure in the copper alloy of the present invention is an intermetallic compound, and has a regularized FCC structure in which an atom positioning at a corner is Al and Si, and an atom positioning at a face center is Ni.

[0013] Since these copper of a parent phase having the FCC structure and γ' phase having the L1₂ structure are both of the FCC structure, they are good in integrity, contribute to improvement in the strength and, at the same time, a solute element concentration of a parent phase is decreased by precipitating the γ' phase, and they also contribute to improvement in electrical conductivity.

5 Further, to explain in detail, since the γ' phase of the L1₂ structure belongs to the GCP (Geometrically close packing) phase, has ductility due to a closed packed structure thereof, and further, is high in integrity, a $\gamma + \gamma'$ structure is formed, in which a γ phase being a fine structure is precipitated, thereby, a copper alloy having high workability with toughness can be obtained.

10 This γ' phase is precipitated finely and spherically in a γ phase containing mainly copper being parent phase. Since the γ ' phase is spherical, a highly workable copper alloy with toughness can be obtained without stress concentration at an interface between the γ ' phase and the γ phase.

Further, by controlling an average particle diameter of the γ' phase small, it is possible to improve the strength more. By reducing an average particle diameter of the γ' phase, a pinning site of moving rearrangement is increased in the number, and the high tensile strength can be obtained.

15 Further, the γ' phase is an intermetallic compound, its own hardness is high, and the tensile strength is also high. Therefore, by preventing rearrangement from moving in the γ' phase, it can contribute to a hardness and the tensile strength of a copper alloy.

[0014] Further, generally, electrical conductivity is lowered as a concentration of a solute element which forms a solid solution in copper, but since a solute element concentration in a parent phase is decreased as compared with the

- *20* solutionized state of a γ monophase by heat- treating an alloy at a low temperature to precipitate a γ' phase, precipitation of the γ ' phase also contributes to improvement in electrical conductivity. In addition, since electrical conductivity of the γ ' phase is lower than electrical conductivity of pure Cu, movement of electrons is reduced by a portion corresponding to a volumetric ratio occupied by this γ phase, but high electrical conductivity can be maintained by adopting an area fraction of a suitable amount of the γ' phase.
- *25* Therefore, when formulated into a copper alloy, the copper alloy greatly contributes to mechanical property such as a hardness, the tensile strength and the like without considerably deteriorating ductility such as cold workability and the like, and as a second phase having the effect of improving electrical conductivity, the γ phase is suitable. Thereupon, it is preferable that an area fraction of the γ ' phase is 5 to 40%.
- *30* This area fraction can be obtained by comparing an area of each metal structure of a certain cross section of a copper alloy. In addition, usually, regarding an area fraction and a volume fraction, if areas of sections when two three dimensionalobjects are cut with a plane parallel with a certain plane are equal in accordance with Cavalier principle, volumes of two three dimensional- objects are equal. Therefore, there is no problem that this area fraction is grasped as a volume fraction. In addition, the area fraction can be measured with a metal microscope, an electron microscope (SEM, TEM), EPMA (X- ray analysis apparatus) or the like.
- *35* Further, it is preferable that an average particle diameter of this γ phase is 100 nm or less. A smaller average particle diameter is preferable, but it is difficult to control a practical precipitation size finer than 1 nm due to coarsening by heat treatment, and when the size is 1 nm or more and 100 nm or less, the sufficient strength can be obtained. An average particle diameter of the γ' phase is obtained by measuring diameters of a plurality of γ' phases by image analysis from structural observation with an electron microscope, and averaging them.
- *40* Thereupon, an intermetallic compound such as Ni₂ (Al, Si), NiAl, Ni₅Si₂ and the like other than the γ' phase of an intermetallic compound of $Ni₃Al$ is precipitated by added Ni, Al and Si, in some cases. However, Ni₂ (Al, Si) is smaller in a precipitation amount as compared with that of Ni₃ (Al, Si), and influences little on a mechanical nature and an electric nature of a copper alloy.
- *45* An intermetallic compound of a β phase represented by NiAl is precipitated. This β phase is of the B2 structure of the BCC regular structure, but a compositional range at which precipitation occurs, is narrow, and if precipitated, an amount thereof is smaller as compared with that of Ni₃ (Al, Si), and the β phase influences little on a mechanical nature and an electric nature of a copper alloy.

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Further, an intermetallic compound of Ni₅Si₂ is precipitated in some cases. This Ni₅Si₂ is also smaller in a precipitation amount as compared with that of Ni₃ (Al, Si), and influences little on a mechanical nature and an electric nature of a copper alloy.

However, precipitation of a number of respective intermetallic compounds other than the γ' phase of Ni₃ (Al, Si) influences on a mechanical nature and an electric nature of a copper alloy, but does not influence thereon more than Ni₃ (Al, Si). However, by combining these all precipitated products, the copper alloy of the present invention is established.

55 **[0015]** Si has the effect of reducing a concentration of a solute element in a matrix, and has the effect of increasing a volume fraction of the γ ' phase and, at the same time, enhancing electrical conductivity. For this reason, the γ ' phase, by becoming an intermetallic compound of $Ni₃(AI, Si)$, is excellent in the strength and electrical conductivity as compared with a single substance of Ni₃Al. It is preferable that an amount ratio of Al and Si is in a range of Al/Si=1 to 5. This is because when the Al/Si ratio is less than 1, other compounds influencing on reduction in ductility and electrical conductivity,

in addition to the γ' phase, are precipitated, and when the ratio is more than 5, a volume fraction of the γ' phase is insufficient, reduction in a concentration of a solute element in a matrix is also insufficient, and increase in the strength and electrical conductivity is not sufficiently obtained.

- *5* Therefore, by adopting a range of A1 : 0.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass% to precipitate the γ' phase, a compositional region excellent in the high strength, high electrical conductivity, and workability can be obtained.
- **[0016]** Further, the copper alloy of the present invention has a compositional range containing Ni: 3.0 to 14.0 mass%, Al: 0.5 to 4.0 mass%, and Si: 0.1 to 1.5 mass%, and has electrical conductivity of 8.5 IACS% or more. By adopting this compositional range to precipitate the γ' phase of 100 nm or less, electrical conductivity can be made
	- to be 8.5 IACS% or more.
- *10* By making electrical conductivity 8.5 IACS% or more, the copper alloy as a copper alloy having high electrical conductivity is applied to a lead frame, a connector, a terminal material and the like of electronic instruments and the like. **[0017]** Further, in the copper alloy of the present invention, by adopting this compositional range to precipitate the γ' phase of 100 nm or less, further, cold workability can be made to be 10 to 95%.
- *15* Cold workability is defined as a reduction ratio of a maximum thickness at which rolling is possible with no cracking without performing annealing in the case of rolling implemented at a temperature of 20°C, and is defined as a maximum area reduction ratio at which wire drawing is possible with no cracking without performing annealing in the case of wire drawing.

Since a Ni₃ (Al, Si) intermetallic compound of the γ' phase has lower workability than that of pure Cu, a working ratio cannot be increased by a portion corresponding to a ratio of a volume occupied by this Ni₃ (Al, Si) intermetallic compound.

20 Therefore, by adopting a compositional range containing Ni: 3.0 to 14.0 mass%, Al: 0.5 to 4.0 mass%, and Si: 0.1 to 1.5 mass%, a precipitation amount of the γ phrase can be controlled to adjust cold workability at 10 to 95% while electrical conductivity is maintained high.

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When cold workability is less than 10%, there is a problem that a material having an objective shape cannot be made. When cold workability exceeds 95%, there is a problem that a burden on a facility is great. Therefore, cold workability is preferably in a range of 10 to 95%, further preferably 20 to 90%.

By adjusting cold workability at 10 to 95%, the copper alloy as a copper alloy having the high strength is applied to a lead frame, a connector, a terminal material and the like of electronic instruments and the like.

[0018] Further, in the copper alloy of the present invention, addition amounts of Ni, Al and Si are in a region A surrounded by four points of (Al: 2.0 mass%, Ni : 3.0 mass%), (Al: 4.0 mass%, Ni: 9.5 mass%), (Al: 1.5 mass%, Ni: 14.0 mass%),

30 and (Al: 0.5 mass%, Ni: 5.0 mass%), in a Ni vs Al equivalent view represented by Al equivalent (mass%) = (Al mass%+1.19Si mass%) and Ni mass%.

The copper alloy of the present invention can afford high electrical conductivity and high cold workability by residing in a range of this region A and adopting 5 to 20% of a volume fraction at which the γ phase is precipitated.

35 In a range of this region A, since electrical conductivity of approximately 10 to 25 IACS% can be obtained, and cold workability of 10 to 95% can be obtained, the copper alloy as a contact material can reduce abrasion even when the material is contacted and sliding- rubbed frequently.

Therefore, the copper alloy can be applied to a lead frame, a connector, a terminal material and the like of electronic instruments and the like, as a copper alloy having high electrical conductivity and high cold workability.

40 **[0019]** Further, in the copper alloy of the present invention, Ni: 9.5 to 29.5mass%, Al: 1.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass% are contained, and a Vickers hardness is in a range of 220 to 450 Hv.

By adding a high amount of Ni to increase a volume and an area occupied by the γ' phase, a Vickers hardness can be enhanced.

In this case, by adjusting a volume fraction at which the γ phase is precipitated, at 20 to 40%, this can contribute to the strength represented by a Vickers hardness on copper.

- *45* Thereupon, an average particle diameter of the γ ' phase is preferably 100 nm or less like the above. A smaller average particle diameter is preferable, but it is difficult to perform practical precipitation completely uniformly, and the sufficient strength can be obtained at an average particle diameter of 1 nm or more and 100 nm or less, and 30 nm or less is more preferable.
- *50* In addition, in the copper alloy of the present invention, since as electrical conductivity in this compositional range, electrical conductivity of approximately 7 to 15 IACS% can be obtained, abrasion is little, and durability is good, the copper alloy can stand use for a long term, even when applied to a lead frame, a connector, a terminal material and the like of electronic instruments and the like, by possession of a high Vickers hardness together..

[0020] In addition, the copper alloy of the present invention is in a region B surrounded by four points of (Al: 4.0 mass%, Ni: 9.5 mass%), (Al: 7.0 mass%, Ni: 16.0 mass%), (Al: 2. 5 mass%, Ni: 29.5 mass%), and (Al: 1.5 mass%, Ni: 14.0

55 mass%, in a Ni vs Al equivalent view represented by Al equivalent (mass%) = (Al mass% +1.19Si) mass%) and Ni mass%. The copper alloy of the present invention can further have the high strength represented by a Vickers hardness by residing in a range of this region B and adjusting a volume fraction at which the γ phase is precipitated, at 25 to 40%. This is derived from that the γ phase is an intermetallic compound, and the strength is very high. However, when an

area ratio of the γ' phase is increased, there is a demerit that electrical conductivity is reduced. Therefore, by residing in a range of this region B, the copper alloy can be also provided with a high Vickers hardness, while high electrical conductivity is obtained.

- *5* Thereby, the copper alloy can be widely applied to a lead frame, a connector, a terminal material and the like of electronic instruments and the like.
- **[0021]** Further, in the copper alloy of the present invention, further, a total amount of 0.01 to 5.0 mass% of one or two or more elements selected from the group consisting of Co, Ti, Sn, Cr, Fe, Zr, Mg and Zn can be contained as an addition element.

10 Since Co, Ti, Cr and Zr stabilize the γ' phase and promote precipitation thereof, they contribute to improvement in the strength, and since they also have the effect of decreasing a concentration of a solute element in Cu, they also contribute to improvement in electrical conductivity.

Since Sn, Mg and Zn have the effect of improving stress relaxation resistance property and, at the same time, dissolve in Cu, they contribute to improvement in the strength.

15 Fe has the effect of miniaturization of a crystal grain by dispersion of a fine grain of Fe in Cu, and contributes to improvement in the strength and improvement in heat resistance.

- An addition amount of an addition element is so that selected one or two more addition elements are contained at a total amount of 0.01 to 5.0 mass%. When a total amount of selected one or two or more addition elements is less than 0.01 mass%, there is a problem that this does not contribute to improvement in electrical conductivity and improvement in the strength, for a copper alloy. Further, when a total amount of addition elements exceeds 5.0 mass%, this contributes
- *20* to improvement in electrical conductivity and improvement in the strength, but there is a problem that it becomes impossible to control electric property such as electrical conductivity and the like, and mechanical property such as a Vickers hardness and the like in a suitable range.

[0022] The copper alloy of the present invention can further contain a total amount of 0.001 to 0.5 mass% of one or two or more elements selected from the group consisting of C, P and B as an addition element.

- *25* C is thought to have the effect on miniaturization of a crystal grain, and contributes to improvement in the strength. Further, C reduces solid solubility of a solute element in Cu, and contributes to improvement in electrical conductivity. P is used as a deoxidant, has the effect of decreasing a concentration of impurities of Cu, and contributes to improvement in electrical conductivity.
- *30* B has the effect of suppressing growth of a crystal grain and, therefore, has the effect of miniaturizing a crystal grain to improve the strength. B can improve heat resistance.

An addition amount is such that selected one or two or more addition elements are contained at a total amount of 0.001 to 0.5 mass% . When a total amount of addition elements is less than 0.001 mass%, there is a problem that addition elements do not contribute to improvement in electrical conductivity and improvement in the strength, for a copper alloy. On the other hand, when a total amount of addition elements exceeds 0. 5 mass%, there is a problem that addition

35 elements contribute to improvement in electrical conductivity and improvement in the strength, but it becomes impossible to control electric property such as electrical conductivity and the like and mechanical property such as a Vickers hardness and the like in a suitable range.

[0023] Further, in the process for producing a copper alloy of the present invention, raw materials are integrated, melted, mixed and cast and, thereafter, the cast product is formed into a shape such as a plate material, a wire material,

- *40* a tube material and the like by hot working such as hot forging and, if necessary, cold working such as cold rolling, cold wire drawing and the like. Then, the formed material is heat- treated in a range of 700 to 1020°C and 0.1 to 10 hours and, thereafter, aging- treated in a range of 400 to 650°C and 0.1 to 48 hours. The process for producing a copper alloy of the present invention has (a) a step of integrating, melting and mixing Ni:
- *45* 3.0 to 29.5 mass%, Al: 0.5 to 7.0 mass%, Si: 0.1 to 1.5 mass% and Cu to form a copper alloy material as an ingot, (b) a step of performing solution treatment of heat- treating the copper alloy material at a temperature in a range of 700°C to 1020°C for a time in a range of 0.1 to 10 hours, after the material is formed by hot working and, if necessary, cold working, and (c) a step of performing aging treatment of heating the copper alloy material after solution treatment at a temperature in a range of 400°C to 650°C for a time in a range of 0.1 to 48 hours.
- *50* **[0024]** In the (a) step of forming a copper alloy material, as a raw material of a copper alloy, a total amount of 0.01 to 5.0 mass% of one or two or more elements selected from the group consisting of Co, Ti, Sn, Cr, Fe, Zr, Mg and Zn can be also further added as an addition element. Further, as raw material of a copper alloy, a total amount of 0.001 to 0.5 mass% of one or two or more elements selected from the group consisting of C, P and B can be also added. In melting and mixing, in order to prevent decrease in Al and Si due to oxidation, for example, a deoxidant such as

55 calcium boride and the like may be used, a bubbling treatment may be performed using an argon gas or a nitrogen gas, or melting may be performed in vacuum in a vacuum container. A method of melting is not particularly limited, but a raw material may be heated at a temperature of a melting point of a copper alloy raw material or higher using the known apparatus such as a high frequency melting furnace and the like.

In the (b) step of performing solution treatment, a copper alloy material is heat-treated at a temperature in a range of

700°C to 1020°C for a time in a range of 0.1 to 10 hours. Thereby, a solid solution in which added alloy elements are uniformly homogenized in a parent phase of Cu without segregation is attained. A method of heating is not particularly limited, but heating may be performed according to the known method.

- *5* By this solution treatment, Ni, Al, Si and the like are dispersed homogeneously, thereby, the γ' phase having a fine average particle diameter of 100 nm or less can be precipitated by aging treatment described later.
- *10* In the (c) step of performing aging treatment, a copper alloy material is aging-treated at 400 to 650°C, for a time in a range of 0.1 to 48 hours. The γ' phase cannot be precipitated at lower than 400°C and/or for shorter than 0.1 hour. At higher than 650°C and/or for longer than 48 hours, a problem arises that the γ phase is grown, an average particle diameter exceeds 100 nm, and desired electrical conductivity and working ratio cannot be obtained. Therefore, in order
- to obtain desired electrical conductivity and hardness, such the aging treatment becomes essential requirement. **[0025]** Further, the process for producing a high strength copper alloy of the present invention is further characterized in that, before or after the aging treatment, cold working of 10 to 95% is performed. In the process for producing a high strength copper alloy of the present invention, in addition to the aforementioned production steps, further, (d) a step of subjecting the copper alloy material to cold working of 10 to 95% before or after
- *15* the aging treatment is provided. By cold- working a copper alloy material before aging treatment, a lattice defect such as a crystal grain boundary, rearrangement, a lamination defect and the like is formed to miniaturize and working- cure a crystal grain and, at the same time, thereafter, disperse and precipitate a number of γ' phases of Ni₃ (Al, Si), thereby, an average particle diameter of the γ ' phase can be made to be 100 nm or less and, at the same time, a temperature of aging treatment can be
- *20* lowered, and a time of aging treatment can be shortened. A method of cold working is not particularly limited, but the method may be performed by the known method such as rolling with a roller and the like. Further, since by cold- working a copper alloy material after aging treatment, rearrangement, a lamination defect and the like can be introduced to working- cure the material, the material can be highly strengthened. Thereupon, working is performed at a working ratio in a range of 10 to 95%. When the working ratio is less than 10%,
- *25* introduction of a defect is little, and the aforementioned effect of working is not sufficiently obtained. When the working ratio exceeds 95%, a burden on a processing facility becomes great, raising a problem. After these steps, in order to impart spring property, low temperature aging may be performed in a range of 100 to 400°C. A method of low temperature aging is not particularly limited, but the method can be performed according to the known method.
- *30* Since a copper alloy obtained by such the production process can precipitate a sufficient amount of a fine γ phase while suppressing coarsening of a γ ' phase of the L1₂ structure precipitating in a copper alloy, electric property such as electrical conductivity and the like, and mechanical property such as cold workability, a Vickers hardness and the like can be easily controlled.
- *35* Examples

(Copper alloy Nos. 1 to 57)

40 **[0026]** In a range of the copper alloy of the present invention, copper alloy materials of compositions of Examples 1 to 57 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as-cast).

(Compositions of Examples 1 to 57)

45 **[0027]**

50 55 [Table 1-1] Alloy No. Ni (mass%) Al (mass%) Si (mass%) [Table 1-2] Alloy No. Ni (mass%) Al (mass%) Si (mass%)

[0028] Thereafter, a γ' phase of the L1₂ structure was precipitated in a parent phase of Cu of the FCC structure.

Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)- solutionizing (900°C, 10 minutes)- cold rolling (20°C, rolling reduction 30%)- aging precipitation treatment (500°C, 18 hours) . Electrical conductivity, workability, a Vickers hardness at each composition thereupon are shown.

5 (Results of electrical conductivity, workability, Vickers hardness)

[0029]

[Table 2-1] Alloy No. Electrical conductivity **Workability Hardness** [Table 2-2] Alloy No. Electrical conductivity **Workability** Hardness

20 From Table 2-1 and Table 2-2, it is seen that electric property such as electrical conductivity and the like, and mechanical property such as cold workability, a Vickers hardness and the like can be controlled in a range of the copper alloy of the present invention.

[0030] Thereafter, a γ' phase of the L1₂ structure was precipitated in a parent phase of the FCC structure via production heat treatment condition steps shown in Table 3.

25

10

15

(Production condition)

[0031]

50 Hot rolling (900°C)

> **[0032]** In Table 4, electrical conductivity and a Vickers hardness at each production condition in Table 3 are shown using copper alloys of compositions of Nos. 16 to 23 as a copper alloy. (Results of electrical conductivity and Vickers hardness under production condition)

55

[Table 4] Heat treatment condition Alloy No.

Electrical conductivity **Hardness**

5 As seen from this Table 4, under all heat treatment working conditions other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Copper alloy Nos. 58 to 70)

10 **[0033]** Then, addition elements were added. Copper alloy materials of compositions of Examples 58 to 70 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast) .

(Composition of addition elements)

15 **[0034]**

20

25

30

[Table 5-1] Alloy No. Ni (mass%) Al (mass%) Si (mass%) Cu (mass%) Remainder [Table 5-2]

Alloy No. Addition element (mass%)

[0035] Thereafter, a γ' phase of the L1₂ structure was precipitated in a parent phase of Cu of the FCC structure. Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)- solutionizing (900°C, 10 minutes)- cold rolling (20°C, rolling reduction 30%)- aging precipitation treatment (500°C, 18 hours) . Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

[0036] As seen in Table 6, under production condition of the production process of the present invention, under all of heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

35

(Results of electrical conductivity and Vickers hardness)

[0037]

40 [Table 6]

Heat treatment condition Alloy No. Electrical conductivity **Hardness**

45

55

(Copper alloy Nos. 71 to 76)

[0038] Then, Sn was added as an addition element.

50 Copper alloy materials of compositions of Examples 71 to 76 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ' phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure. Compositions of Examples 71 to 76 are shown in the following Table 7.

[Table 7]

Alloy No.

Addition element (mass%)

[0039] Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction

90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

As seen from Table 8, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more.

Further, under all heat treatment working conditions essentially including aging treatment other than treatment working conditions 1, 5, 6, 7, 8, 12 and 13, a Vickers hardness was 220 Hv or more.

10 (Results of electrical conductivity and Vickers hardness)

[0040]

5

25

20 (Copper alloy Nos. 77 to 82)

[0041] Then, as an addition element, Ti was added.

Copper alloy materials of compositions of Examples 77 to 82 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure.

Compositions of Examples 77 to 82 are shown in the following Table 9.

30 [Table 9] Alloy No. Addition element (mass%)

> **[0042]** Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

35 Electrical conductivity and a Vickers hardness at each composition thereupon are shown. As seen from Table 10, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

40 (Results of electrical conductivity and Vickers hardness)

[0043]

55

50 (Copper alloy Nos. 83 to 88)

[0044] Then, as an addition element, Zr was added.

Copper alloy materials of compositions of Examples 83 to 88 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ ' phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure.

Compositions of Examples 83 to 88 are shown in the following Table 11.

[Table 11]

Alloy No. Addition element (mass%)

5 **[0045]** Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

As seen from Table 12, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Results of electrical conductivity and Vickers hardness)

15 **[0046]**

10

30

35

40

[Table 12] Heat treatment condition Alloy No. Electrical conductivity **Hardness**

20

(Copper alloy Nos. 89 to 94)

[0047] Then, as an addition element, Cr was added.

25 Copper alloy materials of compositions of Examples 89 to 94 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure.

Compositions of Examples 89 to 94 are shown in the following Table 13.

[Table 13] Alloy No. Addition element (mass%)

[0048] Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%) -aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

As seen from Table 14, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Results of electrical conductivity and Vickers hardness)

45 **[0049]**

[Table 14] Heat treatment condition Alloy Mo. Electrical conductivity Hardness

50

(Copper alloy Nos. 95 to 100)

[0050] Then, as an addition element, Fe was added.

55 Copper alloy materials of compositions of Examples 95 to 100 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as cast). Thereafter, a γ ' phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure. Compositions of Examples 95 to 100 are shown in the following Table 15.

[Table 15] Alloy No. Addition element (mass%)

5 **[0051]** Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction ratio 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

10 As seen from Table 16, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Result of electrical conductivity and Vickers hardness)

15 **[0052]**

> [Table 16] Heat treatment condition Alloy No. Electrical conductivity **Hardness**

(Copper alloy Nos. 101 to 106)

25 **[0053]** Then, as an addition element, P was added.

> Copper alloy materials of compositions of Examples 101 to 106 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure.

Compositions of Examples 101 to 106 are shown in the following Table 17.

30

20

[Table 17] Alloy No. Addition element (mass%)

35 **[0054]** Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

40 As seen from Table 18, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Results of electrical conductivity and Vickers hardness)

45 **[0055]**

50

[Table 18] Heat treatment condition Alloy No. Electrical conductivity **Hardness**

(Copper alloy Nos.107 to 112)

55 **[0056]** Then, as an addition element, Zn was added.

Copper alloy materials of compositions of Examples 107 to 112 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure.

Compositions of Examples 107 to 112 are shown in the following Table 19.

[Table 19] Alloy No. Addition element (mass%)

[0057] Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

- *10* Electrical conductivity and a Vickers hardness at each composition thereupon are shown. As seen from Table 20, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.
- *15* (Results of electrical conductivity and Vickers hardness)

[0058]

5

20

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25 (Copper alloy Nos. 113 to 118)

[0059] Then, as an addition element, Mg was added.

Copper alloy materials of compositions of Examples 113 to 118 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ' phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure.

Compositions of Examples 113 to 118 are shown in the following Table 21.

[Table 21] Alloy No.

35 Addition element (mass%)

> **[0060]** Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

40 Electrical conductivity and a Vickers hardness at each composition thereupon are shown. As seen from Table 22, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5,

12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

45 (Results of electrical conductivity and Vickers hardness)

[0061]

50 [Table 22] Heat treatment condition Alloy No. Electrical conductivity **Hardness**

55 (Copper alloy Nos. 119 to 122)

> **[0062]** Then, as an addition element, B was added. Copper alloy materials of compositions of Examples 119 to 122 were integrally placed into a high frequency induction

melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ' phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure. Compositions of Examples 119 to 122 are shown in the following Table 23.

[Table 23] Alloy No. Addition element (mass%)

10 **[0063]** Heat treatment condition is representative production condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown. As seen from Table 24, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5,

15 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Results of electrical conductivity and Vickers hardness)

[0064]

20

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[Table 24] Heat treatment condition Alloy No. Electrical conductivity

25 **Hardness**

(Copper alloy Nos. 123 to 128)

- **[0065]** Then, as an addition element, Co was added.
- *30* Copper alloy materials of compositions of Examples 123 to 128 were integrally placed into a high frequency induction melting furnace, fused, melted and mixed. This was formulated into a cast ingot (as- cast). Thereafter, a γ phase of the $L1₂$ structure was precipitated in a parent phase of Cu of the FCC structure. Compositions of Examples 123 to 128 are shown in the following Table 25.
- *35*
- [Table 25]

Alloy No. Addition element (mass%)

40 **[0066]** Heat treatment condition is representative productive condition, and is hot rolling (900°C, rolling reduction 90%)-solutionizing (900°C, 10 minutes)-cold rolling (20°C, rolling reduction 30%)-aging precipitation treatment (500°C, 18 hours).

Electrical conductivity and a Vickers hardness at each composition thereupon are shown.

As seen from Table 26, under production condition of the production process of the present invention, under all heat treatment working conditions essentially including aging treatment other than heat treatment working conditions 1, 5, 12 and 13, electrical conductivity was 8.5 IACS% or more, and a Vickers hardness was 220 Hv or more.

(Results of electrical conductivity and Vickers hardness)

[0067]

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[Table 26] Heat treatment Alloy No. Electrical conductivity **Hardness**

[0068] Therefore, the copper alloy of the present invention is a copper alloy having a predetermined composition, which is obtained by a predetermined production process, and since the copper alloy can precipitate a sufficient amount

of a fine γ' phase while coarsening of a γ' phase of the LI₂ structure which is precipitated in a copper alloy is suppressed, it was seen that it can easily control electric property such as electrical conductivity and the like, and mechanical property such as cold workability, a Vickers hardness and the like.

(continued)

[table 2-1]

Alloy No	Electrical conductivity	Workability	Hardness
1	20.8		170
2	17.5	∩	240
3	22.5	∩	225
4	25.3	∩	178
5	14.8	∩	290
6	17.9	∩	285
7	20.7	∩	255
8	13.7	\times	300
9	13.6	\times	307
10	14.4		312

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(continued)

(continued)

[table 3]

25	Heat treatment working condition		
	$\mathbf{1}$	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)	
	2	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-aging precipitation treatment (500°C, 6 hours)	
30	3	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-aging precipitation treatment (500°C, 12 hours)	
	$\overline{4}$	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-aging precipitation treatment (500°C, 18 hours)	
	5	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-cold rolling (rolling reduction 30%)	
35	6	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-cold rolling (rolling reduction 30%)-aging precipitation treatment $(500^{\circ}C, 6 \text{ hours})$	
	$\overline{7}$	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-cold rolling (rolling reduction 30%)-aging precipitation treatment (500°C, 12 hours)	
40	8	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-cold rolling (rousing reduction 30%)-aging precipitation treatment (500°C, 1.8 hours)	
	9	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-aging precipitation treatment (500°C, 6 hours)-cold rolling (rolling reduction 30%)	
45	10	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-aging precipitation treatment (500°C, 12 hours)-cold rolling (rolling reduction 30%)	
	11	Hot rolling (900°C)-solutionizing (900°C, 10 minutes)-aging precipitation treatment (500°C, 18 hours)-cold rolling (rolling reduction 30%)	
	12	As-cast	
	13	Hot rolling $(900^{\circ}C)$	

[table 5-1]

[table 9]

 $\overline{6}$

Electrical
conductivity

 $\overline{7}$

conductivity

Hardness Electrical

Electrical

Hardness

8

conductivity

Hardness

 $\overline{9}$

Hardness

Electrical
conductivity

 $10\,$

Hardness

Electrical
conductivity

 11

conductivity

Electrical

 13.7 289 11.0

Hardness

 $\overline{12}$

Hardness Electrical

 $\overline{265}$

 12.0 266

 10.0 252

Electrical
conductivity

 $\overline{13}$

sonductivity

 7.3 135

 $8,0$ $143\,$

 7.7 $138\,$

Hardness

 $151\,$ 6.9

[table 11] Alloy No. | Addition element (mass%)

83 Zr:0.2 84 Zr:0.5 85 Zr:1.0 86 Zr:0.2 87 (64) Zr:0.5 88 Zr:1.0

*83~85 Ni13Al2Si1 *86~88 Ni13Al1Si1

 $[table 1 0] \centering% \begin{tabular}{cc} \includegraphics[width=0.8\textwidth]{figs/fig_0a}% \label{tab:boxplot}% \end{tabular} \caption{The b-axis is a function of the system with a-axis. The b-axis is the b-axis. The b-axis is the b-axis. The b-axis is the b-axis. The b-axis is the b-axis is the $b$$

Electrical
conductivity

 $\overline{2}$

Hardness

 $\overline{293}$

Electrical conductivity

> 14.9 283 15.4 288 15.7 $\sqrt{ }$ $272\,$ $9, 4$ $231\,$ 15.2 $3\overline{02}$ $16.1\,$ 292 14.9 $\overline{279}$ 14.6 290 15.5 $\overline{275}$ 14.2 273 $|10.4|$ $\sqrt{295}$

 15.3 $\overline{234}$

Hardness

 $\frac{1}{213}$

163

 $\overline{\mathbf{3}}$

conductivity

Electrical

 12.7 291 $11,9$ $279\,$ $7,4$ $\sqrt{239}$ 12.1 $30\bar{5}$ 14.1 $\overline{286}$ 12.6 284 $11.6\,$ 275 12.9 270 12.7 $\overline{277}$ $9, 3$ 276 $7.\,\,2$ 171

 15.7 239 $15,\,9$ $228\,$ $10,\,5$ $\sqrt{206}$ $16,\sqrt{0}$ $\overline{254}$ 16.3 $\overline{237}$ 18.3 $\frac{1}{234}$ 14.1 $\overline{247}$ 15.1 $\overline{241}$ $15, 5$ 234 12.0 $\overline{287}$ 8.4 148

Hardness

 $\overline{4}$

conductivity

Hardness

Electrical

 $\bar{\rm 5}$

Electrical

conductivity

 $7.6\,$ $\sqrt{282}$

Hardness

 $\sqrt{203}$ $\overline{14.9}$ $309\,$ $15.\,2$ $\overline{313}$ 13.4 $\frac{1}{288}$ 10.1 308 11.2 $\overline{300}$

treatment неат

> Alloy $No.$

> > $7\,7$ 10.1

 $\bar{7}8$ 8.1 136 13.0 264 10.4 270 15.4

79 7.9 226 11.6

 80^{\degree} 10.6

 $\bar{8}1$ 10.1 168 15.8 242 15.8 229 $16.\,\,4$ $\overline{233}$ $10.\,2$ $205\,$ 16.7 $265\,$ 16.7 $\overline{247}$ 16.6 $\overline{244}$ $\frac{14.6}{ }$ $\overline{244}$ 14.7 $\overline{242}$ $16.0\,$ 243

 $\overline{\text{82}}$ 10.1 183 14.4 255 15.7 $249\,$ $15,\,6$ $\sqrt{264}$ $8,\,9$ $204\,$ 14.1 $271\,$ 16.4 $\overline{261}$ 14.9 $\overline{256}$ 12.8 $\frac{1}{249}$ 13.3 $\overline{247}$ 14.2 $\overline{241}$

10

	z \sim

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*107~109 Ni13Al2Si1 *110~112 Ni13Al1Si1

 $\bar{7}$

Electrical
conductivity

Hardness

Hardness Electrical $\overline{9}$

Electrical

Hardness

conductivity

Hardness

 $\overline{8}$

conductivity

 $10\,$

conductivity

Electrical

 234 14.7

Hardness

 $\overline{236}$ 12.8 238 10.1 258 6.7 $\frac{147}{147}$

 11

conductivity

Electrical

Hardness

 12°

Electrical
conductivity

 9.4

 $13\,$

sonductivity

Hardness

 $\bar{1}\bar{8}\bar{1}$ $7,\,7$

198

Electrical

Hardness

 260 $11. \; 1$

> 301 6.7

 $\bar{6}$

Electrical
conductivity

 $\bar{5}$

Electrical
conductivity

Hardness

 $[{\rm table}\,2\,\,0\,\,]\quad$

 \mathbf{I}

conductivity

Electrical

 $8,\,9$ 107

Hardness

189 $14.\,8$ $275\,$ 15.1 $275\,$ $15,\sqrt{2}$ $\bar{2}83$ $9,\,9$ $\overline{232}$ 14.1 $\overline{289}$ $\overline{16,1}$ $271\,$ 16.2 262 14.2 $\sqrt{285}$ 15.4 $\sqrt{282}$ 15.5 272

 $\sqrt{134}$ $11,\,6$

 $\bar{2}$

Electrical
conductivity

Hardness

 $\overline{273}$

 $\overline{3}$

conductivity

Electrical

 $12,\,8$ $\sqrt{296}$ $14.1\,$ $\bar{293}$ 7.8 $\overline{231}$ 13.4 $\overline{327}$ 14.8 $\overline{325}$ $\frac{1}{4.8}$ $\overline{322}$ 10.9 306 14.0 297 12.8 $\overline{301}$ $\overline{8.\,\overline{8}}$ $\frac{1}{253}$ 7.9 $\overline{166}$

 $\frac{1}{6}$

Hardness Electrical

 $\bar{2}\bar{3}\bar{3}$ $16,\,0$ $\bar{2}\bar{2}3$ $9, 2$ $187\,$ 14.4 $\overline{256}$ 15.5 $\overline{233}$ 16.1 $\overline{236}$ 13.7 $\overline{233}$ 14.7 $\sqrt{246}$ 14.6 250 10.5 $\overline{292}$ $7.\,\mathrm{8}$ 135

 $\overline{4}$

conductivity Hardness

 $\begin{array}{c}\n\text{Test} \\
\text{treatment}\n\end{array}$

Alloy No.

 $108\,$ $7,6$

109 $8,\,8$ 179 $13,\,5$ $\sqrt{295}$ 14.1 $\bf 287$ $14.\,2$ $287\,$ $9, 0$ $231\,$ 13.9 299 15.7 $\bar{2}83$ 16.1 285 12.6 $\overline{285}$ $14.\,\bar{2}$ $275\,$ 14.8 278

 $110\,$ $9,\,3$ 160 $14,\,6$ $\boldsymbol{233}$

 $111\,$ $9,\,8$ $142\,$ $14,\,3$ $\bar{2}\bar{4}\bar{2}$ 15.7 $\sqrt{236}$ 14.7 $221\,$ 10.0 $\bar{1}88$ 15.7 $250\,$ $15.\ 7$ $\overline{238}$ 15.8 $\overline{236}$ $14. \, 5$ $\overline{257}$ $15.\,2$ $238\,$ 12.7 $235\,$ $|11.3|$ $\overline{277}$ $7,\,6$ 138

 $112\,$ $9,\,8$ $157\,$ $14,\,6$ $234\,$ $13,\,8$ $229\,$ $14,\,6$ $230\,$ $9, 8$ 191 $15,\,0$ $\overline{254}$ $14.9\,$ $247\,$ $\boxed{16.2}$ $\overline{237}$ 15.1

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50

121 **B:0.01**

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[table 21] Alloy No. | Addition element (mass%)

113 Mg:0.2 114 (66) Mg:0.5

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ιιαυισ Ζυι				
Alloy No.	Addition element (mass%)			
123	Co:0.2			
124	Co:0.5			
125	Co:1.0			
126 (60)	Co:0.2			
127	Co:0.5			
128	Co:1.0			
*123~125 Ni13Al2Si1 *126~128 Ni13Al1Si1				

[table 25]

55

Claims

1. A high strength copper alloy of the FCC structure containing Ni: 3.0 to 29. 5 mass%, Al: 0.5 to 7.0 mass%, and Si:

0.1 to 1.5 mass%, with the remainder consisting of Cu and incidental impurities, wherein a γ phase of the L1₂ structure is precipitated with Ni₃Al comprising Si at an average particle diameter of 100 nm or less in a parent phase of the copper alloy.

- *5* **2.** The high strength copper alloy according to claim 1, wherein the high strength copper alloy contains Ni: 3.0 to 14.0 mass%, Al: 0.5 to 4.0 mass%, and Si: 0.1 to 1.5 mass%, and has electrical conductivity of 8.5 IACS% or more.
	- **3.** The high strength copper alloy according to claim 2, wherein cold workability is in a range of 10 to 95%.
- *10* **4.** The high strength copper alloy according to claim 2 or 3, wherein the high strength copper alloy is in a region A surrounded by four points of (Al: 2.0 mass%, Ni: 3.0 mass%), (Al: 4.0 mass%, Ni: 9.5 mass%), (Al: 1.5 mass%, Ni : 14.0 mass%), and (Al: 0.5 mass%, Ni: 5.0 mass%), as a range represented by Al equivalent (mass%) = (Al mass%+1.19Si mass%) and Ni mass% .
- *15* **5.** The high strength copper alloy according to claim 1, wherein the high strength copper alloy contains Ni: 9.5 to 29.5 mass%, Al: 1.5 to 7.0 mass%, and Si: 0.1 to 1.5 mass%, and has a Vickers hardness of 220 Hv or more.
	- **6.** The high strength copper alloy according to claim 5, wherein the high strength copper alloy is in a region B surrounded by four points of (Al: 4.0 mass%, Ni: 9.5 mass%), (Al: 7.0 mass%, Ni,: 16.0 mass%), (Al: 2.5 mass, Ni: 29.5 mass%), and (Al: 1.5 mass%, Ni: 14.0 mass%), as a range represented by Al equivalent (mass%) = (Al mass%+1.19Si mass%) and Ni mass%.
	- **7.** The high strength copper alloy according to any one of claims 1 to 6, wherein the high strength copper alloy further contains a total amount of 0.01 to 5.0 mass% of one or two or more elements selected from the group consisting of Co, Ti, Sn, Cr, Fe, Zr, Mg and Zn, as an addition element.
	- **8.** The high strength copper alloy according to any one of claims 1 to 7, wherein the high strength copper alloy further contains a total amount of 0.001 to 0.5 mass% of one or two or more elements selected from the group consisting of C, P and B, as an addition element.
	- **9.** A process for producing the high strength copper alloy as defined in any one of claims 1 to 8, comprising integrating, melting, mixing, hot-working and cold-working raw materials, then, heat-treating the worked product in a range of 700 to 1020°C and 0.1 to 10 hours and, thereafter, aging-treating this in a range of 400 to 650°C, and 0.1 to 48 hours.
- *35* **10.** The process for producing a high strength copper alloy according to claim 9, wherein before or after the aging treatment, cold working at a working ratio of 10 to 95% is performed.
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REFERENCES CITED IN THE DESCRIPTION

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