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(54) **Cu-Ni-Si-Co COPPER ALLOY FOR ELECTRONIC MATERIAL AND PROCESS FOR PRODUCING SAME**

CU-NI-SI-CO KUPFERLEGIERUNG FÜR EIN ELEKTRONISCHES MATERIAL UND HERSTELLUNGSVERFAHREN DAFÜR

CU-NI-SI-CO ALLIAGE DE CUIVRE POUR MATÉRIEL ÉLECTRONIQUE ET SON PROCÉDÉ DE PRODUCTION

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Description

TECHNICAL FIELD

[0001] The present invention relates to a precipitation hardened copper alloy and particularly, but not exclusively, to a Cu-Ni-Si-Co copper alloy suitable for use in various electronic components.

BACKGROUND ART

[0002] For copper alloys for electronic materials used in various electronic components such as connectors, switches, relays, pins, terminals, lead frames etc., it is desired to satisfy both high strength and high electrical conductivity (or thermal conductivity) as basic properties. In recent years, high integration, as well as reduction in size and thickness of electronic components, has rapidly advanced, and consequently the desired level for copper alloys used in electronic device parts is becoming increasingly sophisticated.

[0003] With regard to high strength and high electrical conductivity, the amount of precipitation hardened copper alloy used as the copper alloy for electronic materials, in place of solid solution strengthened copper alloys such as conventional phosphor bronze and brass, has been increasing. In precipitation hardened copper alloys, microfine precipitates uniformly disperse by age-treating a solutionized supersaturated solid solution to increase alloy strength, and at the same time the amount of solutionized element in copper decreases to improve electrical conductivity. As a result, a material having mechanical characteristics such as strength and spring property as well as good electrical and thermal conductivity is obtained.

[0004] Among precipitation hardened copper alloys, a Cu-Ni-Si copper alloy generally referred to as the Corson alloy is a representative copper alloy that possesses the combination of relatively high electrical conductivity, strength, and bendability, making it one of the alloys that are currently under active development in the industry. In this copper alloy, improvement of strength and electrical conductivity is attempted by allowing microfine Ni-Si intermetallic compound particles to precipitate in the copper matrix.

[0005] In order to improve further properties of the Corson alloy, the addition of Co has been performed.

[0006] It is disclosed in Japanese Laid-open Patent Application 11-222641 (Patent Document 1) that Co is similar to Ni in forming a compound with Si and increasing mechanical strength, and when Cu-Co-Si alloys are aged, they have slightly better mechanical strength and electrical conductivity than Cu-Ni-Si alloys. The document also states that, where acceptable in cost, Cu-Co-Si and Cu-Ni-Co-Si alloys may be also selected. A preparation method of said alloy is described (see claim 10) in which, after a cold working, a recrystallization process is performed at 700-920°C, and then a cold working not more than 25% and an aging treatment at 420-550°C are performed, and then a further cold working not more than 25% and a low-temperature annealing are performed.

[0007] Japanese Translation of PCT International Application Publication No. 2005-532477 (Patent Document 2) describes a wrought copper alloy consisting of, by weight, nickel: 1%-2.5%, cobalt: 0.5-2.0%, silicon: 0.5%-1.5%, and the balance being copper and unavoidable impurities, wherein the total amount of nickel and cobalt contained is 1.7% to 4.3% with a ratio of (Ni + Co)/Si being between 2:1 and 7:1, wherein said wrought copper alloy has an electrical conductivity greater than 40% IACS. Cobalt is combined with silicon to form silicides that are effective for age hardening, to restrict grain growth and to increase softening resistance. As the manufacturing methods thereof, the following sequential steps are described (see claims 25 and 26): hot working at 850-1000°C → solutionizing at 800-1000°C → first aging annealing at 350-600°C, for 30 minutes to 30 hours → a cold working for reducing the sectional area by 10-50% → second aging annealing at lower temperature than first aging annealing.

[0008] In International Publication Pamphlet WO2006/101172 (Patent Document 3) it is described that in a solutionizing treatment, it is effective to set the cooling rate to about 10°C or greater per second because the strength-enhancing effect of the Cu-Ni-Si copper alloy is further demonstrated when the cooling rate after heating is intentionally increased (see paragraph 0028).

[0009] Japanese Patent Application Public Disclosure No. 9-20943 (Patent Document 4) describes a preparation method of Cu-Ni-Si-Co alloy, wherein cold rolling not less than 85% is performed after hot rolling, and then cold rolling not more than 30% is performed after annealing at 450-480°C for 5-30 minutes, and further an aging treatment is performed at 450-500°C, for 30-120 minutes (claim 5).

[0010] US2008/0190524 A1 discloses a range of Cu-Ni-Si alloys suitable for use in electronic parts, based on a particular crystal orientation relationship.

[0011] JP2008-266783A discloses certain Cu-Ni-Si alloys for use in electrical/electronic devices, having a specified mean crystal grain size and standard deviation of crystal grain size.

PROBLEMS TO BE SOLVED BY THE INVENTION

[0012] As described above, it is known that the mechanical strength and electrical conductivity are improved by adding Co into Cu-Ni-Si alloy. However, with regard to the Cu-Ni-Si-Co alloy according to the prior art, there has been a problem that the mechanical properties such as mechanical strength, properties of relaxation of stress and surface roughness when subjected to bending have a tendency to disperse depending on location of measurement even on the same material.

[0013] Therefore, one problem to be solved by the present invention is to provide Cu-Ni-Si-Co alloy which has mechanical and electrical properties that render the alloy suitable for use as a copper alloy for electronic materials and which has even mechanical properties. In addition, another problem to be solved by the present invention is to provide a method for manufacturing such Cu-Ni-Si-Co alloy.

MEANS FOR SOLVING THE PROBLEMS

[0014] The present inventors have found that the Cu-Ni-Si-Co alloys according to the prior art have a tendency to vary the size of crystal grains and therefore big grains and small grains are mixed. The inventors thus have found that the heterogeneity of the mechanical properties is associated with this heterogeneity of size of crystal grains. In the Cu-Ni-Si-Co alloys, it is necessary to perform the solutionizing treatment at higher temperature than usual Cu-Ni-Si alloy because of the addition of Co, and therefore recrystallized particles have a tendency to become oversized. On the other hand, second phase particles such as crystallized material and deposits which have been deposited in the first part of solutionizing process inhibit the growth of crystal grains as obstacles. Therefore, in the Cu-Ni-Si-Co alloys, recrystallized particles have a tendency to vary compared to the usual Cu-Ni-Si alloy.

[0015] The present inventors have, therefore, examined eagerly the means for reducing the dispersion of the recrystallized particles and have thus identified that when fine second phase particles had been allowed to deposit in copper matrix phase at regular intervals and evenly as much as possible, crystalline particles did not so grow due to the pinning effect of the second phase particles. Furthermore, the size of the recrystallized particles also could be homogeneous because the pinning effect acted throughout the copper matrix phase evenly. As the result, it was revealed that Cu-Ni-Si-Co alloy having little dispersion of mechanical properties is obtained.

[0016] In one aspect, the present invention, which was completed based on the above knowledge, provides the copper alloy for electronic materials of claim 1.

[0017] In another aspect, the present invention provides the method of claim 2 for manufacturing the copper alloy.

[0018] In a further aspect, the present invention provides a wrought copper product having the copper alloy according to the present invention.

[0019] In a further aspect, the present invention provides an electronic component having the copper alloy according to the present invention.

EFFECT OF THE INVENTION

[0020] Aspects and embodiments of the present invention provide for a Cu-Ni-Si-Co copper alloy having an even mechanical property, because it has homogeneous crystal-grain diameters within an appropriate range.

BRIEF DESCRIPTION OF THE DRAWINGS

[0021] Embodiments of the present invention will now be described, by way of example only, with reference to the accompanying drawings, in which:

Figure 1 is an illustration of the method for a stress relaxation test; and

Figure 2 is an illustration of the amount of permanent deformation in the stress relaxation test.

DETAILED DESCRIPTION

Addition Amounts of Ni, Co and Si

[0022] Ni, Co and Si form an intermetallic compound by appropriate thermal treatment, and high strengthening can be attempted without deteriorating electrical conductivity.

[0023] Desired strength cannot be obtained if the addition amounts of Ni, Co and Si are Ni: less than 1.0% by mass, Co: less than 0.5% by mass, and Si: less than 0.3% by mass, respectively. On the other hand, with Ni: more than 2.5%

by mass, Co: more than 2.5% by mass, and Si: more than 1.2% by mass, high strengthening can be attempted but electrical conductivity is significantly reduced. Furthermore, hot workability is deteriorated. The addition amounts of Ni, Co and Si are therefore set at Ni: 1.0-2.5% by mass, Co: 0.5-2.5% by mass, and Si: 0.3-1.2% by mass. The addition amounts of Ni, Co and Si are preferably Ni: 1.5-2.0% by mass, Co: 0.5-2.0% by mass, and Si: 0.5-1.0% by mass.

Addition Amount of Cr

[0024] In the cooling process during fusion casting, Cr can strengthen crystal grain boundary because it preferentially precipitates at the grain boundary, allows for less generation of cracks during hot working, and can suppress the reduction of yield. In other words, Cr that underwent grain boundary precipitation during fusion casting will be resolutionized by for example solutionizing, but forms precipitation particles of bcc structure having Cr as the main component or a compound with Si during the subsequent aging precipitation. In an ordinary Cu-Ni-Si alloy, of the amount of Si added, Si that did not contribute to aging precipitation will suppress the increase in electrical conductivity while remaining solutionized in the matrix, but the amount of solutionized Si can be decreased by adding silicide-forming element Cr to further precipitate the silicide, and electrical conductivity can be increased without any loss in strength. However, when Cr concentration is more than 0.5% by mass, coarse second phase particles tend to form and product property is lost. Accordingly, up to 0.5% by mass of Cr can be added to the Cu-Ni-Si-Co alloy according to embodiments of the present invention. However, since less than 0.03% by mass will only have a small effect, preferably 0.03-0.5% by mass, more preferably 0.09-0.3% by mass, may be added.

Addition Amounts of Mg, Mn, Ag and P

[0025] Mg, Mn, Ag and P will improve product properties such as strength and stress relaxation property without any loss of electrical conductivity with the addition of just a trace amount. The effect of addition is mainly exerted by solutionizing into the matrix, but a further effect can also be exerted by being contained in second phase particles. However, when the total concentration of Mg, Mn, Ag and P is more than 0.5%, the effect of improving the property will saturate and in addition manufacturability will be lost. Accordingly, it is possible to add a total of up to 0.5% by mass of one or two or more selected from Mg, Mn, Ag and P to the Cu-Ni-Si-Co alloy according to the present invention. However, since less than 0.01% by mass will only have a small effect, preferably a total of 0.01-0.5% by mass, even more preferably a total of 0.04-0.2% by mass, may be added.

Addition Amounts of Sn and Zn

[0026] Sn and Zn will also improve product properties such as strength, stress relaxation property, and platability without any loss of electrical conductivity with the addition of just a trace amount. The effect of addition is mainly exerted by solutionizing into the matrix. However, when the total concentration of Sn and Zn is more than 2.0% by mass, the effect of improving the property will saturate and in addition manufacturability will be lost. Accordingly, a total of up to 2.0% by mass of one or two selected from Sn and Zn can be added to the Cu-Ni-Si-Co alloy according to the present invention. However, since less than 0.05% by mass will only have a small effect, preferably a total of 0.05-2.0% by mass, more preferably a total of 0.5-1.0% by mass, may be added.

Addition Amounts of As, Sb, Be, B, Ti, Zr, Al and Fe

[0027] As, Sb, Be, B, Ti, Zr, Al and Fe will also improve product properties such as electrical conductivity, strength, stress relaxation property, and platability by adjusting the addition amount according to the desired product property. The effect of addition is mainly exerted by solutionizing into the matrix, but a further effect can also be exerted by being contained in second phase particles, or by forming second phase particles of new composition. However, when the total of these elements is more than 2.0% by mass, the effect of improving the property will saturate and in addition manufacturability will be lost. Accordingly, a total of up to 2.0% by mass of one or two or more selected from As, Sb, Be, B, Ti, Zr, Al and Fe can be added to the Cu-Ni-Si-Co alloy according to embodiments of the present invention. However, since less than 0.001% by mass will only have a small effect, preferably a total of 0.001-2.0% by mass, more preferably a total of 0.05-1.0% by mass, is added.

[0028] Since manufacturability is prone to be lost when the above-described addition amounts of Mg, Mn, Ag P, Sn, Zn, As, Sb, Be, B, Ti, Zr, Al and Fe, exceed 3.0% in total, preferably the total of these is 2.0% by mass or less, more preferably 1.5% by mass or less.

Crystal-grain diameter

[0029] Crystal-grain influences the strength and, in general, the Hall-Petch rule, wherein the strength is proportional to -1/2 power of crystal-grain diameter, is effected. Coarse crystal-grain deteriorates the bendability and causes surface roughness when subjected to bending. Therefore, in general, miniaturization of crystal-diameter is desirable for copper alloy to increase strength. Concretely, 30 μm or less is preferable. 23 μm or less is more preferable.

[0030] On the other hand, with regard to a Cu-Ni-Si-Co alloy such as the present invention, it is also necessary to note the precipitation state of the second phase particles, since said alloy is a precipitation hardened alloy. During aging treatment, while the second phase particles precipitated in crystal-grain contribute to increase of the strength, those precipitated at the crystal-grain boundary rarely contribute to increase of the strength. Accordingly, it is desirable to cause the second phase particles to be precipitated in the crystal-grain for increasing the strength. When crystal-grain diameter is small, the second phase particles preferentially precipitate at the grain boundary at the aging treatment because the area of the grain boundary becomes big. In order to cause the second phase particles to be precipitated in the crystal-grain, it is necessary for the crystal-grain to have a certain size. Concretely, 15 μm or more is preferable. 18 μm or more is more preferable.

[0031] In the present invention, the average crystal-grain diameter is controlled to be set within the range from 15 μm to 30 μm. The average crystal-grain diameter is, preferably, from 18 μm to 23 μm. When the average crystal-grain diameter is controlled to be set within said range, both the effect of increase of the strength obtained by miniaturization of crystal-diameter and the effect of increase of the strength obtained by precipitation hardening can be obtained in a balanced manner. Further, within said range of crystal-grain diameter, it is possible to obtain a good bendability and stress relaxation property.

[0032] In the present invention, crystal-grain diameter indicates a diameter of minimal circle surrounding each crystal-grain which can be observed using a microscope, the average of crystal-grain diameter being an average of said diameters.

[0033] In the present invention, the average of the differences between the maximum crystal-grain diameter and the minimum crystal-grain diameter for 15 fields of view each having an area of 0.5 mm^2 is 7 μm or smaller. The average of the differences is ideally 0 μm. However, this is actually difficult to achieve, and therefore the lower limit is set to 3 μm from the actual minimal value, and 3-7 μm is optimal. The maximum crystal-grain diameter, as used herein, is a maximum crystal-grain diameter observed in the 15 fields of view having an area of 0.5 mm^2, and the minimal crystal-grain diameter observed in the same fields. In the present invention, the average of the differences between the maximum crystal-grain diameter and the minimum crystal-grain diameter is obtained by calculating an average of the differences between the maximum crystal-grain diameter and the minimum crystal-grain diameter which were obtained in 15 fields of view.

[0034] The fact that the difference between the maximum crystal-grain diameter and the minimum crystal-grain diameter is small indicates that the size of crystal-grain is even, which reduces dispersion of mechanical properties, in the same material, depending on location of measurement. As the result, the quality stability of the products made of the rolled copper and electronic device parts obtained by manufacturing the copper alloy according to the present invention will be improved.

Manufacturing Method

[0035] In a general manufacturing process for the Corson copper alloy, first, using an atmosphere furnace, raw materials such as electrolytic copper, Ni, Si, and Co are fused to obtain molten metal of desired composition. Then, this molten metal is cast into ingots. Subsequently, hot rolling is carried out, and cold rolling and thermal treatment are repeated to finish the products into strips and foils having the desired thickness and properties. Thermal treatment includes solutionizing and aging treatment. Solutionizing is carried out by heating at a high temperature of 700 to 1000°C, solutionizing the second phase particles into the Cu matrix, and simultaneously recrystallizing the Cu matrix. Solutionizing is also sometimes performed as hot rolling. Aging treatment is carried out by heating at a temperature range of 350 to 550°C for 1 hour or more, and precipitating the second phase particles that were solutionized in the solutionizing step as microfine particles in the order of nanometers. This aging treatment increases strength and electrical conductivity. Cold rolling may be performed before and/or after aging in order to obtain higher strength. In addition, in a case where cold rolling is carried out after aging, annealing to remove deformation (low temperature annealing) may be performed following cold rolling.

[0036] In between each of the above steps, grinding, polishing, shotblast pickling etc. are suitably performed to remove oxidation scales on the surface as appropriate.

[0037] The above manufacturing process is basically carried out for the copper alloy according to the present invention as well, but in order to control the dispersion of the average crystal-grain diameter and crystal-grain diameter within the range defined by the present invention, it is important to allow the fine second phase particles to deposit in copper matrix

phase at regular intervals and evenly as much as possible in the first part of the solutioning process, as described above. In order to obtain the copper alloys according to the present invention, it is particularly required to produce the same with attention to the following points.

[0038] First, since coarse crystallizations are inevitably produced in the solidification process during casting, and coarse precipitates are inevitably produced in its cooling process, these crystallizations need to be solutionized into the matrix in the subsequent step. If hot rolling is performed after holding at 950°C to 1050°C for 1 hour or more, and the temperature at completion of hot rolling is set at 850°C or above, Co as well as Cr can still be solutionized into the matrix. A temperature condition of 950°C or above is a higher temperature setting compared to other Corson alloys. Solutionizing will be insufficient if the holding temperature before hot rolling is below 950°C, and material may melt if it exceeds 1050°C. In addition, if the temperature at completion of hot rolling is below 850°C, solutionized elements will reprecipitate and it will become difficult to obtain high strength. Accordingly, in order to obtain high strength, it is desirable to complete hot rolling at 850°C and subject it to rapid cooling.

[0039] At this step, if the cooling rate is low, Si compounds including Co and Cr will be reprecipitated. When the heating treatment (aging treatment) is performed for the purpose of increasing strength in said structure, high strength cannot be obtained because coarse crystallizations, which do not contribute any strength, are grown using the precipitated precipitates as a nucleus. Therefore, it is necessary to set the cooling rate as fast as possible, preferably at least 15°C/s. Since precipitation of second-phase particles is considerable until about 400°C, the cooling rate at less than 400°C is not problematic. Therefore, in the present invention, when the temperature of the material is reduced from 850°C to 400°C the average cooling rate is 15°C/s or greater, preferably 20°C/s or greater. The "average cooling rate from 850°C to 400°C" after hot rolling refers to the value (°C/s) obtained by measuring the time when the temperature of the material is reduced from 850°C to 400°C and calculating the expression "(850 - 400) (°C)/Cooling time (s)."

[0040] 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 25°C or lower because the desired cooling rate sometimes cannot be achieved when the water temperature is 25°C or higher. When the material is placed in a tank filled with water, the temperature of the water readily increases to 25°C or higher. Therefore, it is preferred that a spray (shower or mist) be used, cold water be constantly allowed to flow into the water tank, or the water temperature be otherwise prevented from increasing so that the material is cooled at a constant water temperature (25°C or lower). The cooling rate can be increased by providing additional water-cooling nozzles or increasing the flow rate of water per unit of time.

[0041] Cold rolling is carried out after hot rolling. This cold rolling is carried out for the purpose of increasing the distortions which become the precipitation site, in order to allow the precipitate to be precipitated evenly. The cold rolling is preferably carried out with the rolling reduction not less than 85%, more preferably not less than 95%. When the solution treatment is carried out immediately after the hot rolling without the cold rolling, the precipitates do not precipitate evenly. The combination of the hot rolling and subsequent cold rolling may be optionally repeated.

[0042] First aging treatment is carried out after cold rolling. In the case where the second phase particles remain before the present process is performed, such second phase particles further grow when the present process is carried out, and therefore said process results in differences between the particle diameters of the particles generated in the present process and those which remain before the process. However, in the present invention, since the second phase particles have almost disappeared in the first part of the process, it is possible to allow the fine second phase particles having similar size to be precipitated evenly.

[0043] However, when the temperature at the first aging treatment is too low, the amount of the precipitate of the second phase particles which cause the pinning effect decreases, and therefore the size of crystal-grain disperses because the pinning effect caused by solution treatment is only partially obtained. On the other hand, when the temperature at the aging treatment is too high, the second phase particles become oversized and they are precipitated unevenly, and therefore the particle size of the second phase particle diffuses. Further, the longer the time of the aging treatment is, the more the second phase particles grow. Therefore, it is necessary to set an appropriate time of the aging treatment.

[0044] Fine second phase particles can be evenly precipitated in matrix phase by performing the first aging treatment at 350 - 500°C for 1- 24 hours, preferably at 350°C or more and less than 400°C for 12 - 24 hours, at 400°C or more and less than 450°C for 6 - 12 hours, and at 450°C or more and less than 500°C for 3 - 6 hours. In such structure, the growth of recrystallized particles which occurs in the next step of the solution treatment can be evenly prevented by the pinning effect, and therefore sized structure with crystal-grain diameter having little dispersion can be obtained.

[0045] Solution treatment is carried out after the first aging treatment. In the solution treatment, while the second phase particles are solutionized, fine and even recrystallized particles are grown. Therefore, it is required that the solution treatment is performed at 950 - 1050°C. In this treatment, recrystallized particles are firstly grown, and then the second phase particles precipitated in the first aging treatment are solutionized, and therefore the growth of the recrystallized particles can be controlled by the pinning effect. However, the pinning effect disappears after the second phase particles are solutionized, and therefore the recrystallized particles become oversized when the solution treatment is continued

for long term. Accordingly, an appropriate time for solution treatment is 60 - 300 seconds, preferably 120 - 180 seconds, at 950°C or more and less than 1000°C, and 30 - 180 seconds, preferably 60 - 120 seconds, at 1000°C or more and less than 1050°C.

[0046] In the cooling process after solution treatment, average cooling rate when the temperature of material is cooled from 850°C to 400°C should be set to be 15°C/s or more, preferably 20°C/s or more, in order to avoid the precipitate of the second phase particles.

[0047] Second aging treatment is carried out after the solution treatment. As the condition for the second aging treatment, while any traditional condition useful for miniaturization of the precipitates can be employed, it should be noted that temperature and time are set so that the precipitates will not become oversized. 1 - 24 hours at 350 - 550°C, more preferably 1 - 24 hours at 400 - 500°C, is an example of the condition for the aging treatment. Cooling rate after the aging treatment has little effect on the size of the precipitates. Before the second aging treatment, the precipitation sites are increased so that the strength may be increased by promoting the age hardening by using the precipitation site. After the second aging treatment, the precipitates are utilized so that the strength may be increased by promoting work hardening. Cold rolling can be carried out before and/or after the second aging treatment. After the cold rolling after the second aging treatment, stress relief annealing is carried out in order to improve the stress relaxation property. The stress relief annealing can be carried out under the traditional condition for heating. For example, the annealing is carried out for 1 - 24 hours at 250 - 400°C, preferably for 1 - 24 hours at 250 - 300°C.

[0048] The Cu-Ni-Si-Co alloy of the present invention can be processed into various wrought copper and copper alloy products, for example boards, strips, tubes, bars and wires. Furthermore, the Cu-Ni-Si-Co copper alloy according to the present invention can be used in electronic components such as lead frames, connectors, pins, terminals, relays, switches, and foil for secondary battery.

EXAMPLES

[0049] Examples of the present invention will be shown below together with Comparative Examples. However, these Examples are provided to better understand the present invention and its advantages, and do not intend to limit the invention.

[0050] Copper alloys having each of the component compositions listed in Table 1 (Example) and Table 2 (Comparative example) were melted at 1300°C with a high frequency fusion furnace, and cast into ingots having a thickness of 30 mm. Next, these ingots were heated at 1000°C, after which the finishing temperature (temperature at completion of hot rolling) was set to 900°C and hot rolled to 10 mm plates. After completion of hot rolling, the temperature of the material was cooled with water from 850°C to 400°C at the average cooling rate of 18°C/s, and then cooled by leaving it in the air. Next, scales on the surface were removed by facing to a thickness of 9 mm, and cold rolling was carried out to obtain plates having a thickness of 0.15 mm. Subsequently, the first aging treatment was performed at various temperatures for 3 - 12 hours, and then a solution treatment was performed at several temperatures for 120 seconds, immediately after which the temperature of the material was cooled with water from 850°C to 400°C at the average cooling rate of 18°C/s, and then by leaving it in the air. Next, the material was cold rolled to 0.10 mm, and then in an inert atmosphere, a second aging treatment was carried out at 450°C for 3 hours. The material was further subjected to cold rolling to 0.08 mm and finally, in an inert atmosphere, stress relief annealing was carried out at 300°C for three hours. Thus, the test strips were prepared.

[0051] For each test strip obtained as described above, evaluations of each property were performed as follows.

(1) Average crystal-grain diameter

[0052] For obtaining crystal-grain diameter, the test strip was embedded in resin so that the viewing screen thereof would be a cross section which is parallel to the rolling direction, and then the mirror finish of the viewing screen was performed by mechanical polishing. Then, into the solution which was prepared by mixing 10 parts by volume of 36% hydrochloric acid with 100 parts by volume of water, ferric chloride was dissolved so that 5 % by weight of ferric chloride was contained in the solution. In the solution thus prepared, the test strip was immersed for ten seconds to emerge the metal structure. Subsequently, said metal structure was 100 times magnified with an optical microscope and a photo was taken for each field of view having an area of 0.5 mm^2, and the diameters of minimal circle surrounding each crystal-grain were all determined. Then, the average in each field of view was calculated and the average in 15 fields of view was defined as the average crystal-grain diameter.

(2) The average of differences between the maximum crystal-grain diameter and the minimum crystal-grain diameter

[0053] Using the crystal grain diameters measured in determining the average crystal-grain diameter, the difference between the maximum crystal-grain diameter and the minimum crystal-grain diameter was determined for each field of

view. The average of the differences between the maximum crystal-grain diameter and the minimum crystal-grain diameter was defined as the average obtained from 15 fields of view.

(3) Strength

[0054] Strength was tested using a tensile test carried out in the rolling direction, and 0.2% yield strength (YS: MPa) was measured. Dispersion of strength among the measurement points is defined as the difference between maximum strength and minimum strength at 30 measurement points, and the average strength is the average at the 30 measurement points.

(4) Electrical conductivity

[0055] The electrical conductivity (EC: % IACS) was determined by measuring volume resistivity with the aid of double bridge. Dispersion of electrical conductivity among the measurement points is a difference between maximum conductivity and minimum conductivity at 30 measurement points, and the average electrical conductivity is the average at the 30 measurement points.

(5) Stress relaxation property

[0056] For obtaining stress relaxation property, to each test strip which had been fabricated so that it had 10 mm of width and 100 mm of length and thickness t=0.08 mm, as indicated in Figure 1, bending stress was loaded, where gage length l is 25 mm and height y_0 was determined so that load stress would be 80% of 0.2% proof stress, and then the test strip was heated at 150°C for 1000 hours. Subsequently, the permanent set (height) y indicated in Figure 2 was measured, and stress relaxation rate $\{[1-(y-y_1)(mm)/(y_0-y_1)(mm)]\times 100(\%)\}$ was calculated. y_1 is the height of initial bend before the stress is loaded. Dispersion of stress relaxation rate among the measurement points is the differences between maximum strength and minimum strength at 30 sites and the average of stress relaxation rate is an average at these 30 sites.

(6) Bending workability

[0057] Bending workability was estimated by the roughness of the surface at the bending site. In accordance with JIS H 3130, W bending test of Badway (direction of warped axis is identical with rolling direction) was carried out and Ra (μm) defined by JIS B 0601 was obtained by analyzing the surface of the bending site with a confocal laser scanning microscope. Dispersion of bending roughness among the measurement points is defined as the differences between maximum Ra and minimum Ra at the 30 sites, and the average of bending roughness is an average of Ras at these 30 sites.

[Table 1-1]

No	Composition (mass%)					Aging temp.	Solution temp.	Average crystal grain di-am.	Max.diam. -Min.diam. of particles	Average strength	Average electric con-ductivity	Average stress re-laxation rate	Average surface roughnes when bended	Dispersion of strength	Dispersion of stress re-laxation	Dispersion of surface roughness when bend-ed
	Ni	Co	Si	Cr	Others	(°C)	(°C)	(μm)	(μm)	(MPa)	(%IACS)	(%)	(μm)			
2	1.8	1.0	0.65			400	950	25	6	861	47	87	1.95	36	4.6	0.85
3	1.8	1.0	0.65			450	950	20	4	855	46	86	1.91	34	4.2	0.77
4	1.8	1.0	0.65			500	950	18	5	855	46	86	1.88	30	3.8	0.74
5	1.8	1.0	0.65			450	1000	25	5	890	45	87	1.99	33	4	0.82
6	1.8	1.0	0.65			500	1000	20	6	880	45	86	1.94	31	3.9	0.76
7	1.8	1.0	0.65		0.1Mg	450	950	19	3	885	45	92	1.91	34	4.2	0.74
8	1.8	1.0	0.65		0.1Mg	500	950	16	4	885	45	91	1.87	32	3.8	0.68
9	1.8	1.0	0.65		0.1Mg	450	1000	23	4	920	44	93	2.02	32	3.9	0.80
10	1.8	1.0	0.65		0.1Mg	500	1000	19	5	915	44	92	1.94	29	3.5	0.72
12	1.8	1.0	0.65	0.2		400	950	23	4	870	48	87	1.94	35	4.3	0.79
13	1.8	1.0	0.65	0.2		450	950	19	3	865	47	87	1.90	33	4	0.73
14	1.8	1.0	0.65	0.2		500	950	17	5	865	47	86	1.87	31	3.3	0.70
15	1.8	1.0	0.65	0.2		450	1000	23	4	900	46	86	1.98	32	3.9	0.81
16	1.8	1.0	0.65	0.2		500	1000	19	6	890	46	86	1.95	30	3.6	0.65
17	1.8	1.0	0.65	0.2	0.1Mg	450	950	18	5	915	44	92	1.91	35	4.3	0.67
18	1.8	1.0	0.65	0.2	0.1Mg	500	950	16	6	915	44	91	1.87	30	3.6	0.80
19	1.8	1.0	0.65	0.2	0.1Mg	450	1000	22	4	940	43	93	2.01	29	4	0.68
20	1.8	1.0	0.65	0.2	0.1Mg	500	1000	18	5	940	43	91	2.00	37	3.3	0.70

[Table 1-2]

No	Composition (mass%)					Aging temp.	Solution temp.	Average crystal grain di-am.	Max.diam. -Min.diam. of particles	Average strength	Average electric con-ductivity	Average stress re-laxation rate	Average surface roughnes when bended	Dispersion of strength	Dispersion of stress re-laxation	Dispersion of surface roughness when bend-ed
	Ni	Co	Si	Cr	Others	(°C)	(°C)	(μm)	(μm)	(MPa)	(%IACS)	(%)	(μm)			
21	1.8	0.6	0.54			450	950	25	4	835	48	86	1.97	35	4.5	0.82
22	1.8	0.6	0.54			500	950	22	4	830	48	86	1.95	34	4.2	0.70
23	1.8	0.6	0.54	0.2		450	950	24	3	845	49	87	1.98	34	4.3	0.79
24	1.8	0.6	0.54	0.2		500	950	20	5	840	49	86	1.94	33	4.1	0.80
25	1.8	1.5	0.81			450	950	19	5	910	44	87	1.92	33	4.2	0.67
26	1.8	1.5	0.81			500	950	18	6	905	44	88	1.90	32	3.9	0.65
27	1.8	1.5	0.81	0.2		450	950	18	4	920	45	87	1.90	32	4	0.65
28	1.8	1.5	0.81	0.2		500	950	18	5	915	45	86	1.89	29	3.8	0.64
29	1.8	1.0	0.65		0.5Sn	500	950	19	5	870	44	87	1.88	30	3.5	0.75
30	1.8	1.0	0.65		0.5Zn	500	950	20	5	870	43	86	1.90	30	3.5	0.72
31					0.1Ag	500	950	19	4	860	45	88	1.95	33	3.4	0.77
32	1.8	1.0	0.65	0.2	0.5Sn	500	950	18	4	880	45	88	1.90	31	3.4	0.73
33	1.8	1.0	0.65	0.2	0.5Zn	500	950	19	5	875	44	86	1.85	34	3.7	0.71
34	1.8	1.0	0.65	0.2	0.1Ag	500	950	18	4	870	46	88	1.83	30	3.3	0.76

[Table 2]

No	Composition (mass%)					Aging temp.	Solution temp.	Average crystal grain di-am.	Max.diam. -Min.diam. of particles	Average strength	Average electric con-ductivity	Average stress re-laxation rate	Average surface roughnes when bended	Dispersion of strength	Dispersion of stress re-laxation	Dispersion of surface roughness when bend-ed
	Ni	Co	Si	Cr	Others	(°C)	(°C)	(μm)	(μm)	(MPa)	(%IACS)	(%)	(μm)			
1	1.8	1.0	0.65			350	950	28	9	860	47	87	2.00	40	4.8	0.90
11	1.8	1.0	0.65	0.2		350	950	26	8	870	48	88	1.99	38	4.6	0.82
35	1.8	1.0	0.65			-	950	35	10	830	46	87	2.80	45	4.5	0.95
36	1.8	1.0	0.65			-	1000	40	9	820	46	88	2.90	30	3.8	0.80
37	1.8	1.0	0.65			-	1050	65	10	800	46	89	3.00	28	4	0.78
38	1.8	1.0	0.65			300	950	34	14	825	47	87	2.78	55	5.5	1.50
39	1.8	1.0	0.65			300	1000	38	16	820	46	87	2.85	51	5.1	1.10
40	1.8	1.0	0.65			550	950	20	20	855	46	86	2.00	55	7	1.50
41	1.8	1.0	0.65			550	1000	28	22	880	45	86	2.10	60	7.5	2.00
42	1.8	1.0	0.65		0.1Mg	300	950	35	14	865	46	87	2.80	57	5.6	1.60
43	1.8	1.0	0.65		0.1Mg	550	950	19	18	885	43	91	1.90	70	7	2.10
44	1.8	1.0	0.65		0.1Mg	300	1000	37	14	860	43	92	2.87	53	5.3	1.40
45	1.8	1.0	0.65		0.1Mg	550	1000	28	20	910	43	92	2.48	65	7.5	2.10
46	1.8	1.0	0.65	0.2		-	950	34	9	835	47	87	2.77	45	4.4	0.93
47	1.8	1.0	0.65	0.2		-	1000	37	8	825	47	88	2.84	40	4.2	0.81
48	1.8	1.0	0.65	0.2		-	1050	62	9	805	47	89	3.20	32	4	0.77
49	1.8	1.0	0.65	0.2		300	950	33	14	830	47	87	2.75	55	5.4	1.50
50	1.8	1.0	0.65	0.2		300	1000	37	16	825	47	87	2.80	52	5.4	1.20
51	1.8	1.0	0.65	0.2		550	950	20	21	860	47	86	1.95	60	6.8	1.60
52	1.8	1.0	0.65	0.2		550	1000	27	23	885	46	87	2.20	64	6.5	1.80
53	1.8	1.0	0.65	0.2	0.1Mg	550	950	18	19	890	44	91	1.87	65	6.7	1.90

(continued)

No	Composition (mass%)					Aging temp.	Solution temp.	Average crystal grain diam.	Max.diam. -Min.diam. of particles	Average strength	Average electric conductivity	Average stress relaxation rate	Average surface roughnes when bended	Dispersion of strength	Dispersion of stress relaxation	Dispersion of surface roughness when bended
	Ni	Co	Si	Cr	Others	(°C)	(°C)	(μm)	(μm)	(MPa)	(%IACS)	(%)	(μm)			
54	1.8	1.0	0.65	0.2	0.1Mg	550	1000	27	20	930	44	92	2.47	60	7	2.00
55	1.8	2.7	1.02			450	950	17	8	770	33	87	2.20	45	4	0.90
56	1.8	2.7	1.02	0.2		450	950	16	7	780	35	87	2.10	47	4.2	0.85
57	1.8	1.0	0.65			-	900	10	9	770	49	79	1.85	35	4.1	0.96
58	1.8	1.0	0.65			-	850	7	8	730	52	78	1.82	34	4	0.90
59	1.8	1.0	0.65	0.2		-	900	9	8	780	50	78	1.80	35	4	0.95
60	1.8	1.0	0.65	0.2		-	850	6	7	740	53	77	1.79	33	3.8	0.89

[0058] Alloys of Nos. 2 - 10 and 12 - 34 are working examples of the present invention, wherein they have an appropriate strength electric conductivity for electronic materials and dispersion of their properties is little.

[0059] Alloys of Nos. 1 and 11 had two high an average difference between maximum and minimum crystal grain diameter, so were outside the scope of the claimed invention.

[0060] Alloys of Nos. 35 - 37 and 46 - 48 have not been treated with the first aging treatment, and when they underwent the solution treatment, their crystal-grain diameter became oversized and strength and bending workability were deteriorated.

[0061] Alloys of Nos. 38, 39, 42, 44, 49 and 50 underwent the first aging treatment at too low a temperature, and therefore they had small numbers of the second phase particles. Therefore, when they underwent the solution treatment, their crystal-grain diameters became oversized and strength and bending workability were deteriorated. Further, dispersion of crystal-grain diameters increased. As the result, the dispersion of their properties increased.

[0062] Alloys of Nos. 40, 41, 43, 45, and 51 - 54 underwent the first aging treatment at too high a temperature, and therefore they had the second phase particles grown unevenly. Therefore, their crystal-grain diameters dispersed. As the result, the dispersion of their properties increased.

[0063] As for alloys of No. 55 and 56, too much amount of Co was added, and therefore their strength and electric conductivity decreased.

[0064] Alloys of No. 57 - 60 underwent no first aging treatment, and therefore their solutionizing temperatures are low. The second phase particles are not sufficiently solutionized, and the strength and stress relaxation property deteriorated because the crystal-grains were too small.

Claims

1. A copper alloy for electronic materials containing:

Ni: 1.0-2.5% by mass;
Co: 0.5-2.5% by mass;
Si: 0.3-1.2% by mass;
optionally up to 0.5% by mass of Cr;
optionally a total of up to 0.5% by mass of one or more selected from Mg, Mn, Ag and P;
optionally a total of up to 2.0% by mass of one or two selected from Sn and Zn;
optionally a total of up to 2.0% by mass of one or more selected from As, Sb, Be, B, Ti, Zr, Al and Fe;
and the balance being Cu and unavoidable impurities;
and having an average crystal-grain diameter of 15-30 μm;
wherein the average of the differences between a maximum crystal-grain diameter and a minimum crystal-grain diameter obtained in 15 fields of view, each field having an area of 0.5 mm^2, is 7 μm or smaller.

2. A method for manufacturing the copper alloy according to claim 1, comprising the steps of:

- step 1 of fusion casting an ingot having a desired composition;
- step 2 of heating at a material temperature of 950-1050°C for 1 hour or more, and then hot rolling, the temperature at the end of hot rolling being set at 850°C or more, and then cooling the material, the average cooling rate from 850°C to 400°C being 15°C/s or more;
- step 3 of cold rolling of 85% or more of workability;
- step 4 of aging treatment by heating at 350-500°C for 1 to 24 hours;
- step 5 of solutionizing at 950-1050°C, and cooling, the average cooling rate from 850°C to 400°C being 15°C/s or more;
- optional step 6 of cold rolling;
- step 7 of aging treatment;
- optional step 8 of cold rolling; and
- step 9 of stress relief annealing.

3. A wrought copper product having the copper alloy according to claim 1.

4. An electronic component having the copper alloy according to claim 1.

Patentansprüche

1. Kupferlegierung für elektronische Materialien, die Folgendes beinhaltet:

   Ni: 1,0-2,5 Masse-%;
   Co: 0,5-2,5 Masse-%;
   Si: 0,3-1,2 Masse-%;
   optional bis zu 0,5 Masse-% Cr;
   optional ingesamt bis zu 0,5 Masse-% von einem oder mehreren ausgewählt aus Mg, Mn, Ag und P;
   optional insgesamt bis zu 2,0 Masse-% von einem oder zwei ausgewählt aus Sn und Zn;
   optional insgesamt bis zu 2,0 Masse-% von einem oder mehreren ausgewählt aus As, Sb, Be, B, Ti, Zr, Al und Fe;
   wobei der Rest Cu und unvermeidliche Verunreinigungen sind;
   und mit einem durchschnittlichen Kristallkorndurchmesser von 15-30 μm;
   wobei der Durchschnitt der Differenzen zwischen einem maximalen Kristallkorndurchmesser und einem minimalen Kristallkorndurchmesser, erhalten in 15 Blickfeldern, wobei jedes Feld eine Fläche von 0,5 mm^2 hat, 7 μm oder weniger beträgt.

2. Verfahren zur Herstellung der Kupferlegierung nach Anspruch 1, das die folgenden Schritte beinhaltet:

   - Schritt 1 des Schmelzformens eines Ingots mit einer gewünschten Zusammensetzung;
   - Schritt 2 des Erhitzens auf eine Materialtemperatur von 950-1050°C für 1 Stunde oder mehr,
   dann Heißwalzen, wobei die Temperatur am Ende des Heißwalzens auf 850°C oder mehr eingestellt wird, und dann Kühlen des Materials, wobei die durchschnittliche Kühlrate von 850°C auf 400°C 15°C/s oder mehr beträgt;
   - Schritt 3 des Kaltwalzens von 85% oder mehr der Verarbeitbarkeit;
   - Schritt 4 der Altersbehandlung durch Erhitzen auf 350-500°C für 1 bis 24 Stunden;
   - Schritt 5 des Lösungsglühens bei 950-1050°C und Kühlens, wobei die durchschnittliche Kühlrate von 850°C auf 400°C 15°C/s oder mehr beträgt;
   - einen optionalen Schritt 6 des Kaltwalzens;
   - Schritt 7 der Alterungsbehandlung;
   - einen optionalen Schritt 8 des Kaltwalzens; und
   - Schritt 9 des Spannungsfreiglühens.

3. Geschmiedetes Kupferprodukt mit der Kupferlegierung nach Anspruch 1.

4. Elektronische Komponente mit der Kupferlegierung nach Anspruch 1.

Revendications

1. Alliage de cuivre pour matériaux électroniques contenant :

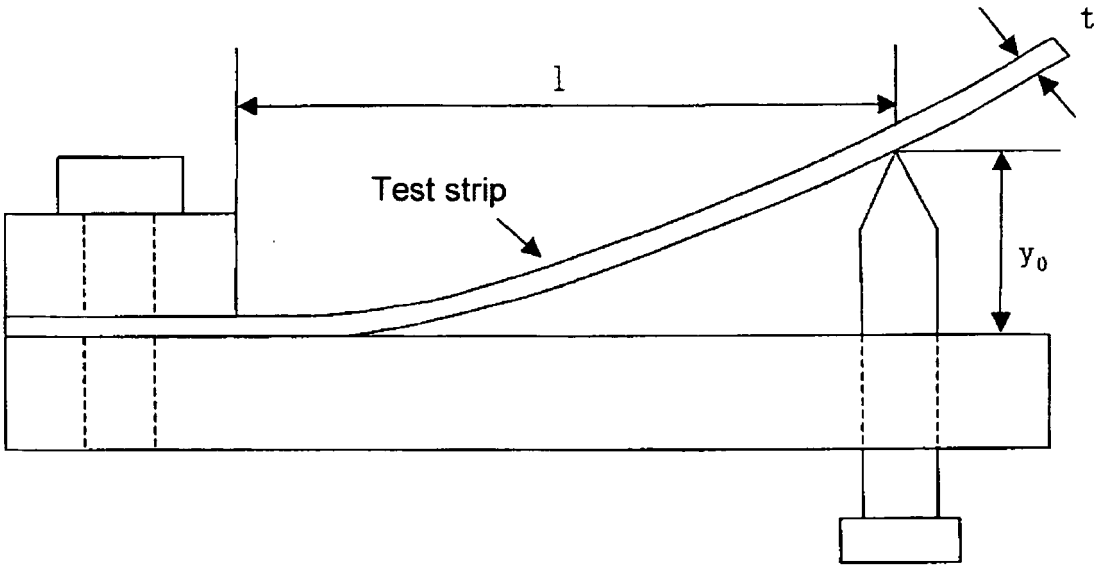
   Ni : 1,0 à 2,5% en masse ;
   Co : 0,5 à 2,5% en masse ;
   Si : 0,3 à 1,2% en masse ;
   éventuellement jusqu'à 0,5% en masse de Cr ;
   éventuellement un total de jusqu'à 0,5% en masse d'un ou plusieurs éléments sélectionnés parmi Mg, Mn, Ag et P ;
   éventuellement un total de jusqu'à 2,0% en masse d'un ou deux éléments sélectionnés parmi Sn et Zn ;
   éventuellement un total de jusqu'à 2,0% en masse d'un ou plusieurs éléments sélectionnés parmi As, Sb, Be, B, Ti, Zr, Al et Fe ;
   et le reste étant du Cu et des impuretés inévitables ;
   et ayant un diamètre moyen de grain cristallin de 15 à 30 μm ;
   dans lequel la moyenne des différences entre un diamètre maximum de grain cristallin et un diamètre minimum de grain cristallin obtenue dans 15 champs de vision, chaque champ ayant une superficie de 0,5 mm^2, est de 7 μm ou moins.

2. Procédé de fabrication de l'alliage de cuivre selon la revendication 1, comprenant les étapes consistant en :

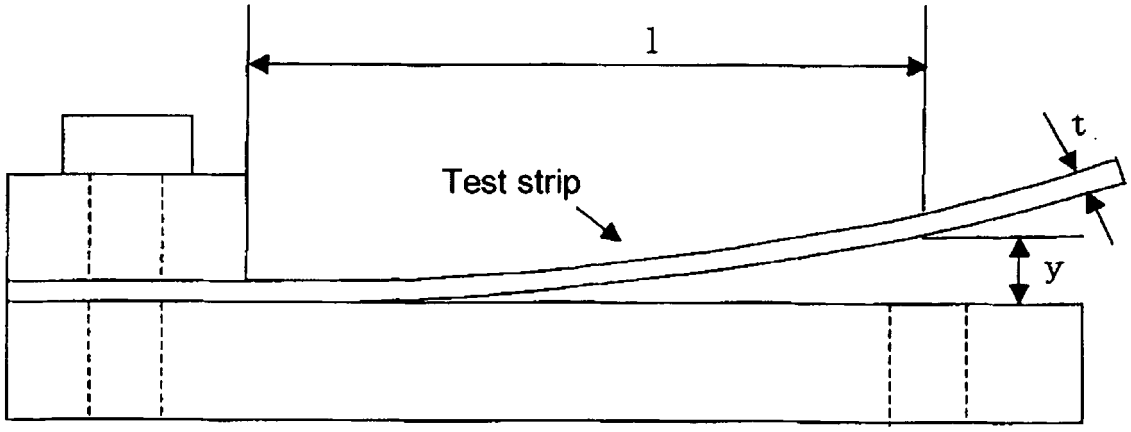
- étape 1, un coulage par fusion d'un lingot ayant une composition souhaitée ;
- étape 2, un chauffage à une température de matériau de 950 à 1050°C pendant 1 heure ou plus, puis un laminage à chaud, la température à la fin du laminage à chaud étant réglée à 850°C ou plus, puis un refroidissement du matériau, le taux de refroidissement moyen de 850°C à 400°C étant de 15°C/s ou plus ;
- étape 3, un laminage à froid de 85% ou plus d'usinabilité ;
- étape 4, un traitement de vieillissement par chauffage à 350 à 500°C pendant 1 à 24 heures ;
- étape 5, une mise en solution à 950 à 1050°C, et le refroidissement, le taux de refroidissement moyen de 850°C à 400°C étant de 15°C/s ou plus ;
- étape 6 éventuelle, un laminage à froid ;
- étape 7, un traitement de vieillissement ;
- étape 8 éventuelle, un laminage à froid ; et
- étape 9, un recuit de détente.

3. Produit de cuivre battu comportant l'alliage de cuivre selon la revendication 1.

4. Composant électronique comportant l'alliage de cuivre selon la revendication 1.



[Figure 1]



[Figure 2]

REFERENCES CITED IN THE DESCRIPTION

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