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(54) CU-CO-SI-ZR ALLOY MATERIAL AND METHOD FOR PRODUCING SAME

(57) The present invention relates to a Cu-Co-Si-Zr alloy material which contains 1.0-2.5 wt% of Co, 0.2-0.7 wt% of Si and 0.001-0.5 wt% of Zr with the elemental ratio Co/Si being 3.5-5.0. The Cu-Co-Si-Zr alloy material contains second phase particles having a diameter of 0.20 μm or more but less than 1.00 μm at a density of 3,000-500,000 particles/mm^2, and has a crystal grain size of 10 μm or less, an electrical conductivity of 60% IACS or more and good bending workability. The alloy material can be produced by setting the temperature of heating that is carried out after casting and before a solution heat treatment to a temperature that is higher than the later-described solution heat treatment temperature by 45 °C or more, by setting the cooling rate from the start temperature of hot rolling to 600 °C to 100 °C/min or less, and by selecting the solution heat treatment temperature from (50 X Co wt% + 775) °C to (50 X Co wt% + 825) °C (inclusive). The aging treatment after the solution heat treatment is preferably carried out at 450-650 ° C for 1-20 hours.

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Description

Technical Field

[0001] The present invention relates to materials for electronic and electrical equipments having excellent bending workability and being able to show high electrical conductivity, in particular, Cu-Co-Si-Zr copper alloy materials suitable for materials for electronic and electrical equipments such as movable connectors.

Background Art

[0002] Materials for electronic and electrical equipments require properties such as electrical conductivity, strength, and bending workability, and a demand for materials that allow high current is increasing in recent years for electric and electronic parts, particularly for movable connectors. In order to avoid movable connectors such as floating type connectors becoming larger, a material having good bendability as well as securing high electrical conductivity and strength, even at a thickness of 0.2 mm or more, is necessary.
Conventionally, Cu-Ni-Si, Cu-Co-Si, Cu-Co-Si-Zr, or Cu-Ni-Co-Si copper alloys are known as precipitation strengthened copper alloys having properties that allow for achieving high strength without deteriorating electrical conductivity. In order to manufacture these copper alloys, supplemented element(s) are solutionized by solution treatment, followed by cold rolling and aging treatment to precipitate or crystallize Ni_2Si and Co_2Si etc. as second phase particles in the matrix. However, since the amount of solubility of Ni_2Si is relatively large, it is difficult to achieve an electrical conductivity of 60% IACS or more with a Cu-Ni-Si copper alloy. For this reason, Cu-Co-Si, Cu-Co-Si-Zr or Cu-Ni-Co-Si alloys containing Co_2Si with low amount of solubility as the main precipitate and showing high electrical conductivity are being researched. The target strength cannot be achieved with these copper alloys unless they are sufficiently solutionized first and then precipitated to form fine precipitates. However, because solution treatment at a high temperature will cause coarsening of crystal grains resulting in problems such as deteriorated bending workability, various countermeasures have been investigated.

[0003] In Japanese Published Unexamined Patent Application Nos. 2009-242814 (Patent Document 1) and 2008-266787 (Patent Document 2), in order to manufacture a precipitation strengthened copper alloy for materials for electric and electronic parts such as a lead frame, the effect of suppressing crystal grain growth by second phase particles is utilized to control grain size and to improve bending workability. In the above documents, second phase particles precipitate during the cooling process in hot working or the temperature elevation process in solution heat treatment, as well as during the aging treatment after grinding ([0025] in Patent Document 1 etc.) In addition, International Publication No. 2010/016429 (Patent Document 3) discloses Cu-Co-Si(-Zr) alloys with certain compositions in which two types of precipitant with different sizes and compositions exist, leading to the suppression of crystal grain growth and the increase in their strength.

[0004]

Patent Document 1
Japanese Published Unexamined Patent Application No. 2009-242814A
Patent Document 2
Japanese Published Unexamined Patent Application No. 2008-266787A
Patent Document 3
WO2010/016429

Disclosure of the Invention

Problems to be Solved by the Invention

[0005] In general, specific target values for preventing the above movable connectors from becoming larger are an electrical conductivity of 60% IACS or more, and a 0.2% yield strength YS of 600 MPa or more, or a tensile strength TS of 630 MPa or more, as well as the threshold of ratio between the bending radius R and the thickness of material t (MBR/t) without generation of cracks, which is considered an indicator of bending workability, is 0.5 or less (0.3 mm thickness of sheet, Bad Way). This bending workability varies depending on the grain size and the size and number etc. of second phase particles, and the grain size to obtain an MBR/t of 0.5 or less at 0.3 mm plate thickness is thought to be generally 10 μm or less for Cu-Co-Si or Cu-Ni-Co-Si alloys. Crystal grains grow by solution treatment, and thus the grain size is determined by the temperature and time of solution treatment, supplemented element(s), and the size or number of second phase particles.

[0006] In Patent Documents 1 and 2, however, Co is not essential and a wide range of second phase particles is targeted. In the method of controlling grain size by second phase particles precipitates described in Patent Document 1, grain size can be controlled but electrical conductivity becomes poor, and high current availability cannot be achieved. Patent Document 2 focuses on second phase particles with diameters of from 50 to 1000 nm as possessing the effect of suppressing the growth of recrystallized grains in solution treatment, but Co second phase particles of this size may sometimes be solutionized and disappear during solution treatment. For this reason, since the temperature and time of solution treatment need to be adjusted so that the precipitates are not solved, only Cu-Co-Si-Zr alloys which are poor in either electrical conductivity or bendability were obtained. In addition, the second phase particles precipitate in this size range may possibly precipitate after solution treatment, and thus it does not show direct controlling effect on grain size. Although the density or diameter and volume density of second phase particles on the crystal grain boundary are evaluated by transmission electron microscope (TEM) observation in the above document, when the second phase was precipitated until grain size could be controlled to 10 μm or less, there was a possibility that accurate values could not be determined due to overlapping of particles and the like.

In addition, although Patent Document 3 focuses on Co second phase particles for the purpose of suppressing crystal grain growth, their grain sizes are 0.005 to 0.05μm and 0.05 to 0.5μm in their diameters. The Cu-Co-Si-Zr alloys in this document are inferior to in their bending workability.

As such, because the purpose of conventional precipitation strengthened copper alloys was utilization of thin sheet for electronic parts such as a lead frame, excellent bending workability at a sheet thickness of approximately 0.3 mm has never been developed.

Means for Solving the Problems

[0007] The present inventors have performed intensive and extensive research in order to solve the above problems, and attained the following inventions.

(1) A Cu-Co-Si-Zr alloy material with good bending workability wherein said material comprises:1.0 to 2.5 wt% of Co; 0.2 to 0.7 wt% of Si; and 0.001 to 0.5 wt% of Zr, and wherein a Co/Si elemental ratio is 3.5 to 5.0 and wherein said material contains 3,000 to 500,000 second phase particles per mm^2 having diameters of from 0.20 μm or more to less than 1.00 μm, and has an electrical conductivity EC of 60% IACS or more, and a grain size of 10 μm or less

(2) The copper alloy material of (1) containing 10 to 2,000 second phase particles per mm^2 having diameters of from 1.00 μm or more to 10.00μm or less.

(3) The copper alloy material of (1) or (2), wherein the 0.2% yield strength YS is 600 MPa or more.

(4) A method of manufacturing the copper alloy material of (1) or (2), wherein the temperature of hot rolling performed after casting and before solution treatment is a temperature that is 45°C or more higher than the solution treatment temperature selected below, the cooling rate from the temperature at the start of hot rolling to 600°C is 100°C/min or lower, and the solution treatment temperature is selected from the range of from (50 x Co wt% + 775)°C or more to (50 x Co wt% + 825)°C or less.

(5) The method of manufacturing the copper alloy material of (4), wherein the aging treatment after solution treatment is at 450 to 650°C for 1 to 20 hours.

[0008] In the present invention, the solution treatment temperature is adjusted, the hot heating temperature before solution treatment is also adjusted to be suitable for the solution treatment temperature, and the cooling rate after hot heating is also adjusted to allow precipitation of a particular amount of second phase particles having a particular grain size in order to prevent coarsening of crystal grains in the manufacturing of a Cu-Co-Si-Zr alloy material having a particular composition. Grain size of 10 μm or less can be obtained by adjusting the above second phase particles, and therefore bending workability, electrical conductivity that allows high current as well as practicable strength, suitable for movable connectors can be achieved.

Brief Description of the Drawings

[0009] Figure 1 is a reference drawing describing a diameter of a second phase particle.

Best Modes for Carrying Out the Invention

(Cu-Co-Si-Zr Alloy Material)

[0010] The alloy material of the present invention contains 1.0 to 2.5 wt% (hereinafter shown as % unless otherwise indicated), preferably 1.5 to 2.2% of Co, and 0.2 to 0.7%, preferably 0.3 to 0.55% of Si. The remainder other than Zr preferably consists of Cu and unavoidable impurities, but various elements employed by those skilled in the art as components ordinarily added to copper alloys, e.g., Cr, Mg, Mn, Ni, Sn, Zn, P, and Ag etc. within the range that allows achievement of the effect targeted by the constitution of the present invention may be further included.

If second phase particles are Co_2Si, the stoichiometric ratio of Co/Si contained is theoretically 4.2, but is 3.5 to 5.0, preferably 3.8 to 4.6 in the present invention. If the ratio is within these ranges, second phase particles Co_2Si and Co-Si-Zr compound suitable for precipitation strengthening and adjustment of grain size is formed. If Co and/or Si are too low, precipitation strengthening effect will be reduced, and if it is too high, it will not be solutionized and electrical conductivity will also be poor. When second phase particles Co_2Si precipitate, precipitation strengthening effect appears, and the purity of the matrix will increase after precipitation, thus improving electrical conductivity. Further, if a particular amount of second phase particles having a particular size is present, the growth of crystal grains is prevented and the grain size can be made to be 10 μm or less.

[0011] An alloy material according to the present invention may contain 0.001 to 0.5 wt% of Zr, preferably 0.01 to 0.4 wt% of Zr, which improves strength and conductivity. These effects are beyond predictions in view of Cu-Co-Si alloy. If the amount of Zr is less than 0.001 wt%, it cannot achieve a desired improvement of strength and conductivity. If the amount of Zr is more than 0.5 wt%, it generates coarse silicides, which deteriorate strength and bending workability.

The grain size of the alloy material of the present invention is 10 μm or less. Ten micrometers or less allows achievement of good bending workability.

The copper alloy material of the present invention may have various shapes, such as for example plates, strips, wires, rods, and foils, and without particular limitation, may be plates or strips for movable connectors.

(Second Phase Particles)

[0012] The second phase particles of the present invention refer to particles that generate when other elements are contained in copper to form a phase different from the copper mother phase (matrix). The number of second phase particles having diameters of 50 nm or more is obtained, after mirror finishing by mechanical polishing followed by electrolytic polishing or acid etching, by counting the number of particles having diameters in the corresponding range on a field of a scanning electron microscope photograph obtained by arbitrary five points selection in a cross-section of a copper alloy sheet parallel to rolling direction. The diameter as used herein refers to the average of L1 and L2 as shown in Figure 1 obtained by measuring the minor axis (L1) and the major axis (L2) of the particle.

Most of the second phase particles of the present invention are Co_2Si and Co-Si-Zr compound, but other intermetallic compounds such as Ni_2Si may also exist as long as the diameter is within the range. Elements that constitute second phase particles can be confirmed for example by using EDX (Energy-Dispersive X-Ray) accompanying FE-SEM (FEI Company Japan, Model XL30SFEG).

[0013] The copper alloy material of the present invention contains 3,000 to 500,000/mm^2, preferably 10,000 to 200,000/mm^2, and further preferably 13,000 to 100,000/mm^2 second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm. The particles may precipitate mainly after hot rolling and before solution treatment, but may also precipitate by solution treatment. The second phase particles that precipitated before solution treatment suppress the growth of grain size in solution treatment, but there is also risk of solid solution thereof. Accordingly, it is preferred to adjust the solution treatment conditions to reduce variation in number as much as possible.

In addition, the material preferably comprises 10 to 2,000/mm^2, further preferably 20 to 1,000/mm^2, and most preferably 30 to 500/mm^2 second phase particles having diameters of from 1.00 μm or more to 10.00 μm or less. The cooling rate after hot rolling (hot heating) may be slowed down for precipitation, and first aging treatment can be applied if necessary in order to adjust grain size for the second phase particles. The above preferred range for diameter of the second phase particles is also linked with the number of second phase particles of from 0.20 μm or more to less than 1.00 μm. High temperature solution treatment is possible under the conditions of the above range and the growth of grain size in solution treatment is suppressed, while the sufficiently solutionized Co, Si and Zr are finely precipitated by a later (second) aging treatment, resulting in high strength, high electrical conductivity, and good bending workability to be achieved. However, the number of second phase particles greater than 2,000/mm^2 is not preferred because bendability will be reduced.

The number of second phase particles having the above diameters of from 0.20 μm or more to less than 1.00 μm and 1.00 μm or more to 10.00 μm or less can be evaluated using a test strip obtained before final rolling or after final working, since the number does not vary considerably before and after solution treatment as well as after second aging treatment.

[0014] Precipitation of fine second phase particles is inhibited and precipitation strengthening effect cannot be obtained

if second phase particles having diameters greater than 10.00 μm exist. Thus, the number of contained particles having diameters greater than 10.00 μm is preferably 1/mm^2 or less, further preferably only 0.01/mm^2 or less.
Although the second phase particles of from 0.05 μm or more to less than 0.20 μm precipitate during hot rolling, the subsequent cooling, and first aging treatment, they are mostly solutionized in solution treatment, and are precipitated by the subsequent cooling and (the second) aging treatment. The second phase particles having diameters of less than 0.05 μm are solutionized in solution treatment, and a large amount thereof is precipitated by (the second) aging treatment. Accordingly, these second phase particles do not show the effect of adjusting grain size, but contribute to improvement in strength.

(Properties of Alloy Material)

[0015] The electrical conductivity EC of the alloy material of the present invention is 60% IACS or more, preferably 65% IACS or more. Parts that allow high current can be manufactured when EC is within this range.
Good bending workability as used in the present invention refers to a minimum bending radius MBR/t of 0.5 or less (Bad Way) at 0.3 mm sheet thickness. If MBR/t is 0.5 or less for at 0.3 mm sheet thickness, properties demanded for manufacture and use of electronic parts, in particular movable connectors are fulfilled. Further, better bending workability is obtained when the alloy material of the present invention is made to be thinner than 0.3 mm thickness.
The 0.2% yield strength YS of the alloy material of the present invention is preferably 600 MPa or more, further preferably 650 MPa or more, and the tensile strength TS is preferably 630 MPa or more, further preferably 660 MPa or more. Values within the above range are sufficient especially for electronic parts material such as a plate material for movable connectors.

(Manufacturing Method)

[0016] The manufacturing process steps of the alloy material of the present invention are the same or similar to those for an ordinary precipitation strengthened copper alloy, i.e., melt casting -> (homogenizing heat treatment) → hot rolling → cooling → (first aging treatment) → grinding → cold rolling → solution treatment → cooling → (cold rolling) → second aging treatment → final cold rolling → (stress relief annealing). Steps in parentheses can be omitted, and final cold rolling may be performed before aging heat treatment.
Although homogenizing heat treatment and hot rolling are performed after casting in the present invention, homogenizing heat treatment may be the heating in hot rolling (in the present specification, heating performed during homogenizing heat treatment and hot rolling is collectively referred to as "hot heating").
The hot heating temperature may be any temperature at which the supplemented elements mostly solutionize, specifically, it may be a temperature that is 40°C or more, preferably 45°C or more higher than the solution treatment temperature selected below. The upper limit of the hot rolling (hot heating) temperature is individually regulated depending on the metal composition and facility, and is ordinarily 1000°C or less. The heating time will depend on plate thickness, and is preferably 30 to 500 minutes, further preferably 60 to 240 minutes. It is preferred that most of the supplemented elements such as Co or Si solve during hot heating.
The cooling rate after hot rolling is 100°C/min or less, preferably 5 to 50°C/min. With this cooling rate, second phase particles ultimately having diameters of from 0.20 μm or more to less than 10.00 μm will precipitate in the target range. However, only fine second phase particles were conventionally precipitated, since quenching by a water-cooling shower etc. with the aim of suppressing the coarsening of second phase particles.
Materials are ground after cooling, and an arbitrary first aging treatment is preferably further performed to allow adjusting of the target size and number of second phase particles. The conditions for this first aging treatment are preferably at 600 to 800°C for 30s to 30h.
[0017] The temperature of solution treatment performed after the above arbitrary first aging treatment is selected from the range of from (50 x Co wt% + 775)°C or more to (50 x Co wt% + 825)°C or less. The preferred treatment time is 30 to 500s, further preferably 60 to 200s. Within this range, the adjusted second phase particles remain resided to prevent the enlargement of grain size, while finely precipitated Co, Si and Zr are sufficiently solutionized and precipitated as fine second phase particles by the later second aging treatment.
The preferred cooling rate after solution treatment is 10°C/s or higher. A cooling rate slower than the above will cause precipitation of second phase particles during cooling, and the amount of solubility will decrease. There is no particularly preferred upper limit for the cooling rate, but e.g. approximately 100°C/s is possible for a generally employed facility.
If the amounts of Co, Si and Zr contained are lower than that in the present invention, or not slowly cooled after hot rolling and second aging treatment heating is not performed, there are only a little second phase particles that are precipitated before solution treatment. When an alloy having only a little precipitated second phase particles is subjected to solution treatment, since an elevated temperature higher than 850°C for a solution treatment time longer than 1 minute will cause coarsening of grain size, heat treatment can be performed only for a short duration of approximately 30

seconds and the actual solutionizable amount is low, and therefore sufficient precipitation strengthening effect cannot be obtained.

[0018] The temperature of second aging treatment after solution treatment is preferably at 450°C to 650°C for 1 to 20 hours. Within this range, the diameters of the second phase particles remaining after solution treatment can be maintained within the range of the present invention, as well as the solutionized supplemented elements will precipitate as fine second phase particles and contribute to strength enhancement.

The final rolling reduction ratio is preferably 5 to 40%, further preferably 10 to 20%. A ratio of less than 5% will result in insufficient increase in strength by work hardening, while greater than 40% will result in decrease in bending workability. Moreover, if final cold rolling is performed before second age treatment, the second age treatment may be performed at 450°C to 600°C for 1 to 20 hours.

The stress release annealing temperature is preferably 250 to 600°C, and the annealing time preferably 10s to 1 hour. Within this range, there is no change in the size and number of second phase particles as well as in grain size.

Examples

(Preparation)

[0019] To a molten metal made of electrolytic copper, Si, Co and Zr as raw materials, supplementing elements were added varying the amount and type, and the molten metal was casted into an ingot having a thickness of 30 mm. The ingot was heated at the temperature shown in the tables for 3 hours, hot rolled into plates having a thickness of 10 mm. Next, oxyded scales on the surface were ground and removed, subjected to aging treatment for 15 hours and then to solution treatment using appropriately varied temperature and time, cooled at the cooling temperature shown in the tables, subjected to 1 to 15 hours of aging treatment at the temperature shown in the tables, and finished to a final thickness of 0.3 mm by final cold rolling. Stress release annealing time is 1 minute.

(Evaluation)

[0020] The concentrations of supplemented elements in the copper alloy matrix were analyzed by ICP-mass spectrometry using samples after the grinding step.

For the diameter and number of second phase particles, a cross-section parallel to the rolling direction of the sample before final cold rolling was mirror finished by means of mechanical polishing, followed by electrolytic polishing or acid etching, and determined from five microscope photographs for each magnification using a scanning electron microscope. Observation magnification is (a) 5 x 10^{4}-power for from 0.05 μm or more to less than 0.20 μm, (b) 1 x 10^{4}-power for from 0.20 μm or more to less than 1.00 μm, and (c) 1 x 10^{3}-power for from 1.00 μm or more to 10.00 μm or less (each of them is represented as "50-200nm","200-1000nm" and "1000-10000nm" respectively in Tables).

For the grain size, average grain size was measured according to JIS H0501 by section method.

For the electrical conductivity EC, specific resistance was measured by a four-terminal method in a thermostatic bath maintained at 20°C (±0.5°C) (distance between terminals: 50 mm).

[0021] For the bending workability MBR/t, a 90° W bend test (JIS H3130, Bad Way) of short test strips (width 10 mm x length 30 mm x thickness 0.3 mm) taken in T.D. (Transverse Direction) so that the bending axis is perpendicular to the rolling direction was performed, and the minimum bending radius without generation of cracks (mm) was referred to as the MBR (Minimum Bend Radius) and the ratio thereof to the plate thickness t (mm), MBR/t was evaluated.

For the 0.2% yield strength YS and tensile strength TS, sample JIS Z2201-13B size out in the direction parallel to the rolling was measured for three times according to JIS Z 2241, and the average was calculated.

[0022] Tables 1A, 1B, and 1C show the result from changes in an additive amount of Zr with the following factors set within the scope of the present invention: a concentration of Co and Si; Co/Si elemental ratio; the number of the second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm; an electrical conductivity EC; and grain size.

Tables 1A and 1B show that comparing to Comparative Example 3 (without Zr), Examples 1 and 2 (with 0.01% of Zr and 0.3% of Zr respectively) showed the increased strength and electrical conductivity or the increased electrical conductivity. In addition, they showed that an electrical conductivity increased in proportion to an additive amount of Zr. However, Comparative Example 4 (with 1.0 % of Zr) showed the decreased strength and bending workability (Table 1C is described hereinafter).

[0023] Tables 2A, 2B and 2C show the result from changes in the compositions and the manufacturing conditions with an amount of Zr set to 0.1 % based on the above results (Table 2C is described hereinafter).

Since Examples 1 to 11 fulfilled the requirements of the present invention, they had excellent properties of an electrical conductivity, strength and bending workability in a thick sheet, which were suitable material for movable connectors allowing high current.

The conditions of Supplementary Example 22 were similar to that of Example 6 but differed in its process as follows: after solution treatment, the material was cooled at the cooling rate according to the table; before aging treatment, the material was finished to a final thickness of 0.3 mm by final cold rolling; the material was subjected to aging treatment at the temperature according to the table for 3 hours; the material was similarly subjected to stress relief annealing. Although the material of Supplementary Example 22 was slightly inferior to Example 6 in its strength, its bending workability was improved.

[0024] As for Comparative Example 12, due to high temperature for solution treatment, second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm disappeared during the solution heat treatment, the effect of suppressing crystal grain growth could not be achieved. As a result, the material had a large grain size to be inferior in bending workability.

The material of Comparative Example 13 had low Co/Si ratio. The material of Comparative Example 14 had high Co/Si ratio. Both of them could not benefit from fine second phase particles having the precipitation strengthened effect and thus had low strength. In addition, an electrical conductivity for both of them was inferior due to high solid solute concentration for Co or Si.

As for Comparative Example 15, cooling rate after hot working was slow. Thus, the number of second phase particles having diameters of from 1.00 μm or more to less than 10.00 μm was large. As a result, bending workability was bad.

As for Comparative Example 16, cooling rate after hot working was fast. Thus, the number of second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm was small. Consequently, the material of Comparative Example 16 could not benefit from second phase particles having the effect of suppressing crystal grain growth and thus had bad bending workability. As for Comparative Example 17, cooling rate after hot working was fast. Thus, the number of second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm was small. To compensate for this, the first aging treatment was performed at high temperature resulting in precipitation of second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm. However, this heat treatment made the grain size large. Consequently, bending workability was bad.

As for Comparative Example 18, the temperatures for hot heating and solution treatment were higher than those of Example 8. The effect of suppressing grain growth could not be achieved. Thus, the grain size was large and bending workability was bad. An electrical conductivity was also inferior to Example 8.

As for Comparative Example 19, the temperature for solution treatment was lower than that of Example 11. Thus, an amount of solid solute for additive elements during solution treatment was small. As a result, the strength was low.

As for Comparative Example 20, a concentration of Co was high. The temperature for solution treatment was relatively high and the treatment time was long. Thus, the number of second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm was large and workability was bad.

As for Comparative Example 21, a concentration of Co was high. The temperature for solution treatment was as high as that of hot working. The effect of suppressing grain size could not be achieved. As a result, the number of second phase particles having diameters of from 0.20 μm or more to less than 1.00 μm was small and the number of second phase particles having diameters of from 1.00 μm or more to 10.00 μm or less was large. Thus, bending workability was bad.

[0025] Although the present invention is not limited by theory, the relationship between the steps of manufacture and the disappearance and precipitation of second phase particles is thought to be as follows. The supplemented element (s) solutionize into copper during hot heating. Second phase particles having a diameter of 0.05 μm or more will precipitate during hot rolling and in the cooling stage after the hot rolling where the cooling rate is adjusted. In first aging treatment after the hot rolling, second phase particles having a diameter of 0.05 μm or more do not precipitate, while second phase particles having a diameter of less than 0.05 μm precipitate in large amounts. The precipitated second phase particles having a diameter of less than 0.20 μm will disappear by solutionization in solution treatment where the temperature is adjusted. In cooling stage after the solution treatment where cooling rate is adjusted, the second phase particles having a diameter of from 0.05 μm or more to less than 0.2 μm will mainly precipitate in small amounts. In second aging treatment after the solution treatment, second phase particles having a diameter of less than 0.05 μm will precipitate in large amounts.

Tables 1C and 2C show the measurement results about how the second phase particles changed during the manufacturing process which had the following ranges of diameter:(a) from 50 nm or more to less than 200 nm; (b) from 200 nm or more to less than 1000 nm; and (c) from 1000 nm or more to 10000 nm or less. Incidentally, any second phase particles having diameter of more than 10000 nm (10.00 μm) was not observed in all of the measurements. Since the number of second phase particles becomes smaller logarithmically as diameter becomes large, the indicated digits were changed.

Particles (a) solutionized under the solution treatment conditions of the present invention and the number was reduced to approximately one fifth to one tenth, and the number after second aging treatment did not vary relatively. There was almost no increase or decrease in the number of particles (b) under the solution treatment conditions and the second aging treatment conditions of the present invention. There was no change in the number of particles (c) before solution treatment and before final cold rolling under hot heating and cooling conditions of the present invention.

Incidentally, high temperature of first aging treatment increased the number for (b) (see Comparative Example 17). High temperature of or long time of solution treatment tended to decrease the number of (b) to be below the lower limit according to the present invention (see Comparative Examples 18 and 21).

Table 1A

	Component				hot rolling	Cooling	Aging	50 x Co wt % + 775	Solution treatment		Cooling	Aging	Final rolling	stress relief annealing
	Co	**Si**	**Zr**	**Co/Si**	Temp.	Rate	Temp.		Temp.	Time	Rate	Temp.	Reduction ratio	Temp.
	wt%	**wt%**	**wt%**		°C /**3h**	°C /**min**	°C /**15h**	Lower limit °C	°C	**S**	°C /**se c**	°C /**1-15 h**	%	°C /**1min**
EXP.1	1.7	0.4	0.01	4.3	980	35	600	860	900	100	20	540	10	500
EXP.2	1.7	0.4	0.3	4.3	980	35	600	860	900	100	20	540	10	500
COMP.3	1.7	0.4	0	4.3	980	35	600	860	900	100	20	540	10	500
COMP.4	1.7	0.4	1.0	4.3	980	35	600	860	900	100	20	540	10	500

Table 1B

	Mechanical and Physical properties					Second phase particles after second aging treatment		
	YS	TS	EC	GS	R/t (B.W.)	50-200nm	200-1000nm	1000-10000nm
	MPa	MPa	%IACS	µm		x 1000000 /mm^2	/mm^2	/mm^2
EXP.1	660	680	67	7	0.1	0.5	80,000	120
EXP.2	650	670	69	6	0.0	0.3	70,000	400
COMP.3	650	670	66	8	0.2	0.5	18,000	80
COMP.4	590	610	70	5	1.0	0.1	4,000	2,500

Table 1C

	Before first aging treatment			After first aging treatment, before solution treatment			After solution treatment			After second aging treatment		
grain size nm	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000
/mm^2	x 1000000	x 1	x 1	x1000000	x 1	x 1	x1000000	x 1	x 1	x1000000	x 1	x 1
EXP.1	0	18,000	140	2	22,000	120	0.4	20,000	120	0.5	20,000	120
EXP.2	0	14,000	400	1.5	16,000	440	0.35	14,000	380	0.3	14,000	400
COMP. 3	0	20,000	80	2.5	22,000	100	0.5	18,000	80	0.5	18,000	80
COMP. 4	0	6,000	2,600	1	4,000	2,500	0.1	4,000	2,600	0.1	4,000	2,500

Table 2A

	Component				hot rolling	Cooling	Aging	50 x Co wt % + 775	Solution treat ment		Cooling	Aging	Final rolling	stress relief anneali ng
	Co	**Si**	**Zr**	**Co/Si**	Temp.	Rate	Temp.		Temp.	Time	Rate	Temp.	Reduction ratio	Temp.
	wt%	**wt%**	**wt%**		°C /**3h**	°C /**min**	°C	Lower limit °C	°C	**S**	°C /**se c**	°C	**%**	°C
EXP.5	1.5	0.40	0.1	3.8	900	10	600	850	860	100	10	550	10	500
EXP.6	1.7	0.40	0.1	4.3	980	35	600	860	875	100	20	540	10	500
EXP.7	1.7	0.40	0.1	4.3	980	35	-	860	875	100	20	540	10	500
EXP.8	1.9	0.45	0.1	4.2	950	30	600	870	900	100	20	530	10	500
EXP.9	2.1	0.50	0.1	4.2	975	35	600	880	925	100	20	520	10	500
EXP.10	2.3	0.46	0.1	5.0	990	40	600	890	940	100	20	510	10	500
EXP.11	2.5	0.70	0.1	3.6	1000	45	600	900	950	100	10	500	10	500
COMP. 12	1.5	0.36	0.1	4.2	980	35	600	850	930	100	20	550	10	500
COMP. 13	1.7	0.60	0.1	2.8	950	30	600	860	875	100	20	520	10	500
COMP. 14	1.7	0.30	0.1	5.7	950	30	600	860	875	100	20	520	10	500
COMP. 15	1.7	0.40	0.1	4.3	950	3	-	860	875	100	20	520	10	500
COMP. 16	1.7	0.40	0.1	4.3	950	200	650	860	875	100	20	540	10	500
COMP. 17	1.7	0.40	0.1	4.3	950	200	800	860	875	100	20	540	10	500
COMP. 18	1.9	0.45	0.1	4.2	1000	45	600	870	950	100	20	530	10	500

(continued)

	wt%	**wt%**	**wt%**		°C /**3h**	°C /**min**	°C	Lower limit °C	°C	**S**	°C /**se c**	°C	**%**	°C
COMP. 19	2.5	0.60	0.1	4.2	1000	45	600	900	800	100	20	510	10	500
COMP. 20	2.7	0.64	0.1	4.2	1000	45	600	910	950	1000	20	500	10	500
COMP. 21	2.7	0.64	0.1	4.2	1000	45	600	910	1000	100	20	500	10	500
SUP.22	1.7	0.40	0.1	4.3	980	35	600	860	875	100	20	500	10	500

Table 2B

	Mechanical and Physical properties					Second phase particles after second aging t reatment		
	YS	TS	EC	GS	R/t (B.W.)	50-200nm	200-1000n m	1000-10000n m
	MPa	MPa	%IAC S	µm		X1000000 /mm^2	/mm^2	/mm^2
EXP.5	610	640	69	5	0.0	0.5	20000	140
EXP.6	650	670	68	7	0.1	0.5	60000	180
EXP.7	650	680	67	7	0.2	1	80000	180
EXP.8	660	680	67	7	0.3	1.5	80000	200
EXP.9	680	710	65	9	0.4	2	140000	300
EXP.10	730	750	64	10	0.4	3	200000	260
EXP.11	760	780	62	10	0.4	3	300000	1800
COMP.12	630	660	67	25	1.5	2	2000	200
COMP.13	580	620	48	7	0.1	0.2	10000	160
COMP.14	570	620	58	7	0.1	0.2	8000	140
COMP.15	620	650	70	7	2.0	0.3	18000	2600
COMP.16	640	660	67	15	1.0	0.1	2000	100
COMP.17	630	660	68	20	1.0	1.5	68000	100
COMP.18	710	740	62	20	1.0	0.2	2000	100
COMP.19	590	620	70	3	0.5	10	400000	1800
COMP.20	760	790	63	8	1.0	3	600000	200
COMP.21	770	800	60	15	2.0	0.1	2000	2100
SUP.22	610	650	68	7	0.0	0.3	60000	180

Table 2C

	Before first aging treatment			After first aging treatment, before solution treatment			After solution treatment			After second aging treatment		
grain size nm	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000
/mm^2	X1000000	X1	X1	X1000000	X1	X1	X1000000	X1	X1	X1000000	X1	X1
EXP.5	0	14000	120	5	24000	140	0.5	20000	140	0.5	20000	140
EXP.6	0	70000	180	4	80000	180	0.45	60000	180	0.5	60000	180
EXP.7	0	80000	180	0	90000	180	0.1	80000	180	0.1	80000	180
EXP.8	0	70000	200	7	80000	240	1.4	80000	200	1.5	80000	200
EXP.9	0	160000	300	10	160000	320	1.5	140000	300	2	140000	300
EXP.10	0	110000	300	15	200000	300	2.5	180000	260	3	200000	260
EXP.11	0	400000	1800	15	400000	1800	3	300000	1600	3	300000	1800
COMP. 12	0	2000	100	5	2000	180	0.2	2000	200	0.2	2000	200
COMP. 13	0	16000	60	4	16000	160	0.2	10000	160	0.2	10000	160
COMP. 14	0	12000	40	4	12000	120	0.2	8000	140	0.2	8000	140
COMP. 15	0	200000	3000	0	200000	3000	0.3	180000	2600	0.3	180000	2600
COMP. 16	0.8	3000	80	10	4000	80	1	2000	100	1	2000	100
COMP. 17	0.8	3000	80	1	110000	60	0.5	70000	100	0.5	68000	100
COMP. 18	0	18000	100	10	18000	100	0.05	2000	100	0.2	2000	100
COMP. 19	0	400000	1800	15	400000	1800	11	400000	1800	10	400000	1800

(continued)

	Before first aging treatment			After first aging treatment, before solution treatment			After solution treatment			After second aging treatment		
grain size nm	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000	50-200	200-1000	1000-10000
/mm^2	X1000000	X1	X1	X1000000	X1	X1	X1000000	X1	X1	X1000000	X1	X1
COMP. 20	0	600000	240	12	600000	200	3	600000	180	3	600000	200
COMP. 21	0	2000	2400	1.5	4000	2200	0.05	2000	2100	0.1	2000	2100
SUP.22	0	70000	180	4	80000	180	0.45	60000	180	0.5	60000	180

Industrial Applicability

[0026] A copper alloy according to the present invention may achieve practicable strength as well as bending workability suitable for movable connector and electrical conductivity allowing high current.

Explanation of References

[0027]

L1: minor axis for particles
L2: major axis for particles

Claims

1. A Cu-Co-Si-Zr alloy material with good bending workability wherein said material comprises:1.0 to 2.5 wt% of Co; 0.2 to 0.7 wt% of Si; and 0.001 to 0.5 wt% of Zr, and wherein a Co/Si elemental ratio is 3.5 to 5.0 and wherein said material contains 3,000 to 500,000 second phase particles per mm^2 having diameters of from 0.20 μm or more to less than 1.00 μm, and has an electrical conductivity EC of 60% IACS or more, and a grain size of 10 μm or less

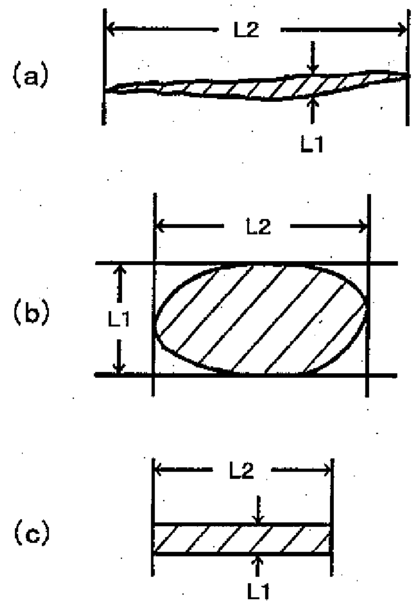
2. The copper alloy material of Claim 1 containing 10 to 2,000 second phase particles per mm^2 having diameters of from 1.00 μm or more to 10.00μm or less.

3. The copper alloy material of claim 1 or 2, wherein the 0.2% yield strength YS is 600 MPa or more.

4. A method of manufacturing the copper alloy material of claim 1 or 2, wherein the temperature of hot rolling (hot heating) performed after casting and before solution treatment is a temperature that is 45°C or more higher than the solution treatment temperature selected below, the cooling rate from the temperature at the start of hot rolling to 600°C is 100°C/min or lower, and the solution treatment temperature is selected from the range of from (50 x Co wt% + 775)°C or more to (50 x Co wt% + 825)°C or less.

5. The method of manufacturing the copper alloy material of claim 4, wherein the aging treatment after solution treatment is at 450 to 650°C for 1 to 20 hours.

Figure 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/050508

A. CLASSIFICATION OF SUBJECT MATTER
C22C9/06(2006.01)i, *C22F1/08*(2006.01)i, *H01B1/02*(2006.01)i, *H01B13/00*(2006.01)i, *C22F1/00*(2006.01)n

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C9/06, C22F1/08, H01B1/02, H01B13/00, 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	1996-2012
Kokai Jitsuyo Shinan Koho	1971-2012	Toroku Jitsuyo Shinan Koho	1994-2012

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	WO 2009/116649 A1 (The Furukawa Electric Co., Ltd.), 24 September 2009 (24.09.2009), claims; paragraphs [0009] to [0016] & US 2011/0005644 A1 & EP 2267172 A1 & CN 101978081 A	1-5
A	JP 2008-056977 A (Mitsubishi Electric Corp.), 13 March 2008 (13.03.2008), claims; paragraphs [0019] to [0023] & US 2008/0056930 A1 & DE 102007040822 A	1-5

☒ 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 02 April, 2012 (02.04.12)	Date of mailing of the international search report 10 April, 2012 (10.04.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

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PCT/JP2012/050508

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-088512 A (Nippon Mining & Metals Co., Ltd.), 17 April 2008 (17.04.2008), claims; paragraph [0011] & WO 2008/041696 A1 & KR 10-2009-0050101 A & CN 101522927 A	1-5

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