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(54) **CU-CO-SI COPPER ALLOY FOR USE IN ELECTRONICS, AND MANUFACTURING METHOD THEREFOR**

(57) The present invention provides Cu-Co-Si system alloys that have desirable mechanical and electrical characteristics as a copper alloy for electronic materials, and have uniform mechanical characteristics. The copper alloys for electronic materials contain 0.5 to 4.0 mass% Co, 0.1 to 1.2 mass% Si, and the balance being

Cu and unavoidable impurities. An average grain size is 15 to 30 μm and an average difference between maximum grain size and minimum grain size in every observation field of 0.5 mm^2 is not more than 10 μm .

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Description

FIELD OF THE INVENTION

5 **[0001]** The present invention relates to precipitation hardening copper alloys, in particular, to Cu-Co-Si system alloys suitable for use in a variety of electronic components.

BACKGROUND OF THE INVENTION

10 **[0002]** A copper alloy for electronic materials that are used in a connector, switch, relay, pin, terminal, lead frame, and various other electronic components is required to satisfy both high strength and high electrical conductivity (or thermal conductivity) as basic characteristics. In recent years, as high integration and reduction in size and thickness of an electronic component have been rapidly advancing, requirements for copper alloys used in these electronic components have been increasingly becoming severe.

15 **[0003]** Because of considerations related to high strength and high electrical conductivity, the amount in which precipitation-hardened copper alloys are used has been increasing, replacing conventional solid-solution strengthened copper alloys typified by phosphor bronze and brass as copper alloys for electronic components. With a precipitation-hardened copper alloy, the aging of a solution-treated supersaturated solid solution causes fine precipitates to be uniformly dispersed and the strength of the alloys to increase. At the same time, the amount of solved elements in the copper is reduced and electrical conductivity is improved. For this reason, it is possible to obtain materials having excellent strength, spring property, and other mechanical characteristics, as well as high electrical and thermal conductivity.

20 **[0004]** Among precipitation hardening copper alloys, Cu-Ni-Si system alloys commonly referred to as Corson alloys are typical copper alloys having relatively high electrical conductivity, strength, and bending workability, and are among the alloys that are currently being actively developed in the industry. In these copper alloys, fine particles of Ni-Si intermetallic compounds are precipitated in the copper matrix, thereby increasing strength and electrical conductivity.

25 **[0005]** Various experiments have been made with the aim of further improving the characteristics of Corson alloys by adding Co.

30 **[0006]** Patent document 1 discloses that Co is similar to Ni in forming a compound with Si and increasing mechanical strength, and when Cu-Co-Si system alloys are aged, they have better mechanical strength and electrical conductivity than Cu-Ni-Si system alloys, and where acceptable in cost, Cu-Co-Si system alloys may be also selected. The document also discloses that the optimum additive amount of Co is 0.05 to 2.0 wt%.

35 **[0007]** Patent document 2 discloses that cobalt content should be 0.5 to 2.5 wt% because the precipitation of the cobalt-containing silicide as second-phase is insufficient when the cobalt content is less than 0.5 wt%, and excessive second-phase particles precipitate, formability is reduced, and the copper alloy is endowed with undesirable ferromagnetic properties when the cobalt content exceeds 2.5 wt%. The document discloses that the cobalt content is preferably about 0.5 wt% to about 1.5 wt%, and the cobalt content is about 0.7 wt% to about 1.2 wt% in the most preferable embodiment.

40 **[0008]** Copper alloys disclosed in Patent document 3 have been developed with the aim of applications mainly for an end terminal of vehicle installation, communication instrument, and the like, or connector materials. The copper alloys are Cu-Co-Si system alloys in which cobalt concentration is 0.5 to 2.5 wt% and high electrical conductivity and moderate strength are achieved. The document discloses that the cobalt concentration is limited within the above described range because desirable strength cannot be provided when additive amount of cobalt is less than 0.5 wt%, and high strength can be provided, but electrical conductivity remarkably deteriorates and further hot processing characteristics deteriorates when cobalt concentration exceeds 2.5 wt%. The document discloses that the cobalt concentration is preferably 0.5 to 2.0 wt%.

45 **[0009]** Copper alloys disclosed in Patent document 4 have been developed with the aim of achieving high strength, high electrical conductivity and high bending workability and limit cobalt concentration to 0.1 to 3.0 wt%. The document discloses that the cobalt concentration is limited within the above described range because it is undesirable that the alloys do not have the above described effects when the cobalt concentration is less than the range, and the crystallized phase is generated at casting and it leads to breaks at casting when the cobalt concentration exceeds the range.

50 [Patent document 1] Japanese patent laid-open publication No. 11-222641

[Patent document 2] Japanese Domestic Republication No. 2005-532477

[Patent document 3] Japanese patent laid-open publication No. 2008-248333

[Patent document 4] Japanese patent laid-open publication No. 9-20943

SUMMARY OF THE INVENTION

PROBLEMS TO BE SOLVED BY THE INVENTION

[0010] Though it is known that the addition of Co contributes to an improvement of copper alloys properties as discussed previously, having Co in high concentration negatively affects manufacturing properties and alloys properties as disclosed in the above prior documents, and improvements of Cu-Co-Si system alloys properties in which cobalt is added in high concentration have not been discussed sufficiently. However, Co improves mechanical strength and electrical conductivity more than Ni, and then possibility that Cu-Co-Si system alloys properties can be improved by increasing Co concentration more is considered to remain. On the other hand, to increase Co concentration more requires an operation of a solution treatment at higher temperature. In such cases, recrystallized grains are liable to increase in size. Further, secondary-phase particles such as crystalloid components and precipitated components precipitated before the solution treatment step act as obstacles and block grain growth. Accordingly, ununiformity of recrystallized grains in alloys increases and a problem of increase on a variability of mechanical characteristics of alloys occurs.

[0011] The object of the invention is to provide Cu-Co-Si system alloys containing high concentration Co, having high electrical conductivity, high strength and high bending workability, and having uniform mechanical characteristics. Another object of the invention is to provide a method for manufacturing such Cu-Co-Si system alloys.

MEANS FOR SOLVING THE PROBLEM

[0012] The inventors have diligently studied means for decrease in variability of recrystallized grains, and eventually have found out that, in a manufacturing process for Cu-Co-Si system alloys that contain Co in high concentration, when the solution treatment is conducted in relatively-high temperature, the grain size does not increase so much because of pinning effect of the second-phase particles and the pinning effect works evenly in an entire copper base matrix, resulting in uniformization of the size of growing recrystallized grains by precipitating fine second-phase particles in copper base matrix as equally spaced apart and uniformly as possible before the solution treatment step. As a result, Cu-Co-Si system alloys having small variability of mechanical characteristics can be provided.

[0013] In one aspect, the present invention that has been made based on these findings is a copper alloy for electronic materials, containing 0.5 to 4.0 mass% Co, 0.1 to 1.2 mass% Si, the balance being Cu and unavoidable impurities, wherein an average grain size is 15 to 30 μm and an average difference between maximum grain size and minimum grain size in every observation field of 0.5 mm^2 is not more than 10 μm .

[0014] In another aspect, the present invention is the copper alloy wherein Cr is furthermore contained in a maximum amount of 0.5 mass%.

[0015] In an embodiment, the present invention is the copper alloy wherein a single element or two or more elements selected from Mg, Mn, Ag and P are furthermore contained in total in a maximum amount of 0.5 mass%.

[0016] In another embodiment, the present invention is the copper alloy wherein one or two elements selected from Sn and Zn are furthermore contained in total in a maximum amount of 2.0 mass%.

[0017] In a further embodiment, the present invention is the copper alloy wherein a single element or two or more elements selected from As, Sb, Be, B, Ti, Zr, Al and Fe are furthermore contained in total in a maximum amount of 2.0 mass%.

[0018] In a further aspect, the present invention is a method for manufacturing the copper alloy, comprising sequentially conducting:

- step 1 for casting an ingot having a desired composition;
- step 2 for heating the ingot for not less than 1 hour at 950 °C to 1050 °C, thereafter hot rolling the ingot, setting the temperature to not less than 850 °C when hot rolling is completed, and cooling the ingot at an average cooling rate being not less than 15 °C/s from 850 °C to 400 °C;
- step 3 for cold rolling at a reduction ratio being not less than 85 %;
- step 4 for conducting aging by heating at 350 °C to 500 °C for 1 to 24 hours;
- step 5 for conducting a solution treatment at 950 °C to 1050 °C, and cooling the material at an average cooling rate being not less than 15 °C/s when the material temperature is reduced from 850 °C to 400 °C;
- step 6 for conducting optional cold rolling;
- step 7 for conducting aging; and
- step 8 for conducting optional cold rolling.

[0019] In a further aspect, the present invention is a copper alloy product using the copper alloy according to the present invention.

[0020] In a further aspect, the present invention is an electronic component using the copper alloy according to the present invention.

ADVANTAGEOUS EFFECT OF THE INVENTION

[0021] The invention can provide Cu-Co-Si system alloys that have desirable mechanical and electrical characteristics as a copper alloy for electronic materials, and have uniform mechanical characteristics.

BRIEF DESCRIPTION OF THE FIGURES

[0022]

Fig.1 is an illustration to explain the method of the stress relaxation test.

Fig.2 is an illustration to explain the amount of permanent set in the method of the stress relaxation test.

PREFERRED EMBODIMENT OF THE INVENTION

(Additive amount of Co and Si)

[0023] Co and Si form an intermetallic compound with appropriate heat-treatment, and make it possible to increase strength without adversely affecting electrical conductivity.

[0024] When the additive amount of Co and Si are such that Co is less than 0.5 mass% and Si is less than 0.1 mass% respectively, the desired strength cannot be achieved, and conversely, when the additive amount of Co and Si are such that Co is more than 4.0 mass% and Si is more than 1.2 mass% respectively, higher strength can be achieved, but electrical conductivity is dramatically reduced and hot workability furthermore deteriorates. Therefore, the additive amounts of Co and Si are such that Co is 0.5 to 4.0 mass% and Si is 0.1 to 1.2 mass% in the present invention.

[0025] The high strength is more desired in Cu-Co-Si system alloys than in Cu-Ni-Si system alloys and in Cu-Ni-Si-Co system alloys. Therefore, the high concentration of Co is desired and the concentration of Co is preferably not less than 2.5 mass%, more preferably not less than 3.2 mass%. That is, the additive amounts of Co and Si are such that, preferably, Co is 2.5 to 4.0 mass% and Si is 0.5 to 1.0 mass%, and more preferably, Co is 3.2 to 4.0 mass% and Si is 0.65 to 1.0 mass%.

(Additive amount of Cr)

[0026] Cr preferentially precipitates along crystal grain boundaries in the cooling process at the time of casting. Therefore, the grain boundaries can be strengthened, cracking during hot rolling is less liable to occur, and a reduction in yield can be limited. That is, Cr that has precipitated along the grain boundaries during casting is solved again by solution treatment and the like, resulting in producing precipitated particles or compounds with Si, having a bcc structure mainly composed of Cr in the subsequent aging precipitation. With an ordinary Cu-Ni-Si system alloy, the portion of the added Si solved in the matrix, which has not contributed to aging precipitation, suppresses an increase in electrical conductivity, but the Si content solved in the matrix can be reduced and electrical conductivity can be increased without compromising strength by adding Cr as a silicide-forming element and causing silicide to further precipitate. However, when the Cr concentration exceeds 0.5 mass%, coarse second-phase particles are more easily formed and product characteristics are compromised. Therefore, in the Cu-Co-Si system alloys according to the present invention, Cr can be added in a maximum amount of 0.5 mass%. However, since the effect of the addition is low at less than 0.03 mass%, it is preferred that the additive amount be 0.03 to 0.5 mass%, and more preferably 0.09 to 0.3 mass%.

(Additive amount of Mg, Mn, Ag and P)

[0027] The addition of traces of Mg, Mn, Ag and P can improve strength, stress relaxation characteristics, and other manufacturing characteristics without compromising electrical conductivity. The effect of the addition is mainly produced by the formation of a solid solution in the matrix, but the effect can be further produced when the elements are contained in the second-phase particles. However, when the total concentration of Mg, Mn, Ag and P exceeds 0.5 mass%, the effect of improving the characteristics becomes saturated and manufacturability is compromised. Therefore, in the Cu-Co-Si system alloys according to the present invention, a single element or two or more elements selected from Mg, Mn, Ag and P can be added in total in a maximum amount of 0.5 mass%. However, since the effect of the addition is low at less than 0.01 mass%, it is preferred that the additive amount be a total of 0.01 to 0.5 mass%, and more preferably a total of 0.04 to 0.2 mass%.

(Additive amount of Sn and Zn)

[0028] The addition of traces of Sn and Zn also improves the strength, stress relaxation characteristics, plating properties, and other product characteristics without compromising electrical conductivity. The effect of the addition is mainly produced by the formation of a solid solution in the matrix. However, when the total amount of Sn and Zn exceeds 2.0 mass%, the characteristics improvement effect becomes saturated and manufacturability is compromised. Therefore, in the Cu-Co-Si system alloys according to the present invention, one or two elements selected from Sn and Zn can be added in total in a maximum amount of 2.0 mass%. However, since the effect of the addition is low at less than 0.05 mass%, it is preferred that the additive amount be a total of 0.05 to 2.0 mass%, and more preferably a total of 0.5 to 1.0 mass%.

(Additive amount of As, Sb, Be, B, Ti, Zr, Al and Fe)

[0029] Electrical conductivity, strength, stress relaxation characteristics, plating properties, and other product characteristics are improved by adjusting the additive amount of As, Sb, Be, B, Ti, Zr, Al and Fe in accordance with the required product characteristics. The effect of the addition is mainly produced by the formation of a solid solution in the matrix, but a further effect can be produced when the above-described elements are added to the second-phase particles or when second-phase particles having a new composition are formed. However, when the total concentration of these elements exceeds 2.0 mass%, the characteristics improvement effect becomes saturated and manufacturability is compromised. Therefore, in the Cu-Co-Si system alloys according to the present invention, a single element or one or greater elements selected from As, Sb, Be, B, Ti, Zr, Al and Fe can be added in total in a maximum amount of 2.0 mass%. However, since the effect of the addition is low at less than 0.001 mass%, it is preferred that the additive amount be a total of 0.001 to 2.0 mass%, and more preferably a total of 0.05 to 1.0 mass%.

[0030] Manufacturability is readily compromised when the additive amount of the Mg, Mn, Ag, P, Sn, Zn, As, Sb, Be, B, Ti, Zr, Al and Fe described above exceeds 3.0 mass% as a total. Therefore, it is preferred that the total be not more than 2.0 mass%, and more preferably not more than 1.5 mass%.

(Grain size)

[0031] Hall-Petch rule in which a crystal grain has an influence on the strength and the strength is proportional to (the grain size)^{-1/2} is generally effected. Further, a coarse crystal grain deteriorates bending workability and it triggers rough surface at bending work. Accordingly, a refinement of the crystal grain is generally desirable for an improvement of strength of copper alloys. In particular, the crystal grain is preferably not more than 30 μm, and more preferably not more than 23 μm.

[0032] On the other hand, Cu-Co-Si system alloys according to the present invention are precipitation-hardened copper alloys, and then it is also necessary to note precipitation state of second-phase particles. The second-phase particles precipitated in the crystal grain at aging treatment endow improvement of strength of copper alloys. However, the second-phase particles precipitated in the crystal grain boundary hardly endow improvement of strength of copper alloys. Therefore, in order to improve strength of copper alloys, it is desirable to precipitate the second-phase particles in the crystal grain. When the grain size decreases, the crystal grain boundary area increases. Accordingly, the second-phase particles become easy to be precipitated preferentially in the crystal grain boundary at aging treatment. In order to precipitate the second-phase particles in the crystal grain, it is necessary that the crystal grain has a certain level of size. In particular, the grain size is preferably not less than 15 μm, and more preferably not less than 18 μm.

[0033] In the present invention, the average grain size is controlled within the range of 15 to 30 μm. The average grain size is preferably 18 to 23 μm. By controlling the average grain size within such a range, both the improvement effects of strength caused by the refinement of crystal grain and caused by the precipitation hardening can be achieved in a balanced manner. Further, when the average grain size is within the range, excellent bending workability and stress relaxation characteristics can be provided.

[0034] In the present invention, the grain size indicates a diameter of a minimum circle surrounding individual crystal grain, being provided by a microscope observation of a cross-section surface in the thickness direction parallel to the rolling direction. The average grain size indicates an average amount of those grain sizes.

[0035] In the present invention, an average difference between maximum grain size and minimum grain size in every observation field of 0.5 mm² is not more than 10 μm, and preferably not more than 7 μm. Though the average difference is ideally 0 μm, it is realistically difficult to be achieved. Therefore, a lower limit of the average difference is 3 μm from an actual minimum value, and typically 3 to 7 μm is optimum. The maximum grain size indicates a maximum grain size observed in an observation field of 0.5 mm². The minimum grain size indicates a minimum grain size observed in the same observation field. In the present invention, differences between maximum grain size and minimum grain size are measured in plural observation fields, and an average value of the differences indicates the average difference between

maximum grain size and minimum grain size.

[0036] The crystal grain size is uniform when the difference between maximum grain size and minimum grain size is small, and then variability of mechanical characteristics at every measuring point in the same materials is reduced. As a result, quality stability of copper alloy products or electronic components produced by using copper alloys of the present invention is improved.

(Method for manufacturing)

[0037] In general manufacturing process for Corson copper alloys, firstly, electrolytic cathode copper, Si and Co, and other starting materials are melted in a atmospheric melting furnace to obtain a molten metal having the desired composition. Then the molten metal is cast in a mold to produce an ingot. Hot rolling is conducted thereafter, cold rolling and heat treatment are repeated, and a strip or a foil having a desired thickness and characteristics are finished. The heat treatment includes solution treatment and aging treatment. In the solution treatment, material is heated at a high temperature of about 700 to about 1000 °C, the second-phase particles are solved in the Cu base matrix, and the Cu base matrix is simultaneously re-crystallized. Hot rolling sometimes doubles as the solution treatment. In an aging treatment, material is heated for not less than 1 hour in a temperature range of about 350 to about 550 °C, and second-phase particles formed into a solid solution in the solution treatment are precipitated as microparticles on a nanometer order. The aging treatment results in increased strength and electrical conductivity. Cold rolling is sometimes performed before and/or after the aging treatment in order to obtain higher strength. Further, stress relief annealing (low-temperature annealing) is sometimes performed after cold rolling in the case that cold rolling is conducted after aging.

[0038] Grinding, polishing, shot blast pickling and the like may be conducted as needed in order to remove oxidized scale on the surface between each of the above-described steps.

[0039] The manufacturing process described above is also used basically in the copper alloys according to the present invention, and it is important to precipitate fine second-phase particles in copper base matrix as equally spaced and uniformly as possible before the solution treatment step as described above in order to control the average grain size and the variability of grain size within the range as defined in the present invention. In order to provide copper alloys according to the present invention, it is necessary to produce them with particular attention to the following points.

[0040] First, coarse crystallites are unavoidably generated in the solidification process at the time of casting, and coarse precipitates are unavoidably generated in the cooling process. Therefore, the crystallites must form a solid solution in the matrix in the steps that follow. The material is held for not less than 1 hour at 950 °C to 1050 °C and then subjected to hot rolling, and when the temperature at the end of hot rolling is set to not less than 850 °C, a solid solution can be formed in the matrix even when Co, and Cr as well, are added. The temperature condition of not less than 950 °C is a higher temperature setting than in the case of other Corson alloys. When the holding temperature before hot rolling is less than 950 °C, solid solution is not sufficient. When the holding temperature before hot rolling exceeds 1050 °C, the material may melt. When the temperature at the end of hot rolling is less than 850 °C, it is difficult to obtain high strength because the elements, which have formed a solid solution, will precipitate again. Therefore, it is preferred that hot rolling be ended at 850 °C and the material be rapidly cooled in order to obtain high strength.

[0041] In this process, when the cooling rate is low, Si system compounds containing Co and Cr are precipitated again. When a heating treatment (aging treatment) is conducted in such compositions with the aim of improvement of strength, precipitates in the cooling process become growth cores, and coarse precipitates which do not contribute to strength grow from the cores, and then high strength cannot be provided. Accordingly, it is necessary that the cooling rate should be as high as possible, in particular, not less than 15 °C/s. However, the secondary-phase particles remarkably precipitates until the temperature increases to about 400 °C, and then the cooling rate in the temperature of less than 400 °C does not make any difference. Therefore, in the present invention, the cooling is conducted at the average cooling rate of not less than 15 °C/s, preferably not less than 20 °C/s when the material temperature is reduced from 850 °C to 400 °C. "The average cooling rate when the material temperature is reduced from 850 °C to 400 °C" indicates a value (°C/s) being calculated by a formula of $(850-400) (^{\circ}\text{C})/\text{cooling time (s)}$, wherein the cooling time is measured as time when the material temperature is reduced from 850 °C to 400 °C.

[0042] Water cooling is the most effective method for increasing the cooling rate. However, the cooling rate can be increased by managing the water temperature because the cooling rate varies due to the temperature of the water to be used for water-cooling. The water temperature is preferably kept at not more than 25 °C because the desired cooling rate sometimes cannot be achieved when the water temperature is not less than 25 °C. When the material is placed in a tank filled with water, the temperature of the water readily increases to not less than 25 °C. Therefore, it is preferred that a spray (shower or mist) be used or cold water be constantly allowed to flow into the water tank to prevent the water temperature from increasing, so that the material is cooled at a constant water temperature (not more than 25 °C). The cooling rate can be increased by providing additional water-cooling nozzles or increasing the flow rate of water per unit of time.

[0043] The cold rolling is conducted after the hot rolling. The cold rolling is conducted with the aim of increasing strains

which will be precipitation sites in order to generate precipitates uniformly. The cold rolling is preferably conducted at reduction rate of not less than 70 %, and more preferably not less than 85 %. When the cold rolling is not conducted and the solution treatment is conducted just after the hot rolling, precipitates cannot be generated uniformly. A combination of the hot rolling and the subsequent cold rolling may be repeated accordingly.

[0044] The first aging treatment is conducted after the cold rolling. If the secondary-phase particles remain before conducting the step, such secondary-phase particles grow further when the step is conducted, and then the sizes of the secondary-phase particles is different from those of secondary-phase particles which are generated first in the step. However, in the present invention, fine secondary-phase particles can be precipitated in uniform size and uniformly because remaining secondary-phase particles are discredited in the former step.

[0045] When the aging temperature of the first aging treatment is too low, however, precipitation amount of the secondary-phase particles providing pinning effect decreases and pinning effect generated in the solution treatment can be provided partially. Accordingly, the sizes of the crystal grains vary. On the other hand, when the aging temperature is too high, the secondary-phase particles become coarse and precipitate ununiformly, and then the sizes of the crystal grains vary. Further, the longer the aging time is, the larger the secondary-phase particles grow, and then it is necessary to set the aging time appropriately.

[0046] The first aging treatment is conducted at 350 to 500 °C for 1 to 24 hours, preferably at not less than 350 °C to less than 400 °C for 12 to 24 hours, at not less than 400 °C to less than 450 °C for 6 to 12 hours, and at not less than 450 °C to less than 500 °C for 3 to 6 hours, and then fine secondary-phase particles can be precipitated uniformly in the matrix. In such compositions, the growth of recrystallized grains generated in the solution treatment of the next step can be pinned uniformly, and then refined grain compositions having little variability of grain size can be provided.

[0047] The solution treatment is conducted after the first aging treatment. In this treatment, fine and uniform recrystallized grains are grown with a solid solution of the second-phase particles. Accordingly, it is necessary that the temperature of the solution treatment is 950 to 1050 °C. In this treatment, the recrystallized grains grow first and then the second-phase particles precipitated in the first aging treatment form solid solution. Accordingly, the growth of the recrystallized grains can be controlled by the pinning effect. However, the pinning effect disappears after the second-phase particles form the solid solution, and then the recrystallized grains grow when the solution treatment is conducted for a long time. Therefore, an appropriate solution treatment time is 60 to 300 seconds at not less than 950 °C to less than 1000 °C, preferably 120 to 180 seconds, and 30 to 180 seconds at not less than 1000 °C to less than 1050 °C, preferably 60 to 120 seconds.

[0048] Also in the cooling step after the solution treatment, the average cooling rate in the material temperature being reduced from 850 °C to 400 °C should be not less than 15 °C/s, preferably not less than 20 °C/s in order not to precipitate the second-phase particles.

[0049] The second aging treatment is conducted after the solution treatment. Conditions of the second aging treatment may be such that are generally used because of their availability for refinement of the precipitates. However, it is necessary to note that the temperature and time should be set so that the precipitates may not coarsen. The aging conditions are, for example, the temperature is in the range of 350 to 550 °C and the time is 1 to 24 hours, more preferably the temperature is in the range of 400 to 500 °C and the time is 1 to 24 hours. In addition, the cooling rate after the aging treatment has little influences on small or large for sizes of the precipitates. Before conducting the second aging treatment, precipitation sites may be increased and age hardening may be advanced by using the precipitation sites in order to improve strength. After conducting the second aging treatment, work hardening may be advanced by using the precipitates in order to improve strength. The cold rolling may be conducted before and/or after the second aging treatment.

[0050] The Cu-Co-Si system alloys according to the present invention can be used to produce various wrought copper alloy products, for example, plates, strips, tubes, rods, and wires. Further, the Cu-Co-Si system alloys according to the present invention can be used in lead frames, connectors, pins, terminals, relays, switches, foil material for secondary batteries, and other electronic components and the like.

EXAMPLES

[0051] Hereinafter, working examples will be described with comparative examples in order to understand the present invention and advantages thereof better. However, the present invention is not limited to these examples.

[0052] Copper alloys having the compositions shown in Table 1 (working examples) and Table 2 (comparative examples) were melted in a high-frequency melting furnace at 1300 °C and then cast in a mold to produce ingots having a thickness of 30 mm. Next, the ingots were heated to 1000 °C, hot rolled thereafter to a plate thickness of 10 mm at finishing temperature (the temperature at the completion of hot rolling) of 900 °C, water-cooled to 850 °C to 400 °C at average cooling rate of 18 °C/s after the completion of hot rolling, and then cooled by being left in the atmosphere. Next, the metals were faced to a thickness of 9 mm in order to remove scales from the surface, and sheets having a thickness of 0.15 mm were then formed by cold rolling. First aging treatment was subsequently conducted at various aging temperatures for 3 to 12 hours (this aging treatment was not conducted on some of comparative examples), and then solution

treatment was conducted at various temperatures for 120 seconds, and immediately water-cooled to 850 °C to 400 °C at average cooling rate of 18 °C/s, and then cooled by being left in the atmosphere. The sheets were then cold rolled to 0.10 mm, subjected to second age treatment in an inert atmosphere at 450 °C for 3 hours, and lastly cold rolled to 0.08 mm to produce test pieces.

[0053] The following various evaluation tests were conducted on the provided test pieces.

(1) Average grain size

[0054] Resin filling was conducted to the test pieces in such a manner that their observation surfaces were cross-section surfaces in the thickness direction parallel to the rolling direction, and mirror finish was conducted on the observation surfaces by mechanical polish. Next, solution was prepared by blending hydrochloric acid and water by a ratio of 10 volume parts of hydrochloric acid of 36 % to 100 volume parts of water, and then ferric chloride having weight of 5% of the solution weight was dissolved to the solution. The test pieces were immersed in the prepared solution for 10 seconds, and then metal structures appeared. Next, the metal structures were magnified 100 times by an optical microscope, pictures of their observation fields of 0.5 mm² were taken, each diameter of minimum circle surrounding individual crystal grain was measured, and then mean value was calculated on every observation field. The average grain size is mean value of the grain sizes in 15 observation fields.

(2) Average difference between maximum grain size and minimum grain size

[0055] With respect to measured grain sizes which were provided in measuring the average grain size, differences between maximum and minimum were measured in every observation field. The average difference between maximum grain size and minimum grain size is mean value of the differences in 15 observation fields.

(3) Strength

[0056] With respect to strength, a tensile test was conducted in the rolling direction, and 0.2 % yield strength (YS: MPa) was measured. Variability of strength according to measurement spots corresponds to a difference between maximum strength and minimum strength of 30 points. The average strength is mean value of strengths in these 30 points.

(4) Electrical conductivity

[0057] Electrical conductivity (EC:% IACS) was determined by measuring volume resistivity with the aid of double bridge. Variability of electrical conductivity according to measurement spots corresponds to a difference between maximum electrical conductivity and minimum electrical conductivity of 30 points. The average electrical conductivity is mean value of electrical conductivities in these 30 points.

(5) Stress relaxation performance

[0058] In measuring the stress relaxation performance, as described in Fig.1 bending stress was loaded to each test piece processed to with:10 mm and length: 100 mm and thickness (t):0.08 mm in the condition that gauge length (l) is 25 mm and height (y₀) is determined to be such that load stress is 80 % of 0.2 % yield strength. Next, the test pieces were heated at 150 °C for 1000 hours and then the amounts of permanent set (height: y) as described in Fig.2 were measured and the stress relaxation performances $\{[1 - (y - y_1) / (y_0 - y_1)] \times 100 (\%) \}$ were calculated. In addition, y₁ indicates height of an initial warpage before loading stress. Variability of stress relaxation performance according to measurement spots corresponds to a difference between maximum stress relaxation performance and minimum stress relaxation performance of 30 points. The average stress relaxation performance is mean value of stress relaxation performances in these 30 points.

(6) Bending workability

[0059] Bending workability was measured by a surface roughness of bending part. W bending test was conducted to Bad Way (BW: a direction where the bending axis is parallel to the rolling direction) with reference to JIS-H3130. Then the surface of the bending part was analyzed by a confocal laser scanning microscope and Ra (μm) regulated in JIS-B0601 was calculated. Variability of roughness of bending according to measurement spots corresponds to a difference between maximum Ra and minimum Ra of 30 points. The average roughness of bending is mean value of Ra in these 30 points.

(Table 1-1)

No.	composition(mass%)				aging temperature (°C)	solution treatment temperature (°C)	average grain size (μm)	max grain size - min grain size (μm)	average strength (MPa)	average electrical conductivity (%IACS)	average stress relaxation performance (%)	average roughness of bending (μm)	variability of strength (MPa)	variability of stress relaxation performance (%)	variability of roughness of bending (μm)
	Co	Si	Cr	others											
1	0.7	0.17			450	950	17	7	675	62	82	1.70	25	2.6	0.55
2	0.7	0.17	0.2		450	950	15	8	671	63	81	1.82	28	2.5	0.67
3	2.0	0.48	0	0	450	1020	23	8	777	57	82	2.14	30	3.8	0.67
4	2.0	0.48	0	0	500	1020	19	9	776	56	84	2.05	36	2.4	0.68
5	2.0	0.48	0.2	0	450	1020	19	5	788	58	83	2.13	37	3.1	0.71
6	2.0	0.48	0.2	0	500	1020	19	6	785	58	85	2.12	28	2.8	0.64
7	3.0	0.71	0	0	350	1020	25	8	867	53	86	2.06	43	3.5	0.90
8	3.0	0.71	0	0	400	1020	25	8	867	52	82	2.11	35	3.1	0.79
9	3.0	0.71	0	0	450	1020	18	6	861	50	85	2.08	39	3.7	0.77
10	3.0	0.71	0	0	500	1020	17	6	863	50	83	2.15	36	3.7	0.74
11	3.0	0.71	0	0	450	1050	22	7	902	52	82	2.24	38	2.8	0.82
12	3.0	0.71	0	0	500	1050	19	9	900	52	82	2.12	37	3.0	0.75
13	3.0	0.71	0	0.1 Mg	450	1020	16	6	890	50	90	2.22	40	3.1	0.74
14	3.0	0.71	0	0.1 Mg	500	1020	15	7	891	50	87	2.18	39	3.0	0.70
15	3.0	0.71	0	0.1 Mg	450	1050	19	7	931	50	89	2.31	38	4.2	0.84
16	3.0	0.71	0	0.1 Mg	500	1050	18	9	928	48	87	2.05	31	2.0	0.67
17	3.0	0.71	0.2	0	350	1020	21	8	877	53	86	2.32	45	3.6	0.79
18	3.0	0.71	0.2	0	400	1020	21	6	891	54	86	2.22	40	3.8	0.81

(Table 1-2)

No	composition (mass%)				aging temperature (°C)	solution treatment temperature (°C)	average grain size (μm)	max grain size - min grain size (μm)	average strength (MPa)	average electrical conductivity (%IACS)	average stress relaxation performance (%)	average roughness of bending (μm)	variability of strength (MPa)	variability of stress relaxation performance (%)	variability of roughness of bending (μm)
	Co	Si	Cr	others											
19	3.0	0.71	0.2	0	450	1020	15	8	871	53	84	2.08	36	2.6	0.71
20	3.0	0.71	0.2	0	500	1020	15	8	870	53	81	2.17	32	3.0	0.74
21	3.0	0.71	0.2	0	450	1050	23	7	912	53	85	2.16	39	2.9	0.84
22	3.0	0.71	0.2	0	500	1050	17	8	905	53	82	2.29	30	2.4	0.66
23	3.0	0.71	0.2	0.1Mg	450	1020	18	6	934	50	89	2.04	34	4.6	0.70
24	3.0	0.71	0.2	0.1Mg	500	1020	15	7	927	50	88	2.08	30	3.4	0.83
25	3.0	0.71	0.2	0.1Mg	450	1050	21	7	948	49	90	2.11	30	2.5	0.66
26	3.0	0.71	0.2	0.1Mg	500	1050	15	5	948	49	89	2.33	39	2.2	0.67
27	3.0	0.71	0	0.5Sn	500	1020	17	8	885	46	84	2.08	29	1.7	0.72
28	3.0	0.71	0	0.5Zn	500	1020	19	6	886	48	81	2.18	29	3.4	0.72
29	3.0	0.71	0	0.1Ag	500	1020	16	6	874	49	87	2.26	33	2.9	0.34
30	3.0	0.71	0.2	0.5Sn	500	1020	17	8	888	51	87	2.04	33	2.4	0.71
31	3.0	0.71	0.2	0.5Zn	500	1020	16	6	880	49	84	2.12	37	3.8	0.74
32	3.0	0.71	0.2	0.1Ag	500	1020	17	5	878	52	83	2.09	31	3.3	0.78
33	3.8	0.90	0	0	450	1050	16	9	952	45	85	2.34	35	3.6	0.66
34	3.8	0.90	0	0	500	1050	16	9	946	44	83	2.44	37	3.2	0.59
35	3.8	0.90	0.2	0	450	1050	16	7	967	48	82	2.39	38	3.4	0.64
36	3.8	0.90	0.2	0	500	1050	16	6	961	47	82	2.44	29	3.1	0.60

(Table 2-1)

No.	composition(mass%)				aging temperature (°C)	solution treatment temperature (°C)	average grain size (μm)	max grain size - min grain size (μm)	average strength (MPa)	average electrical conductivity (%IACS)	average stress relaxation performance (%)	average roughness of bending (μm)	Variability of strength (MPa)	variability of stress relaxation performance (%)	variability of roughness of bending (μm)
	Co	Si	Cr	others											
37	0.7	0.17	0	0	-	950	24	16	659	58	81	3.58	48	5.0	1.40
38	2.0	0.48	0	0	-	1020	32	20	765	57	83	3.24	57	6.4	1.46
39	3.0	0.71	0	0	-	1020	22	12	849	53	86	3.03	55	5.6	1.96
40	3.0	0.71	0	0	-	1050	36	36	830	51	85	3.12	51	5.8	1.99
41	3.0	0.71	0	0	-	1070	50	44	807	52	87	3.34	50	4.6	2.01
42	3.0	0.71	0.2	0	-	1020	22	14	847	54	84	3.10	48	5.5	1.87
43	3.0	0.71	0.2	0	-	1050	32	21	830	53	83	2.94	43	4.2	1.92
44	3.0	0.71	0.2	0	-	1070	46	33	817	53	86	3.38	52	6.1	2.14
45	3.0	0.71	0	0	-	950	9	8	777	55	76	2.05	39	4.1	1.13
46	3.0	0.71	0	0	-	900	7	4	743	59	77	2.05	35	3.3	1.09
47	3.0	0.71	0.2	0	-	950	8	7	792	54	76	1.96	38	4.5	1.30
48	3.0	0.71	0.2	0	-	900	6	4	753	57	73	1.90	38	3.6	1.15
49	3.0	0.71	0	0	300	1020	21	19	834	52	83	2.95	62	5.4	1.40
50	3.0	0.71	0	0	300	1050	34	28	837	52	85	3.06	52	4.8	1.46

(Table 2-2)

No.	composition(mass%)				aging temperature (°C)	solution treatment temperature (°C)	Average grain size (μm)	max grain size - min grain size (μm)	average strength (MPa)	average electrical conductivity (%IACS)	average stress relaxation performance (%)	average roughness of bending (μm)	variability of strength (MPa)	variability of stress relaxation performance (%)	variability of roughness of bending (μm)
	Co	Si	Cr	others											
51	3.0	0.71	0	0.1Mg	300	1020	20	21	882	51	83	3.14	63	5.1	2.04
52	3.0	0.71	0	0.1Mg	300	1050	31	35	868	49	82	2.97	59	49	1.50
53	3.0	0.71	0.2	0	300	1020	19	15	839	51	83	2.95	57	5.3	1.11
54	3.0	0.71	0.2	0	300	1050	29	22	845	51	82	2.92	55	4.4	1.83
55	4.7	1.12	0	0	450	1020	14	11	780	38	81	2.31	46	5.5	1.41
56	4.7	1.12	0.2	0	450	1020	15	9	795	40	85	2.31	52	5.8	1.38
57	3.0	0.71	0	0	550	1020	28	19	860	50	81	2.10	54	50	0.82
58	3.0	0.71	0	0	550	1050	34	25	888	51	82	2.36	60	4.9	1.29
59	3.0	0.71	0	0.1Mg	550	1020	23	18	900	48	80	2.24	71	6.4	1.18
60	3.0	0.71	0	0.1Mg	550	1050	31	22	926	50	82	2.66	72	5.4	1.42
61	3.0	0.71	0.2	0	550	1020	25	25	866	52	83	2.06	60	6.2	1.10
62	3.0	0.71	0.2	0	550	1050	29	27	897	51	85	2.40	69	64	1.06
63	3.0	0.71	0.2	0.1Mg	550	1020	27	20	906	50	84	2.17	72	5.4	1.02
64	3.0	0.71	0.2	0.1Mg	550	1050	31	21	935	50	83	2.67	62	5.9	1.62

[0060] Alloys of No.1 to 6 are working examples according to the present invention wherein concentrations of Co are relatively low (0.7 and 0.2 mass%). Those average strengths are low because of low concentrations of Co and variabilities of all kinds of characteristics are small.

[0061] Alloys of No.7 to 36 are working examples according to the present invention wherein concentrations of Co are high (not less than 3.0 mass%). All of them have appropriate strength and electrical conductivity for electronic materials and variabilities of all kinds of characteristics are small.

[0062] With respect to alloys of No.37 to 44, strength and bending workability deteriorated because the first aging treatment was not conducted and then the grain size increased in the solution treatment.

[0063] With respect to alloys of No.45 to 48, strength and stress relaxation characteristics deteriorated because the first aging treatment was not conducted and the temperature of the solution treatment was low, and then the second-phase particles did not form into a solid solution sufficiently and the grain size was too small.

[0064] With respect to alloys of No.49 to 54, strength and bending workability deteriorated because the temperature of the solution treatment was too low and number of the second-phase particles was small, and then grain size increased in the solution treatment. Further, variability of grain size increased, and then variability of characteristics increased.

[0065] With respect to alloys of No.55 to 56, strength and electrical conductivity deteriorated because additive amount of Co was too large.

[0066] With respect to alloys of No.57 to 64, variability of grain size increased because the temperature of the first aging treatment was too high and then the second-phase particles grew ununiformly. As a result, variability of characteristics increased.

Claims

1. A copper alloy for electronic materials, containing 0.5 to 4.0 mass% Co, 0.1 to 1.2 mass% Si, the balance being Cu and unavoidable impurities, wherein an average grain size is 15 to 30 μm and an average difference between maximum grain size and minimum grain size in every observation field of 0.5 mm^2 is not more than 10 μm .
2. The copper alloy for electronic materials of claim 1, wherein Cr is furthermore contained in a maximum amount of 0.5 mass%.
3. The copper alloy for electronic materials of claim 1 or 2, wherein a single element or two or more elements selected from Mg, Mn, Ag and P are furthermore contained in total in a maximum amount of 0.5 mass%.
4. The copper alloy for electronic materials of any one of claims 1 to 3, wherein one or two elements selected from Sn and Zn are furthermore contained in total in a maximum amount of 2.0 mass%.
5. The copper alloy for electronic materials of any one of claims 1 to 4, wherein a single element or two or more elements selected from As, Sb, Be, B, Ti, Zr, Al and Fe are furthermore contained in total in a maximum amount of 2.0 mass%.
6. A method for manufacturing the copper alloy according to any one of claims 1 to 5, comprising sequentially conducting:
 - step 1 for casting an ingot having a desired composition;
 - step 2 for heating the ingot for not less than 1 hour at 950 °C to 1050 °C, thereafter hot rolling the ingot, setting the temperature to not less than 850 °C when hot rolling is completed, and cooling the ingot at an average cooling rate being not less than 15 °C/s from 850 °C to 400 °C;
 - step 3 for cold rolling at a reduction ratio being not less than 70 %;
 - step 4 for conducting aging by heating at 350 °C to 500 °C for 1 to 24 hours;
 - step 5 for conducting a solution treatment at 950 °C to 1050 °C, and cooling the material at an average cooling rate being not less than 15 °C/s when the material temperature is reduced from 850 °C to 400 °C;
 - step 6 for conducting optional cold rolling;
 - step 7 for conducting aging; and
 - step 8 for conducting optional cold rolling.
7. A copper alloy product using the copper alloy of any one of claims 1 to 5.
8. An electronic component using the copper alloy of any one of claims 1 to 5.

Fig.1

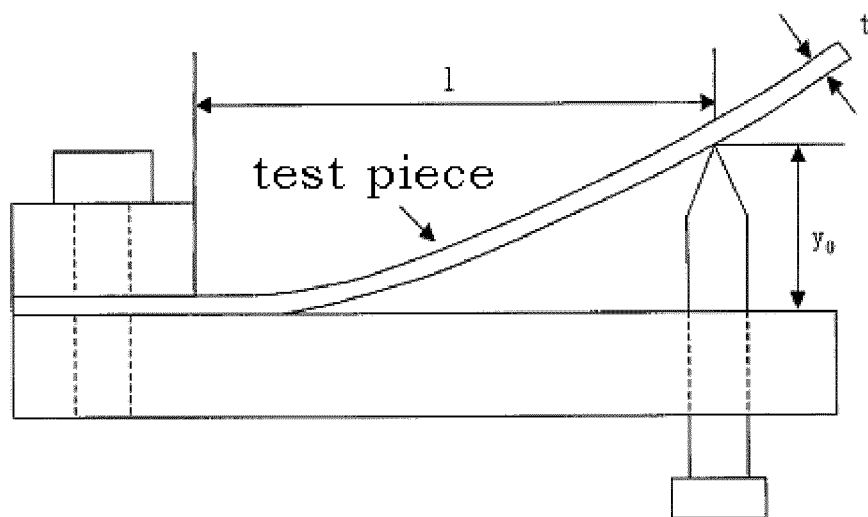
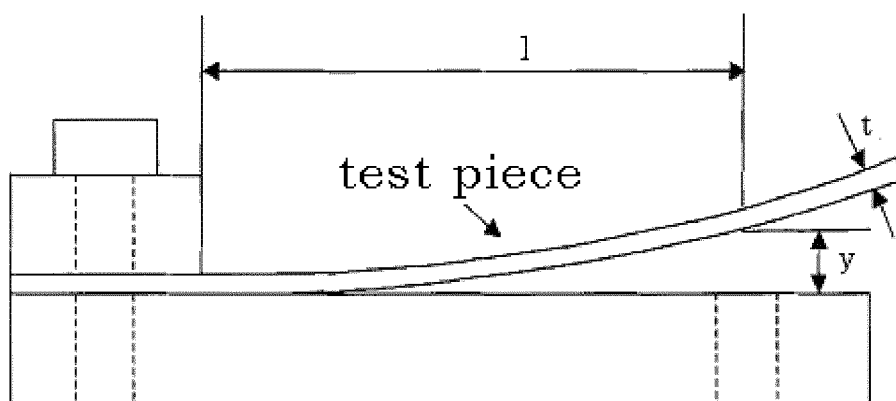


Fig.2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/052375

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/06(2006.01)i, C22C9/00(2006.01)i, C22C9/01(2006.01)i, C22C9/02(2006.01)i, C22C9/04(2006.01)i, C22C9/05(2006.01)i, C22C9/10(2006.01)i, C22F1/08(2006.01)i, H01B1/02(2006.01)i, C22F1/00(2006.01)n,

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C22C9/00-9/10, C22F1/08, H01B1/02, C22F1/00, C22F1/02

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 1996-2010

Kokai Jitsuyo Shinan Koho 1971-2010 Toroku Jitsuyo Shinan Koho 1994-2010

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2008-88512 A (Nippon Mining & Metals Co., Ltd.), 17 April 2008 (17.04.2008), entire text & WO 2008/041696 A1 & KR 10-2009-0050101 A & CN 101522927 A	1-8
A	JP 9-20943 A (The Furukawa Electric Co., Ltd.), 21 January 1997 (21.01.1997), entire text (Family: none)	4-8

☒ Further documents are listed in the continuation of Box C.

☐ See patent family annex.

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"&" document member of the same patent family

Date of the actual completion of the international search
10 May, 2010 (10.05.10)

Date of mailing of the international search report
18 May, 2010 (18.05.10)

Name and mailing address of the ISA/
Japanese Patent Office

Authorized officer

Facsimile No.

Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/052375

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 2008-266783 A (The Furukawa Electric Co., Ltd.), 06 November 2008 (06.11.2008), entire text & EP 2143810 A1 & WO 2008/126681 A1 & CN 101680057 A	1-8
E,X E,A	JP 2010-59543 A (The Furukawa Electric Co., Ltd.), 18 March 2010 (18.03.2010), claims; paragraphs [0013] to [0025] (Family: none)	1-5, 7, 8 6
P,A	WO 2009/148101 A1 (The Furukawa Electric Co., Ltd.), 10 December 2009 (10.12.2009), entire text (Family: none)	1-8

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

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2010/052375

Continuation of A. CLASSIFICATION OF SUBJECT MATTER
(International Patent Classification (IPC))

C22F1/02(2006.01)n

(According to International Patent Classification (IPC) or to both national
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REFERENCES CITED IN THE DESCRIPTION

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- JP 2005532477 A [0009]
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- JP 9020943 A [0009]