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(54) COPPER ALLOY

(57) A copper alloy, containing: Ni and/or Si, and at least one or more of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, with a balance being Cu and inevitable impurities; the copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of Ni and/or Si, and at least one or more of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, in which a grain diameter of the precipitate Y is 0.01 to 2 μm.

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Description

TECHNICAL FIELD

[0001] The present invention relates to a copper alloy applicable as materials for electric and electronic instruments.

BACKGROUND ART

[0002] Heretofore, generally, in addition to iron-based materials, copper-based materials, such as phosphor bronze, red brass, and brass, which are excellent in electrical conductivity and thermal conductivity, have been used widely as materials for electric and electronic instruments (electrical and electronic machinery and tools).

Recently, demands for miniaturization, weight saving, and associated high-density packaging of parts of electric and electronic instruments have increased, and various characteristics of higher levels are required for the copper-based materials applied thereto. Examples of basic characteristics required include mechanical properties, electrical conductivity, stress relaxation resistance, bending property, and spring property. Of those, improvements in stress relaxation resistance, tensile strength, and bending property are strongly required, for satisfying the recent demands for the miniaturization of parts or components for the products described above. In particular, for miniaturizing electronic parts, for example, tensile strength and bending property are necessary for lead frame materials, while stress relaxation resistance as well as tensile strength is necessary for connectors and terminal materials.

[0003] The requirements for those materials differ form each other little by little, depending on uses, kinds, shapes, or the like of the parts, and specific requirements include: a tensile strength of 700 MPa or more and a bending property of $R/t \leq 1.0$ (in which R represents a bending radius, and t represents a sheet thickness), or a tensile strength of 800 MPa or more and a bending property of $R/t \leq 2.0$; more preferably a tensile strength of 800 MPa or more and a bending property of $R/t < 1.5$, or a tensile strength of 900 MPa or more and a bending property of $R/t < 2.0$.

Thinning of the material is inevitable in association with miniaturization of the parts. Accordingly, conventional copper alloys are not always durable to long term uses due to increased stress loaded on the material and increased temperatures of working environments. Under these situations, more improved stress relaxation resistance is desired. Minimum stress relaxation resistance is a value defined by the Standard of the Electronic Materials Manufacturers Association of Japan (EMAS-3003), wherein the copper alloy material is desired to satisfy a stress relaxation ratio of less than 20% at a temperature condition of 150°C.

The required characteristics have reached a level that cannot be satisfied with conventional commercially available, mass-produced alloys, such as phosphor bronze, red brass, and brass. Thus, conventionally, such alloys each have an increased strength by: allowing Sn or Zn having a very different atomic radius from that of copper as a matrix phase, to be contained as a solid solution in Cu; and subjecting the resultant alloy having the solid solution to cold-working such as rolling or drawing. The method can provide high-strength materials by employing a large cold-working ratio, but employment of a large cold-working ratio (generally 50% or more) is known to conspicuously degrade bending property of the resultant alloy material. The method generally involves a combination of solid solution strengthening and working strengthening.

[0004] An alternative strengthening method is a precipitation strengthening method (a precipitation hardening method) that involves formation of a precipitate of a nanometer order in the materials. The precipitation strengthening method has merits of increasing strength and improving electrical conductivity at the same time, and is used for many alloys.

Of those, a strengthened alloy prepared by forming a precipitate composed of Ni and Si by adding Ni and Si into Cu, so-called a Corson alloy, has a remarkably high strengthening ability compared with many other precipitation-type alloys. This strengthening method is also used for some commercially available alloys (e.g. CDA70250, a registered alloy of Copper Development Association (CDA)). When the alloy generally subjected to precipitating strengthening is used for terminal/connector materials, the alloy is produced through a production process incorporating the following two important heat treatments. One is a heat treatment which involves heat treatment at a high temperature (generally 700°C or higher) near a melting point, so-called solution treatment, to allow Ni and Si precipitated through casting or hot-rolling to be contained as a solid solution into a Cu matrix. The other is a heat treatment which involves heat treatment at a lower temperature than that of the solution treatment, so-called aging treatment, to precipitate Ni and Si, which are in the solid solution caused at the high temperature, as a precipitate. The strengthening method utilizes a difference in concentrations of Ni and Si entering Cu as a solid solution at high temperatures and low temperatures.

[0005] An example of the Corson alloy applicable for electric and electronic instruments includes an alloy having a defined grain size of precipitate (see, for example, Patent Document 1). However, the precipitation-type alloy has such problems that the crystal grain size increases to cause giant crystal grains upon the solution treatment, and that the crystal grain size upon the solution treatment remains unchanged and becomes the crystal grain size of a product since the aging treatment generally does not involve recrystallization. An increased amount of Ni or Si to be added requires a solution treatment at a higher temperature, and it results in that the crystal grain size tends to increase to cause giant crystal grains, through a heat treatment in a short period of time. The resultant giant crystal grains occurred in this way cause problems of conspicuous deterioration in bending property.

Alternatively, a method of improving the bending property of a copper alloy involves addition of Mn, Ni, and P for a mutual reaction to precipitate a compound, without use of a Ni-Si precipitate (see, for example, Patent Document 2). However, the resultant alloy has a tensile strength of about 640 MPa at most, which is not sufficient for satisfying the recent demands for high strength through miniaturization of parts. Addition of Si to the copper alloy decreases the amount of the Ni-P precipitate, to thereby reduce the mechanical strength and electrical conductivity. Further, excess Si and P cause problems of occurrence of crack upon hot working.

As is apparent from the above, the bending property is hardly maintained with increasing tensile strength. Accordingly, it is desired to develop the copper alloy allowing tensile strength, bending property, electrical conductivity, and stress relaxation resistance to be compatible at high levels to one another or keeping a good balance among them, while these properties are able to be controlled depending on the uses.

Other and further features and advantages of the present invention will appear more fully from the following description.

[0006]

Patent Document 1: JP-A-11-43731 ("JP-A" means unexamined published Japanese patent application)
Patent Document 2: JP-A-2003-82425

DISCLOSURE OF INVENTION

[0007] For solving the above-mentioned problems, the present invention contemplates providing a copper alloy having high bending property and excellent tensile strength, electrical conductivity and stress relaxation resistance, wherein characteristics of the copper alloy may be readily balanced depending on uses, and the copper alloy is favorable for materials of lead frames, connectors, terminals or the like of electric and electronic instruments, particularly for materials of vehicle connectors, terminals, relays and switches or the like.

[0008] The inventors of the present invention have conducted intensive studies on a copper alloy suitably used for electrical and electronic parts, and have noticed the relations between characteristics of the alloy and grain diameters of Ni-Si precipitates and other precipitates in a copper alloy structure, and between the proportions of the distribution density of the precipitates and suppression of coarsening of crystal grains. As a result, the inventors have completed, through intensive studies, the copper alloy of the present invention that is able to form a material having excellent tensile strength and being excellent in bending property, electrical conductivity, and stress relaxation resistance.

According to the present invention, there is provided the following means:

(1) A copper alloy, having: a precipitate Y composed of Ni and/or Si, and at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be; and a precipitate X composed of Ni and Si, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm;

(2) The copper alloy, wherein the grain diameter of the precipitate Y is 0.02 to 0.9 μm;

(3) A copper alloy, having: a precipitate X composed of Ni and Si; and at least one precipitate selected from the group consisting of a precipitate Y1 composed of Ni, Si, and Cr, a precipitate Y2 composed of Ni, Si, and Co, a precipitate Y3 composed of Ni, Si, and Zr, and a precipitate Z composed of Ni, Si, and B, wherein a grain diameter of the at least one precipitate selected from the group consisting of the precipitates Y1, Y2, Y3, and Z is 0.1 to 2 μm;

(4) A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of Ni, Si, and at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm;

(5) A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of Ni or Si, and at least two or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm;

(6) A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of at least three or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein

a grain diameter of the precipitate Y is 0.01 to 2 μm;

(7) The copper alloy according to any one of Claims (1) to (6), wherein the melting point of the precipitate Y is higher than a solid solution treatment temperature;

(8) The copper alloy according to any one of (1) to (7), wherein the number of precipitates X per mm^2 is 20 to 2,000 times the number of precipitates Y per mm^2;

(9) The copper alloy according to any one of Claims (1) to (8), wherein the number of precipitates X is 10^8 to 10^{12} per mm^2, and the number of precipitates Y is 10^4 to 10^8 per mm^2;

(10) The copper alloy according to any one of Claims (1) to (9), wherein a composition of the copper alloy further comprises at least one or more selected from Sn 0.1 to 1.0 mass%, Zn 0.1 to 1,0 mass%, and Mg 0.05 to 0.5 mass%;

(11) The copper alloy according to any one of (1) to (10), which has a stress relaxation ratio of less than 20%; and

(12) The copper alloy according to any one of (1) to (11), which is for use as a material of an electric or electronic instrument.

[0009] The copper alloy of the present invention compatibly has a tensile strength and a bending property (R/t) at high levels, without impairing electrical conductivity, while stress relaxation resistance that may largely affect reliability of connectors and terminals is further improved. The copper alloy of the present invention is excellent in bending property and stress relaxation resistance, as compared with conventional copper alloys having the same level of tensile strength. The copper alloy of the present invention is a copper alloy favorable for use in electric and electronic instruments that are required for higher characteristics upon miniaturization. In addition to the above, the copper alloy of the present invention is excellent in other properties such as spring property.

BEST MODE FOR CARRYING OUT THE INVENTION

[0010] Preferable embodiments of the copper alloy of the present invention will be described in detail.

The copper alloy of the present invention is an inexpensive, high-performance copper alloy maintaining high electrical conductivity, having excellent bending property and other favorable properties, and it is preferable for a variety of electric and electronic instruments including electronic parts, e.g. vehicle terminals/connectors, relays, and switches.

[0011] Preferable embodiments of the copper alloy of the present invention will be described in detail.

The present invention relates to controlling of a grain size of a precipitate of a copper alloy. To be specific, a method of controlling a grain size has been realized from two standpoints.

First, the method of controlling a grain size can be realized by using an element that does not allow a crystal grain size to increase to cause giant grains upon a solution treatment. Each of precipitates composed of Ni, Si and α; Ni, α and β; Si, α and β; and α, β and γ (herein α, β and γ each are an element other than Ni and Si) does not form any solid solution in a Cu matrix phase even at high temperatures of the solution treatment, and that the precipitate exists in crystal grains of the Cu matrix phase and the precipitate grains, to exhibit an action and effect of suppressing growth of the crystal grains of the matrix.

[0012] Second, the method of controlling a grain size can be realized by using an element that serves as a nucleus at initial recrystallization upon the solution treatment. An intermetallic compound which is a precipitate composed of Ni, Si and α; Ni, α and β; Si, α and β; and α, β and γ (herein α, β and γ each are an element other than Ni and Si) serves as a nucleation site for recrystallization at a solution treatment temperature, and that more crystal grains are formed (nucleation) than that in the case where the precipitate is not added. Formation of more crystal grains causes mutual interference of the crystal grains during grain growth, to thereby suppress the grain growth. Multi-component precipitates are preferable for the action and effect of the nucleation site for recrystallization.

In the present invention, the term "precipitate" means to include intermetallic compounds, carbides, oxides, sulfides, nitride, compounds (solid solutions), and element metals.

[0013] The aforementioned precipitate is not to form any solid solution in the Cu matrix even during the solution treatment. That is, the precipitate must have a melting point higher than the solution treatment temperature. The precipitate is not limited to the aforementioned precipitates as long as it has a melting point higher than the solution treatment temperature. Further, the precipitate is not limited as long as it provides an effect of preventing growth of too large crystal grains during the solution treatment or forming many crystal grains (nucleation) by serving as a nucleation site for recrystallization.

The copper alloy of the present invention is an inexpensive, high-performance copper alloy maintaining high electrical conductivity, having excellent bending property and other favorable properties, and it is preferable for a variety of electric and electronic instruments including electronic parts, e.g. vehicle terminals/connectors, relays, and switches.

[0014] Next, an alloy structure of the copper alloy of the present invention will be described.

The grain diameter of the precipitate X composed of Ni and Si is preferably 0.001 to 0.1 μm, more preferably from 0.003 to 0.05 μm, and further preferably 0.005 to 0.02 μm. The strength is not improved when the grain diameter is too small, while the bending property decreases when the grain diameter is too large.

[0015] The precipitate Y composed of Ni and/or Si and at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co and Be; the precipitate Y1 composed of Ni, Si and Cr; the precipitate Y2 composed of Ni, Si and Co; and the precipitate Y3 composed of Ni, Si and Zr each have larger effects for fining crystal grains than Ni-Si precipitate X does, during the solid solution treatment as a heat treatment at high temperatures. Those effects become particularly large by the precipitate Y1 and the precipitate Y2. This effect acts for improving bending property. Since solid solution treatment can be applied at higher temperatures than temperatures of the conventional solid solution treatment, this effect can contribute to improvements of the tensile strength and the stress relaxation resistance by increasing the amount of the solid solution in the copper alloy as well as the amount of precipitates during aging treatments. This effect is particularly enhanced when the melting point of precipitate Y is higher than the melting point of precipitate X. The melting point of precipitate X is preferably from 650 to 1,050°C, and the melting point of precipitate Y is preferably higher than the melting point of precipitate X and 1,100°C or less.

[0016] The grain diameter of precipitate Y is preferably 0.01 to 2.0 μm, more preferably 0.05 to 0.5 μm, and most preferably from 0.05 to 0.13 μm. This is because an effect for suppressing growth of crystal grains and an effect for increasing the number of nucleation sites are not exhibited when the grain diameter is too small, while the bending property decreases when the grain diameter is too large. In the present invention, the grain diameter of precipitate Y is preferably larger than the grain diameter of precipitate X. The ratio of the grain diameters between Y and X (Y/X) preferably exceeds 1 and 2,000 or less, more preferably 5 to 500.

[0017] Next, the action and effect of each alloy element and a range of addition amount of the alloy element will be described.

Ni and Si are elements that can be added in a controlled addition ratio of Ni to Si for forming a Ni-Si precipitate for precipitation strengthening, to thereby enhance the mechanical strength of the copper alloy. The amount of Ni to be added is generally 2.0 to 5.0 mass%, preferably 2.1 to 4.6 mass%. The Ni amount is more preferably 3.5 to 4.6 mass%, for satisfying a tensile strength of 800 MPa or more and a bending property of $R/t < 1.5$, or a tensile strength of 900 MPa or more and a bending property of $R/t < 2$. A too small Ni amount provides a small precipitated and hardened amount that results in insufficient mechanical strength, and a too large Ni amount results in a conspicuously low electrical conductivity.

Further, the ratio of the addition amount of Ni to Si of about 1 to 4 (i.e. the amount of Ni to be added being 4 vs. that of Si being about 1) in terms of mass ratio, is known to provide the largest strengthening effect. When the Si addition amount exceeds 1.5 mass%, it is apt to cause cracking of an ingot of the copper alloy during hot working. Thus, the Si addition amount is generally 0.3 to 1.5 mass%, preferably 0.5 to 1.1 mass%, more preferably 0.8 to 1.1 mass%.

[0018] B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be form precipitate Y by themselves or in combination with Ni and/or Si. While precipitate Y serves for suppressing crystal grains from coarsening during the solid solution treatment as described above, it is not responsible for or does not largely contribute to precipitation strengthening. The content of each of the above-mentioned elements is generally 0.005 to 1.0 mass%, preferably 0.007 to 0.5 mass%, and more preferably 0.01 to 0.1 mass%. The quality of an ingot is impaired by forming large crystals during melt-casting when the amount of addition of these elements is too large, while attainment of desired effects is impossible when the amount is too small.

[0019] Further, in particularly, Cr, Co and Zr form precipitates in combination with main components, Ni and Si. While the effect is to suppress crystal grains from being coarsened during the solid solution treatment, to thereby control the crystal grain diameter as described above, it does not largely contribute to precipitation strengthening. The amount of addition of these elements is preferably 0.005 to 1.0 mass%, more preferably 0.1 to 0.3 mass% for permitting the effect to be exhibited. The quality of the ingot may be impaired by forming large crystals during melt-casting when the amount of addition of these elements is too large, while the effect of addition is not exhibited when the amount is too small.

[0020] B forms a precipitate with main constituents Ni and Si. The effect of B as the same manner as the above Cr, Co or Zr is that B is an element for suppressing increase of the crystal grain size to become too large (giant) during the solution treatment, but B takes no part in the precipitation strengthening. The B addition amount is preferably 0.005 to 0.1 mass%, more preferably 0.01 to 0.07 mass%, for exhibiting the effect. A too large B addition amount results in too large crystallized product during melt-casting to cause problems in ingot quality, and a too small B addition amount provides no addition effect.

[0021] Further, Zn, Sn, and/or Mg are preferably added to further improve the characteristics.

Zn is an element which forms a solid solution in a matrix, but Zn addition significantly alleviates solder embrittlement. Thus, Zn is added preferably in an amount of 0.1 to 1.0 mass%. The preferable primary uses of the alloy of the present invention are electric and electronic instruments and electronic part terminal materials such as vehicle terminals/connectors, relays, and switches. Most of them are joined by solder, and thus the enhancement of reliability in the joined portions is one of the important elemental techniques.

Further, Zn addition may lower the melting point of the alloy, to control the states of formation of the precipitate composed of Ni and B and the precipitate composed of Mn and P. Both the precipitates are formed during solidification. Thus, a high solidification temperature of the alloy increases the grain size, to provide a small contribution of the precipitates to the effects of suppressing increase of the crystal grain size and forming a nucleation site for the crystal grains. The lower limit of Zn addition is defined as 0.1 mass%, because it is a minimum necessary amount that provides alleviations in solder embrittlement. The upper limit of Zn addition is defined as 1.0 mass%, because a Zn addition amount more than 1.0 mass% may degrade the electrical conductivity.

[0022] Sn and Mg to be added are also preferable elements for their uses. Sn and Mg addition provides an effect of improving creep resistance, which is emphasized in electronic instrument terminals/connectors. The effect is also referred to as stress relaxing resistance, and it is an important characteristic that assumes reliability of the terminals/connectors. Solely addition of Sn or Mg may improve the creep resistance, but the use in combination of Sn and Mg can further improve the creep resistance by a synergetic effect. The lower limit of Sn addition is defined as 0.1 mass%, because it is a minimum necessary amount that provides improvements in creep resistance. The upper limit of Sn addition is defined as 1 mass%, because a Sn addition amount more than 1 mass% may degrade the electrical conductivity. The lower limit of Mg addition is defined as 0.05 mass%, because an addition amount of Mg less than 0.05 mass% provides no effect of improving the creep resistance. The upper limit of Mg addition is defined as 0.5 mass%, because an Mg addition amount of more than 0.5 mass% not only saturates the effect. Further, when an Mg addition amount is more than 0.5 mass%, it may degrade hot-workability at a particularly-high temperature, depending on the composition of the alloy.

Sn and Mg have a function of accelerating formation of a precipitate composed of Ni and Si. It is important to add preferable amounts of these Sn and Mg, serving as fine nucleation sites for the precipitate.

[0023] Next, the relationship between the number of precipitate X (the number of grains of the precipitate X) and the number of precipitate Y as another precipitate will be described below.

The number of precipitate X per mm^2 on an arbitrary cross section in the copper alloy is preferably 20 to 2,000 times the number of corresponding precipitate Y per mm^2. This is because the bending property is particularly enhanced among the characteristics, and a sufficient mechanical strength can be obtained. The number of the precipitate X is more preferably 100 to 1,500 times the number of the precipitate Y.

[0024] Specifically, the number of precipitates X is preferably 10^8 to 10^{12} per mm^2, and the number of precipitates Y that correspond to the precipitates X is preferably 10^4 to 10^8 per mm^2. This is because the aforementioned ranges provide particularly excellent bending property. If the number of precipitates is too small, the resultant alloy may not have a targeted mechanical strength. On the other hand, if the number of precipitates is too large, the resultant alloy may be poor in bending property. The number of precipitates X is more preferably 5×10^9 to 6×10^{11} per mm^2, and the number of precipitates Y is more preferably 10^4 to 4×10^7 per mm^2.

The effect of precipitates becomes remarkable as the amounts of Ni and Si are increased. A tensile strength of 800 MPa or more with the bending property of $R/t \leq 2.0$, or a tensile strength of 700 MPa or more with the bending property of $R/t \leq 1.0$ may be attained, by controlling the number of precipitates Y as described above. It is also possible to attain a tensile strength of 800 MPa or more with the bending property of $R/t < 1.5$, or a tensile strength of 900 MPa or more with the bending property of $R/t < 2$. With respect to the stress relaxation resistance, the stress relaxation ratio of the copper alloy is preferably less than 20%, more preferably less than 18%, and further preferably 15% or less, in which an open-sided block method prescribed in the Standard of the Electronic Materials Manufacturers Association of Japan (EMAS-3003) is employed with load stress set to be a surface maximum stress of 80%-yield strength (80%-YS, 0.2%-proof stress), and the stress relaxation ratio is measured under the conditions of at 150°C for 1,000 hours. The number of precipitates is represented by an average number per unit area.

[0025] The copper alloy of the present invention may have a crystal grain diameter (i.e. an average of a minor axis diameter and a major axis diameter) of generally 20 μm or less, preferably 10.0 μm or less. If the crystal grain diameter is longer than 10.0 μm, it may be impossible to obtain a tensile strength of 720 MPa or more and a bending property of $R/t < 2$. More preferably, the crystal grain diameter of the copper alloy is 8.5 μm or less. The lower limit of the crystal grain diameter may be generally 0.5 μm or more. The aforementioned crystal grain diameters are measured in the following manner: The crystal grain diameters are measured in two directions parallel to or perpendicular to the finally cold-rolled direction, respectively, on cross sections parallel to the direction of thickness of the alloy sheet and parallel to the finally cold-rolled direction (the direction of the final plastic-working), thereby to determine larger lengths as major axis diameters and smaller lengths as minor axis diameters in respective directions. An average value of each four lengths of the major axis diameters and minor axis diameters is rounded up as a product of multiplying 0.005 mm times an integer, to determine the crystal grain diameter.

[0026] Next, a specific example of a preferable production method for the copper alloy according to the present invention involves: melting a copper alloy having the aforementioned preferable element composition; casting into an ingot; and hot-rolling the ingot. More specifically, the production method involves: heating the ingot at a temperature rising rate of 20 to 200°C/hr; holding the resultant ingot at 850 to 1,050°C for 0.5 to 5 hours; hot-rolling; and, after finishing the hot-rolling at a finishing temperature of 300 to 700°C, quenching the hot-rolled product. In this way, the precipitate X, and the precipitate Y corresponding to the element composition are formed. After hot-rolling, for example, the resultant alloy is formed into a given thickness, through a combination of solution treatment, annealing, and cold-rolling.

The purpose of the solution treatment is to allow Ni and Si precipitated during casting or hot-rolling, to form a solid solution again and to recrystallize at the same time. This permits the amount of the elements in the solid solution to be increased and accumulated distortion during working to be removed, and a basic treatment for improving the strength and bending property can be provided. The temperature of the solution treatment may be adjusted according to a Ni addition amount. As preferable embodiments, the solution treatment temperature is preferably 600 to 820°C for an Ni amount of 2.0 mass% or more but less than 2.5 mass%, 700 to 870°C for an Ni amount of 2.5 mass% or more but less than 3.0 mass%, 750 to 920°C for an Ni amount of 3.0 mass% or more but less than 3.5 mass%, 800 to 970°C for an Ni amount of 3.5 mass% or more but less than 4.0 mass%, 850 to 1,020°C for an Ni amount of 4.0 mass% or more but less than 4.5 mass%, and 920 to 1,050°C for an Ni amount of from 4.5 mass% or more but less than 5.0 mass%. Since crystal grains are suppressed from being coarsened at high temperatures in the alloy of the present invention to which the above-mentioned elements are added, the amount of elements in the solid solution is increased by applying the solid solution treatment at higher temperatures, to thereby enable a high strength to be obtained.

[0027] For example, the heat treatment at 900°C of an alloy material composed of Ni 3.0 mass% and Si 0.7 mass%, allows sufficient Ni-Si precipitates that have already been precipitated, to form again the solid solution. However, the size of the crystal grain far exceeds 10 μm, and the bending property is conspicuously decreased. However, crystal grains with a size of 10 μm or less may be obtained, even by a solid solution treatment at 900°C, from an alloy material to which any one of Cr, Co, Zr, and B is further added.

Further, for example, the heat treatment at 850°C of an alloy material whose Ni content is 3.0 mass% and Si content is 0.7 mass%, allows sufficiently precipitated Ni and Si, to form again the solid solution and thereby to give crystal grains of 10 μm or less. However, the heat treatment at the same temperature of an alloy having a too small Ni amount causes growth of crystal grains into too large grains to thereby fail in obtaining a grain size of 10 μm or less. Further, on the other hand, a too large Ni amount may not provide an ideal solution state, and the mechanical strength may not be enhanced through the subsequent aging treatment.

The size of the precipitate (e.g. precipitate Y) may be changed, by changing the conditions of the solid solution treatment, i.e. by appropriately selecting the temperature of the solid solution treatment, as described above.

For example, a higher temperature of the solid solution treatment (a temperature higher by 50°C than a standard temperature) is selected for the heat treatment when the size of precipitate Y1 is to be increased, while a lower temperature of solid solution treatment (a temperature lower by 50°C than a standard temperature) is selected for the heat treatment when the size of precipitate Y1 is to be decreased. In addition, the change of the density is coupled with the change of the crystal grain size, and the density becomes lower as the size is larger, while the density becomes higher as the size is smaller.

[0028] The copper alloy of the present invention apparently provides improvement in, in particular, bending property, and optionally stress relaxation resistance, of a high strength copper alloy having a tensile strength of 800 MPa or more, while high electrical conductivity is maintained. Further, the copper alloy of the present invention provides similar improvement in bending property of a copper alloy having a tensile strength of less than 800 MPa. The copper alloy according to the present invention is also excellent in other properties, such as spring property and the like.

EXAMPLES

[0029] The present invention will be described in more detail based on examples given below, but the invention is not meant to be limited by these.

(Example 1)

[0030] An alloy component containing Ni, Si, Cr, and other elements in the amounts, as shown in Table 1, with the balance being Cu and inevitable impurities, was melted with a high frequency melting furnace, and the thus-molten alloy was cast at a cooling rate from 10 to 30°C/second, to give an ingot with a size: thickness 30 mm, width 100 mm, and length 150 mm. After holding the ingot at 900°C for 1 hour, the resultant ingot was subjected to hot-rolling, to give a hot-rolled sheet with a sheet thickness (t) of 12 mm, each of the surfaces of the sheet was chamfered by 1 mm, to adjust the thickness (t) at 10 mm, and then the sheet was finished at a thickness (t) of 0.167 mm by cold-rolling. The sheet material was then subjected to solid solution treatment. The temperature of the solid solution treatment was selected, in accordance with the conditions described in the foregoing paragraph [0026]. For changing the size of precipitate Y1, a higher solid solution treatment temperature (a temperature higher by 50°C than a standard temperature) was selected when the size of precipitate Y1 was to be increased, while a lower solid solution temperature (a temperature lower by 50°C than a standard temperature) was selected when the size of precipitate Y1 was to be decreased, for conducting the heat treatment. The change of the density was coupled with the change of the crystal grain size, and the density became lower as the size was larger, while the density became higher as the size was smaller.

Immediately after the solution treatment, the sheet material was subjected to water quenching. Then, each of the resultant alloys was subjected to aging at a temperature of 450 to 500°C for 2 hours and cold-rolling with a working ratio of 10%, to thereby obtain a sample of t = 0.15 mm.

[0031] The following characteristics of the thus-obtained samples were tested and evaluated as mentioned in below, and the results are shown in Table 2.

a. Electrical conductivity (EC):

Electrical conductivity was calculated by measuring a specific resistance of the sample through a four terminal method in a thermostatic bath maintained at 20°C (±0.5°C). The distance between the terminals was set to 100 mm.

b. Tensile strength (TS):

Tensile strengths of 3 test pieces prepared according to JIS Z 2201-13B cut out from the sample in a direction parallel to the rolling direction, were measured according to JIS Z 2241, and an average value thereof was obtained.

c. Bending property:

A test piece was cut out from the sample in a direction parallel to the rolling direction into a size of width 10 mm and length 25 mm. The resultant test piece was W-bent at 90° at a bending radius R that would be 0, 0.1, 0.15, 0.2, 0.25, 0.3, 0.4, 0.5, or 0.6 (mm), with a bending axis being perpendicular to the rolling direction. Whether cracks were occurred or not at the bent portion, was observed with the naked eye through observation with an optical microscope of 50 times magnification, and the bent sites were observed with a scanning electron microscope to examine whether cracks were observed or not.

Evaluation results are designated by R/t (in which R represents a bending radius (mm), and t represents a sheet thickness(mm)), and the R/t was calculated by employing a (limit) maximum R at which cracks were occurred. If no crack is formed at R = 0.15 and cracks are formed at R = 0.1, since the sample had a thickness (t) = 0.15 mm, R/t = 0.15/0.15 = 1 is obtained, which is shown in the following table. As the value of R/t is smaller, the bending property is improved.

d. Grain size of precipitate and distribution density:

The sample was punched out into a shape of a disc of diameter 3 mm, and the resultant was subjected to thin-film-polishing by using a twinjet polishing method. Photographs (5,000 and 100,000 times magnification) of the resultant sample were taken at 3 arbitrary positions with a transmission electron microscope at accelerating voltage 300 kV, and the grain size of the precipitate and the density thereof were measured on the photographs. Measurement of the grain size and density of the precipitate were carried out in the following manner: setting an incident electron beam azimuth to [001], and measuring the number of fine grains of the precipitate X composed of Ni-Si in a high-power photograph (100,000 times magnification) at n = 100 (n represents the number of viewing fields for observation), since the precipitate X was fine; and, on the other hand, measuring the number of grains of the precipitate Y1 in a low-power photograph (5,000 times magnification) at n = 10; thereby to eliminate the localized bias on the numbers. The numbers were calculated into numbers per unit area (/mm^2).

e. Crystal grain diameter:

The crystal grain diameter was measured according to JIS H 0501 (cutting method). The crystal grain diameters were measured in two directions parallel to and perpendicular to the finally cold-rolled direction, respectively, on cross sections parallel to the direction of thickness of the alloy sheet and parallel to the finally cold-rolled direction (the direction of the final plastic-working). The thus-measured lengths were classified into larger lengths as major axis diameters and smaller lengths as minor axis diameters in respective directions. An average value of each four lengths of the major axis diameters and minor axis diameters was rounded up as a product of multiplying 0.005 mm times an integer, to determine the crystal grain diameter.

[0032] [Table 1]

Table 1

Classification	No.	Ni [mass%]	Si [mass%]	Cr [mass%]	Other [mass%]
Example according to this invention	1	2.31	0.52	0.08	-
	2	3.22	0.73	0.62	-
	3	3.82	0.86	0.19	Zn:0.51
	4	4.22	0.95	0.22	Zn:0.49 Sn:0.15 Mg:0.11
	5	4.81	1.09	0.41	Zn:0.50 Sn:0.12
Comparative example	100	2.37	0.56	0.09	-
	101	3.5	0.80	0.13	-
	102	3.94	0.94	0.19	Zn:0.52 Sn:0.15
	103	4.29	1.02	0.22	-

[0033] [Table 2]

Table 2

Classification	No.	Grain size of precipitate X [μm]	Grain size of precipitate Y1 [μm]	Number of Y1/ number of X	Crystal grain diameter [μm]	TS [MPa]	EC [%IACS]	Bending property [R/t]
Example according to this invention	1	0.02	0.21	330	5	722	44	1.0
	2	0.03	0.19	430	6	764	40	1.0
	3	0.05	0.22	58	8	805	38	1.5
	4	0.04	0.17	890	7	846	36	2.0
	5	0.04	0.19	1020	5	887	33	2.0
Comparative example	100	0.02	2.20	19	18	725	44	1.5
	101	0.03	0.001	16	22	764	41	2.5
	102	0.03	0.004	18	19	803	39	3.0
	103	0.04	2.92	10	27	841	36	3.5

[0034] From the results shown in Tables 1 and 2, it is understood that the samples according to the present invention have excellent properties in both of the mechanical strength and the bending property. However, since the grain diameter of precipitate Y1 was outside of the range defined in the present invention, the samples in Comparative examples 100, 101, 102 and 103 each were poor in the bending property, as compared with the samples in the examples according to the present invention having the same level of mechanical strength, and the mechanical strength in the comparative examples was not compatible to the bending property. Thus, it is possible to improve the bending property (R/t) while high strength is maintained, by controlling the grain diameter of precipitate Y1 in the Cu alloy system containing Ni, Si, and Cr. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable for materials of lead frames or the like. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property.

(Example 2)

[0035] With respect to the copper alloys containing the elements in the amounts, as shown in Table 3, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1, except that the measurement was made on the precipitate Y2 in place of the precipitate Y1. The results are shown in Table 4. The production and measurement methods were also performed in the same manner as in Example 1.

[0036] [Table 3]

Table 3

Classification	No.	Ni [mass%]	Si [mass%]	Co [mass%]	Other [mass%]
Example according to this invention	6	2.33	0.48	0.09	-
	7	3.20	0.67	0.55	-
	8	3.84	0.93	0.17	Zn:0.51
	9	4.29	1.02	0.14	Zn:0.49 Sn:0.15 Mg:0.12
	10	4.82	1.09	0.37	Zn:0.50 Sn:0.12
Comparative example	105	2.40	0.52	0.04	-
	106	3.26	0.77	0.19	-
	107	3.94	0.86	0.19	Zn:0.52 Sn:0.15
	108	4.32	1.00	0.31	-

[0037] [Table 4]

Table 4

Classification	No.	Grain size of precipitate X [μm]	Grain size of precipitate Y2 [μm]	Number of Y2/ number of X	Crystal grain diameter [μm]	TS [MPa]	EC [%IACS]	Bending property [R/t]
Example according to this invention	6	0.016	0.209	331	6	718	45	1.0
	7	0.021	0.189	442	6	759	40	1.0
	8	0.045	0.212	60	9	805	38	1.5
	9	0.034	0.170	902	7	843	37	2.0
	10	0.041	0.195	1035	5	877	34	2.0
Comparative example	105	0.021	2.150	34	19	723	44	1.5
	106	0.031	0.009	19	22	763	41	2.5
	107	0.029	0.005	19	20	799	39	3.0
	108	0.047	2.918	17	27	830	36	3.5

[0038] From the results shown in Tables 3 and 4, it is understood that the samples according to the present invention have excellent properties in both of the mechanical strength and the bending property. However, since the grain diameter of precipitate Y2 was outside of the range defined in the present invention, the samples in Comparative examples 105, 106, 107 and 108 each were poor in the bending property, as compared with the samples in the examples according to the present invention having the same level of mechanical strength, and the mechanical strength in the comparative examples was not compatible to the bending property. Thus, it is possible to improve the bending property (R/t) while high strength is maintained, by controlling the grain diameter of precipitate Y2 in the Cu alloy system containing Ni, Si, and Co. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable for materials of lead frames or the like. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property.

(Example 3)

[0039] With respect to the copper alloys containing the elements in the amounts, as shown in Table 5, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1, except that the measurement was made on the precipitate Y3 in place of the precipitate Y1. The results are shown in Table 6. The production and measurement methods were also performed in the same manner as in Example 1.

[0040] [Table 5]

Table 5

Classification	No.	Ni [mass%]	Si [mass%]	Zr [mass%]	Other [mass%]
Example according to this invention	11	2.42	0.59	0.07	-
	12	3.18	0.84	0.69	-
	13	3.81	0.79	0.21	Zn:0.51
	14	4.31	1.01	0.30	Zn:0.49 Sn:0.14 Mg:0.10
	15	4.77	1.08	0.36	Zn:0.50 Sn:0.13
Comparative example	109	2.30	0.63	0.06	-
	110	3.28	0.83	0.15	-
	111	3.90	0.78	0.20	Zn:0.53 Sn:0.15
	112	4.37	1.08	0.18	-

[0041] [Table 6]

Table 6

Classification	No.	Grain size of precipitate X [μm]	Grain size of precipitate Y3 [μm]	Number of Y3/ number of X	Crystal grain diameter [μm]	TS [MPa]	EC [%IACS]	Bending [R/t]
Example according to this invention	11	0.022	0.204	361	7	709	45	1.0
	12	0.021	0.195	448	7	747	42	1.0
	13	0.050	0.225	80	9	802	39	1.5
	14	0.035	0.174	916	8	835	37	2.0
	15	0.046	0.181	1048	5	875	33	2.0
Comparative example	109	0.021	2.250	43	19	715	45	1.5
	110	0.031	0.009	19	23	751	42	2.5
	111	0.038	0.004	28	20	796	40	3.0
	112	0.036	2.929	52	28	828	38	3.5

[0042] From the results shown in Tables 5 and 6, it is understood that the samples according to the present invention have excellent properties in both of the mechanical strength and the bending property. However, since the grain diameter of precipitate Y3 was outside of the range defined in the present invention, the samples in Comparative examples 109, 110, 111 and 112 each were poor in the bending property, as compared with the samples in the examples according to the present invention having the same level of mechanical strength, and the mechanical strength in the comparative examples was not compatible to the bending property. Thus, it is possible to improve the bending property (R/t) while high strength is maintained, by controlling the grain diameter of precipitate Y3 in the Cu alloy system containing Ni, Si, and Zr. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable for materials of lead frames or the like. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property.

(Example 4)

[0043] With respect to the copper alloys containing the elements in the amounts, as shown in Table 7, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1, except that the measurement was made on the precipitate Z in place of the precipitate Y1. The results are shown in Table 8. The production and measurement methods were also performed in the same manner as in Example 1.

[0044] [Table 7]

Table 7

Classification	No.	Ni [mass%]	Si [mass%]	B [mass%]	Other [mass%]
Example according to this invention this invention	16	2.36	0.38	0.08	-
	17	3.20	0.78	0.01	-
	18	3.87	0.86	0.10	Zn:0.50
	19	4.21	0.77	0.29	Zn:0.49 Sn:0.15 Mg:0.11
	20	4.95	1.11	0.21	Zn:0.48 Sn:0.13
Comparative example	113	2.44	0.59	0.21	-
	114	3.43	0.86	0.02	-
	115	3.91	0.92	0.18	Zn:0.50 Sn:0.15
	116	4.31	0.89	0.08	-

[0045] [Table 8]

Table 8

Classification	No.	Grain size of precipitate X [µm]	Grain size of precipitate Z [µm]	Number of Z/ number of X	Crystal grain diameter [µm]	TS [MPa]	EC [%IACS]	Bending property [R/t]
Example according to this invention	15	0.016	0.210	348	7	707	45	1.0
	16	0.023	0.187	441	8	743	41	1.0
	17	0.044	0.232	106	9	802	39	1.5
	18	0.036	0.170	921	9	829	36	2.0
	19	0.045	0.192	1054	6	870	34	2.0

(continued)

Classification	No.	Grain size of precipitate X [μm]	Grain size of precipitate Z [μm]	Number of Z/ number of X	Crystal grain diameter [μm]	TS [MPa]	EC [%IACS]	Bending property [R/t]
Comparative example	113	0.021	2.250	59	20	712	46	1.5
	114	0.030	0.007	42	23	750	43	2.5
	115	0.042	0.003	38	20	790	40	3.0
	116	0.037	2.931	61	28	820	38	3.5

[0046] From the results shown in Tables 7 and 8, it is understood that the samples according to the present invention have excellent properties in both of the mechanical strength and the bending property. However, since the grain diameter of precipitate Z was outside of the range defined in the present invention, the samples in Comparative examples 113, 114, 115 and 116 each were poor in the bending property, as compared with the samples in the examples according to the present invention having the same level of mechanical strength, and the mechanical strength in the comparative examples was not compatible to the bending property. Thus, it is possible to improve the bending property (R/t) while high strength is maintained, by controlling the grain diameter of precipitate Z in the Cu alloy containing Ni, Si, and B. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable for materials of lead frames or the like. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property.

(Example 5)

[0047] With respect to the copper alloys containing the elements in the amounts, as shown in Table 9, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1, except that the measurement was made on the precipitate Y2, Y3 or Z in place of a part of the precipitate Y1. The results are shown in Table 10. The production and measurement methods were also performed in the same manner as in Example 1.
[0048] [Table 9]

Table 9

Classification	No.	Ni [mass%]	Si [mass%]	Cr, Co, Zr, B [mass%]	Zn [mass%]	Sn [mass%]	Mg [mass%]
Example according to this invention	21	2.25	0.54	Cr:0.08	0.2	0.10	0.20
	22	3.24	0.78	Co:0.08	0.3	0.15	0.15
	23	3.45	0.83	Cr:0.2 Zr: 0.1	0.5	0.10	0.10
	24	3.66	0.88	Zr: 0.1 B: 0.02	0.5	0.12	0.12
	25	3.87	0.93	Cr: 0.7	0.4	0.15	0.15
	26	4.02	0.97	Cr: 0.2 Co: 0.1	0.2	0.18	0.11
	27	4.27	1.02	Co: 0.8 Zr: 0.1	0.5	0.22	0.21
	28	4.48	1.07	Cr:0.4	0.4	0.40	0.15
	29	4.94	1.18	Cr:0.3 Co:0.1	0.5	0.32	0.14

(continued)

Classification	No.	Ni [mass%]	Si [mass%]	Cr, Co, Zr, B [mass%]	Zn [mass%]	Sn [mass%]	Mg [mass%]
Comparative example	117	2.44	0.59	Cr:0.09	0.4	0.25	0.12
	118	3.20	0.77	Co:0.25	0.5	0.15	0.17
	119	3.77	0.91	Zr:0.2 Cr: 0.1	0.2	0.20	0.09
	120	3.94	0.95	Cr:0.25	0.2	0.15	0.21
	121	4.23	1.01	Cr:0.3 Co: 0.1	0.3	0.12	0.14
	122	4.70	1.13	Cr:0.25	0.4	0.20	0.21

[0049] [Table 10]

Table 10

Classification	No.	Grain size of precipitate X [μm]	Grain size of precipitate Y1, Y2, Y3, Z [μm]	Number of Y1, Y2, Y3, Z/ number of X	Crystal grain diameter [μm]	TS [MPa]	EC [%IACS]	Bending property [R/t]
Example according to this invention	21	0.023	0.204	333	6	705	44	1.0
	22	0.032	0.191	444	6	727	39	1.0
	23	0.051	0.223	80	9	728	37	1.0
	24	0.039	0.163	891	8	801	36	1.5
	25	0.045	0.195	1031	5	809	34	1.5
	26	0.018	0.208	365	6	811	33	2.0
	27	0.031	0.197	443	8	833	31	2.0
	28	0.053	0.219	94	9	854	30	2.0
	29	0.036	0.166	914	8	875	28	2.0
Comparative example	117	0.021	2.270	21	19	765	43	1.5
	118	0.031	0.006	23	23	786	39	2.0
	119	0.304	2.103	26	23	807	35	2.5
	120	0.044	0.001	28	20	828	33	3.0
	121	0.032	0.008	35	20	850	31	3.0
	122	0.047	2.916	26	28	871	27	3.0

[0050] From the results shown in Tables 9 and 10, it is understood that the samples according to the present invention have excellent properties in both of the mechanical strength and the bending property. However, since the grain diameter of precipitate Y1, Y2, Y3 or Z was outside of the range defined in the present invention, the samples in Comparative examples 117, 118, 119, 120, 121 and 122 each were poor in the bending property, as compared with the samples in the examples according to the present invention having the same level of mechanical strength, and the mechanical strength in the comparative examples was not compatible to the bending property. Thus, it is possible to improve the bending property (R/t) while high strength is maintained, by controlling the grain diameter of precipitate Y1 or the like. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable for materials of lead frames or the like. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property.

[0051] In the following examples, it is shown that it is possible to control the stress relaxation resistance that has a large influence on the reliability particularly of connectors and terminal materials, by controlling the grain diameter of precipitate Y. While the copper alloys in the following examples according to the present invention are particularly favorable as connectors and terminal materials, they are also applicable to other uses, such as lead frame materials.

(Example 6)

[0052] With respect to the copper alloys containing Ni, Si, and elements in the given amounts as shown in Table 11, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1. The contents of Ni and Si were as follows: 3.5 mass% of Ni and 0.8 mass% of Si in the samples of Examples according to the present invention Nos. 1-4 and 1-11; 4.0 mass% of Ni and 0.95 mass% of Si in the sample of Example according to the present invention No. 1-6; and 3.8 mass% of Ni and 0.86 mass% of Si in the samples of other Examples according to the present invention and Comparative examples. The production and measurement methods for the samples were also performed in the same manner as in Example 1. Further, the stress relaxation resistance was evaluated by the following manner.

f. Stress relaxation resistance:

[0053] An open-sided block method prescribed in the Standard of the Electronic Materials Manufacturers Association of Japan (EMAS-3003) was employed with load stress set to be a surface maximum stress of 80%-yield strength (80%-YS, 0.2%-proof stress), and the stress relaxation ratio (S.R.R.) was measured by placing the sample in a thermostat bath at 150 °C for 1,000 hours. When the stress relaxation ratio of the copper alloy was less than 20%, it is judged that the stress relaxation resistance is "good", while when the S.R.R. was 20% or more, it is judged that the stress relaxation resistance is "poor".

Herein, the terms 'GW' and 'BW' in the following tables are defined as follows. GW denotes bending with a bend axis perpendicular to the direction of rolling, by using a test piece sampled in parallel to the direction of rolling; and BW denotes bending with a bend axis parallel to the direction of rolling, by using a test piece sampled perpendicular to the direction of rolling. In other words, GW means that the longitudinal direction of the test piece is parallel to the direction of rolling, and BW means that the longitudinal direction of the test piece is perpendicular to the direction of rolling.

[0054] As is apparent from the results in Table 11, the samples according to the present invention each have excellent properties with respect to the mechanical strength, electrical conductivity, bending property, and stress relaxation resistance. In particular, it is possible to control the stress relaxation resistance by the grain size of precipitate Y, to make the stress relaxation ratio be less than 20%. In the examples according to the present invention, by making the grain size of Y within the range from 0.02 to 0.9 μm, it was possible to attain a good stress relaxation ratio, which was a stress relaxation ratio of 13% or less, while maintaining excellent mechanical strength, electrical conductivity, and bending property. Based on the above, the alloys of the examples according to the present invention can be considered to be favorable, for example, for materials of terminals and connectors. Furthermore, although not shown in the examples, the similar effects can be exhibited when the grain size of Y is within the range from 0.01 to 2.0 μm. Contrary to the above, since the grain size of precipitate Y was too large due to a too large amount of B, the sample in Comparative example 1-1 was poor in the mechanical strength and the stress relaxation resistance. Since the grain size of precipitate Y was too small due to a too small amount of Fe, the sample in Comparative example 1-2 was poor in the stress relaxation resistance. Since the amount of P was too large, the sample in Comparative example 1-3 was poor in the stress relaxation resistance. Since the grain size of precipitate Y was too small, the sample in Comparative example 1-4 was poor in the bending property and the stress relaxation resistance. Since the grain size of precipitate Y was too small, the sample in Comparative example 1-5 was poor in the stress relaxation resistance. Since the grain size of precipitate Y was too small, the sample in Comparative example 1-6 was poor in the stress relaxation resistance.

[0055] [Table 11]

Table 11

	Component	Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	Size	Density	Composition	Size	Density				GW	BW	
	mass%	μm	/mm^2	Compound	μm	/mm^2		MPa	%IACS	R/t	R/t	%
This invention 1-1	Cr=0.2	0.03	3×10^{9}	Ni-Si-Cr	0.2	2×10^{7}	150	862	36	1.0	1.0	9
This invention 1-2	Cr=0.1 Zr=0.1	0.03	8×10^{9}	Ni-Si-Cr Ni-Si-Zr Ni-Si-Cr-Zr	0.3	6×10^{10}	0.1	855	38	1.5	1.0	10
This invention 1-3	B=0.008	0.04	1×10^{10}	Ni-Si-B	0.8	2×10^{9}	5	833	40	1.5	1.0	12
This invention 1-4	Fe=0.15 P=0.09	0.08	2×10^{7}	Ni-Si-Fe Ni-Si-Fe-P	0.2	1×10^{5}	200	821	40	1.5	1.0	11
This invention 1-5	MM=0.008	0.09	7×10^{7}	Ni-Si-MM	0.5	3×10^{6}	25	833	39	1.5	1.0	10
This invention 1-6	Ti=0.2	0.05	5×10^{9}	Ni-Si-Ti	0.2	2×10^{3}	250000	882	33	1.5	1.0	7
This invention 1-7	O=0.006	0.04	3×10^{9}	Ni-Si-O	0.8	7×10^{2}	430000	832	37	1.5	1.0	11
This invention 1-8	Be=0.01	0.05	6×10^{9}	Ni-Si-Be	0.5	4×10^{7}	150	855	39	1.0	1.0	12
This invention 1-9	Cr=0.3 Hf=0.2	0.02	7×10^{10}	Ni-Si-Cr Ni-Si-Hf Ni-Si-Cr-Hf	0.7	4×10^{8}	175	852	37	1.0	1.0	11
This invention 1-10	C=0.009	0.09	3×10^{8}	Ni-Si-C	0.5	3×10^{3}	10000	830	41	1.5	1.0	12
This invention 1-11	N=0.01	0.07	2×10^{8}	Ni-Si-N	0.9	5×10^{5}	400	820	38	1.0	1.0	12
This invention 1-12	Mn=0.2	0.08	4×10^{9}	Ni-Si-Mn	0.5	5×10^{7}	80	842	38	1.0	1.0	13
This invention 1-13	In=0.49 Cr=0.1	0.06	5×10^{9}	Ni-Si-In Ni-Si-Cr Ni-Si-In-Cr	0.3	2×10^{8}	25	845	36	1.0	1.0	12
This invention 1-14	Al=0.3	0.08	8×10^{8}	Ni-Si-Al	0.02	2×10^{6}	400	839	37	1.0	1.0	10
This invention 1-15	Co=0.2	0.04	7×10^{9}	Ni-Si-Co	0.7	4×10^{7}	175	862	39	1.0	1.0	9
Comparative example 1-1	B=1.1	1.25	2×10^{6}	Ni-Si-B	2.2	2×10^{3}	1000	789	40	2.0	1.5	22

(continued)

	Component	Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	Size	Density	Composition	Size	Density				GW	BW	
	mass%	µm	/mm^2	Compound	µm	/mm^2		MPa	%IACS	R/t	R/t	%
Comparative example 1-2	Fe=0.002	0.04	3x10^7	Ni-Si-Fe	0.005	3x10^3	10000	812	43	2.0	2.0	27
Comparative example 1-3	P=1.2	0.06	6x10^9	Ni-Si-P	2.4	2x10^3	3000000	812	36	2.0	2.0	23
Comparative example 1-4	C=0.005	0.03	4x10^9	Ni-Si-C	0.007	1x10^8	40	845	39	2.5	2.0	28
Comparative example 1-5	Cr=0.5	0.04	5x10^9	Ni-Ti-Cr	0.003	5x10^9	1	854	38	2.0	2.0	35
Comparative example 1-6	Be=0.05	0.03	7x10^{10}	Ni-Ti-Be	0.007	6x10^7	1200	809	37	2.0	2.0	21

(Example 7)

[0056] With respect to the copper alloys containing Ni, Si, and elements in the given amounts as shown in Table 12, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1. The contents of Ni and Si were as follows: 3.5 mass% of Ni and 0.8 mass% of Si in the samples of Examples according to the present invention Nos. 2-4 and 2-11; 4.0 mass% of Ni and 0.95 mass% of Si in the sample of Example according to the present invention No. 2-2; and 3.8 mass% of Ni and 0.86 mass% of Si in the samples of other Examples according to the present invention and Comparative examples. The production and measurement methods for the samples were also performed in the same manner as in Example 1. Further, the stress relaxation resistance was evaluated in the same manner as in Example 6.
As is apparent from the results in Table 12, the samples according to the present invention each have excellent properties with respect to the mechanical strength, electrical conductivity, bending property, and stress relaxation resistance. In particular, in the examples according to the present invention, by making the grain size of Y within the range from 0.05 to 0.9 μm, it was possible to attain a stress relaxation ratio of 14% or less, while maintaining excellent mechanical strength, electrical conductivity, and bending property. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable, for example, for materials of terminals and connectors. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property. Contrary to the above, since the values of the precipitates Y were outside of the range of from 0.01 to 2.0 μm, the samples in Comparative examples each were poor in the stress relaxation ratio of 21% or more.

[0057] [Table 12]

Table 12

	Component		Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	β	Size	Density	Composition	Size	Density				GW	BW	
	mass%	mass%	μm	/mm^{2}	Compound	μm	/mm^{2}		MPa	%IACS	R/t	R/t	%
This invention 2-1	Cr=0.2	Ti=0.01	0.04	2 x 10^{9}	Ni-Cr-Ti	0.3	3 x 10^{7}	70	851	37	1.0	1.0	9
This invention 2-2	Cr=0.1	Zr=0.2	0.02	4 x 10^{9}	Ni-Cr-Zr	0.2	5 x 10^{10}	0.1	862	39	1.5	1.0	11
This invention 2-3	B=0.01	Mn=0.02	0.05	x 10^{10}	Ni-Mn-B	0.9	5 x 10^{9}	4	839	40	1.5	1.0	12
This invention 2-4	Fe=0.18	P=0.09	0.07	5 x 10^{7}	Ni-Fe-P	0.4	3 x 10^{5}	170	829	40	1.5	1.0	12
This invention 2-5	MM=0.008	O=0.006	0.10	5x10^{7}	Ni-MM-O	0.3	4x10^{6}	13	841	39	1.5	1.0	10
This invention 2-6	Ti=0.2	B=0.02	0.04	6 x 10^{9}	Ni-Ti-B	0.5	5 x 10^{3}	1200000	843	33	1.5	1.0	8
This invention 2-7	O=0.004	Cr=0.3	0.03	2x10^{9}	Ni-Cr-O	0.3	2x10^{2}	10000000	833	38	1.5	1.0	12
This invention 2-8	Be=0.02	Al=0.02	0.06	7 x 10^{9}	Ni-Be-Al	0.6	7 x 10^{7}	100	834	39	1.0	1.0	12
This invention 2-9	Cr=0.45	Hf=0.1	0.03	8 x 10^{10}	Ni-Cr-Hf	0.6	7 x 10^{8}	115	857	37	1.0	1.0	11
This invention 2-10	C=0.009	Ti=0.03	0.08	2 x 10^{8}	Ni-Ti-C	0.6	3 x 10^{3}	67000	834	41	1.5	1.0	12
This invention 2-11	N=0.01	S=0.006	0.08	7 x 10^{8}	Ni-N-S	0.4	4 x 10^{5}	1750	825	39	1.0	1.0	12
This invention 2-12	Mn=0.2	Cr=0.3	0.09	8 x 10^{9}	Ni-Mn-Cr	0.6	7 x 10^{7}	115	846	40	1.0	1.0	14
This invention 2-13	In=0.2	Cr=0.5	0.09	9 x 10^{9}	Ni-In-Cr	0.2	2 x 10^{8}	45	848	36	1.0	1.0	13

(continued)

	Component		Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	β	Size	Density	Composition	Size	Density				GW	BW	
	mass%	mass%	μm	/mm^2	Compound	μm	/mm^2		MPa	%IACS	R/t	R/t	%
This invention 2-14	Al=0.3	P=0.03	0.03	6×10^8	Ni-Al-P	0.05	3×10^6	200	846	38	1.0	1.0	10
This invention 2-15	Co=0.2	Cr=0.3	0.02	7×10^8	Ni-Co-Cr	0.30	7×10^6	100	859	38	1.0	1.0	11
Comparative example 2-1	B=1.2	Mn=0.19	2.25	6×10^6	Ni-B-Mn	4.2	6×10^3	100	796	40	2.0	1.5	23
Comparative example 2-2	Fe=0.002	P=0.001	0.09	6×10^7	Ni-Fe-P	0.005	5×10^3	12000	816	43	2.0	2.0	27
Comparative example 2-3	P=0.3	Fe=0.4	0.03	9×10^9	Ni-Fe-P	3.3	3×10^3	3000000	815	36	2.0	2.0	23
Comparative example 2-4	C=0.05	Ti=0.4	0.02	8×10^9	Ni-C-Ti	0.005	3×10^8	25	852	40	2.5	2.0	29
Comparative example 2-5	Cr=0.45	P=0.03	0.03	3×10^9	Ni-Cr-P	0.002	7×10^9	0.4	854	38	2.0	2.0	35
Comparative example 2-6	Zr=0.4	Fe=0.2	0.07	8×10^{10}	Ni-Fe-Zr	0.009	7×10^7	1150	813	36	2.0	2.0	21

(Example 8)

[0058] With respect to the copper alloys containing Ni, Si, and elements in the given amounts as shown in Table 13, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1. The contents of Ni and Si were as follows: 3.5 mass% of Ni and 0.8 mass% of Si in the samples of Examples according to the present invention Nos. 3-4 and 3-11; 4.0 mass% of Ni and 0.95 mass% of Si in the samples of Examples according to the present invention Nos. 3-8 and 3-15; and 3.8 mass% of Ni and 0.86 mass% of Si in the samples of other Examples according to the present invention and Comparative examples. The production and measurement methods for the samples were also performed in the same manner as in Example 1. Further, the stress relaxation resistance was evaluated in the same manner as in Example 6.

As is apparent from the results in Table 13, the samples according to the present invention each have excellent properties with respect to the mechanical strength, electrical conductivity, bending property, and stress relaxation resistance. In particular, in the examples according to the present invention, by making the grain size of Y within the range from 0.2 to 0.6 μm, it was possible to attain a stress relaxation ratio of 15% or less, while maintaining excellent mechanical strength, bending property, and electrical conductivity. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable, for example, for materials of terminals and connectors. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property. Contrary to the above, since the values of the precipitates Y were outside of the range of from 0.01 to 2.0 μm, the samples in Comparative examples each were poor in the stress relaxation ratio of 21% or more.

[0059] [Table 13]

Table 13

	Component		Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	β	Size	Density	Composition	Size	Density				GW	BW	
	mass%	mass%	μm	/mm^2	Compound	μm	/mm^2		MPa	%IACS	R/t	R/t	%
This invention 3-1	Cr=0.45	Ti=0.2	0.04	5x10^9	Si-Cr-Ti	0.2	6x107	85	854	38	1.0	1.0	10
This invention 3-2	Cr=0.3	Zr=0.15	0.01	2x10^9	Si-Cr-Zr	0.3	4x10^{10}	0.05	867	40	1.5	1.0	11
This invention 3-3	B=0.008	Mn=0.2	0.03	4 x 10^{10}	Si-Mn-B	0.6	9 x 10^9	4	844	41	1.5	1.0	13
This invention 3-4	Fe=0.28	P=0.19	0.06	3 x 10^7	Si-Fe-P	0.5	4 x 10^5	75	834	41	1.5	1.0	13
This invention 3-5	MM=0.005	O=0.005	0.10	4x10^7	Si-MM-O	0.4	1x10^6	40	843	40	1.5	1.0	11
This invention 3-6	Ti=0.25	B=0.03	0.03	3x10^9	Si-Ti-B	0.2	9x10^3	330000	866	33	1.5	1.0	8
This invention 3-7	O=0.004	Cr=0.45	0.02	9 x 10^9	Si-Cr-O	0.6	8 x 10^2	11250000	839	39	1.5	1.0	13
This invention 3-8	Be=0.008	Al=0.012	0.02	5x10^9	Si-Be-Al	0.4	2x10^7	250	888	41	1.0	1.0	13
This invention 3-9	Cr=0.3	Hf=0.05	0.02	6 x 10^{10}	Si-Cr-Hf	0.5	5 x 10^8	120	867	37	1.0	1.0	12
This invention 3-10	C=0.01	Ti=0.06	0.07	5x10^8	Si-Ti-C	0.2	6 x 10^3	83000	838	43	1.5	1.0	13
This invention 3-11	N=0.007	S=0.008	0.05	9x10^8	Si-N-S	0.4	5 x 10^5	1800	828	39	1.0	1.0	12
This invention 3-12	Mn=0.25	Cr=0.5	0.04	8 x 10^9	Si-Mn-Cr	0.3	2 x 10^7	400	848	40	1.0	1.0	15
This invention 3-13	In=0.4	Cr=0.3	0.09	6 x 10^9	Si-In-Cr	0.2	2 x 10^8	30	853	36	1.0	1.0	13

(continued)

	Component		Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	β	Size	Density	Composition	Size	Density				GW	BW	
	mass%	mass%	μm	/mm^2	Compound	μm	/mm^2		MPa	%IACS	R/t	R/t	%
This invention 3-14	Al=0.1	P=0.06	0.02	4×10^8	Si-Al-P	0.4	3×10^6	130	848	38	1.0	1.0	11
This invention 3-15	Co=0.2	Cr=0.15	0.03	3×10^{10}	Si-Co-Cr	0.3	9×10^8	35	873	32	1.0	1.0	8
Comparative example 3-1	B=0.2	Mn=0.5	0.37	9×10^6	Si-B-Mn	3.2	8×10^3	1100	805	41	2.0	1.5	23
Comparative example 3-2	Fe=0.02	P=0.008	0.07	3×10^7	Si-Fe-P	0.001	3×10^3	10000	818	44	2.0	2.0	28
Comparative example 3-3	P=0.04	Fe=0.1	0.01	1×10^9	Si-Fe-P	3.3	6×10^3	170000	823	37	2.0	2.0	24
Comparative example 3-4	C=0.005	Ti=0.35	0.05	2×10^9	Si-C-Ti	0.005	1×10^8	20	856	41	2.5	2.0	29
Comparative example 3-5	Cr=0.25	P=0.3	0.01	3×10^9	Si-Cr-P	0.004	4×10^9	0.8	859	39	2.0	2.0	36
Comparative example 3-6	Zr=0.24	Fe=0.12	0.06	4×10^{10}	Si-Fe-Zr	0.005	2×10^7	2000	821	37	2.0	2.0	21

(Example 9)

[0060] With respect to the copper alloys containing Ni, Si, and elements in the given amounts as shown in Table 14, with the balance being made of Cu and inevitable impurities, the test was conducted in the same manner as in Example 1. The contents of Ni and Si were as follows: 3.5 mass% of Ni and 0.8 mass% of Si in the samples of Examples according to the present invention Nos. 4-1 and 4-4; 4.0 mass% of Ni and 0.95 mass% of Si in the samples of Examples according to the present invention Nos. 4-2 and 4-9; and 3.8 mass% of Ni and 0.86 mass% of Si in the samples of other Examples according to the present invention and Comparative examples. The production and measurement methods for the samples were also performed in the same manner as in Example 1. Further, the stress relaxation resistance was evaluated in the same manner as in Example 6.
As is apparent from the results in Table 14, the samples according to the present invention each have excellent properties with respect to the mechanical strength, electrical conductivity, bending property, and stress relaxation resistance. In particular, in the examples according to the present invention, by making the grain size of Y within the range from 0.1 to 0.6 μm, it was possible to attain a stress relaxation ratio of 15% or less, while maintaining excellent mechanical strength, bending property, and electrical conductivity. Based on the above, the copper alloys of the examples according to the present invention can be considered to be favorable, for example, for materials of terminals and connectors. Further, the copper alloys of the examples according to the present invention are also excellent in other properties, such as spring property. Contrary to the above, since the values of the precipitates Y were outside of the range of from 0.01 to 2.0 μm, the samples in Comparative examples each were poor in the stress relaxation ratio of 21% or more.

[0061] [Table 14]

Table 14

	Component			Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	β	γ	Size	Density	Composition	Size	Density				GW	BW	
	mass%	mass%	mass%	µm	/mm^{2}	Compound	µm	/mm^{2}		MPa	%IACS	R/t	R/t	%
This invention 4-1	Cr=0.5	Ti=0.1	Zr=0.2	0.02	1x10^{9}	Zr-Cr-Ti	0.1	1x10^{7}	100	822	39	1.0	1.0	10
This invention 4-2	Cr= 0.25	Zr=0.1	P= 0.05	0.02	5x10^{9}	P-Cr-Zr	0.2	5x10^{10}	0.1	877	40	1.5	1.0	12
This invention 4-3	B= 0.01	Mn= 0.15	P=0.2	0.06	9x10^{10}	P-Mn-B	0.5	2x10^{9}	45	846	41	1.5	1.0	13
This invention 4-4	MM= 0.005	O= 0.005	S= 0.005	0.08	5 x 10^{7}	MM-O-S	0.4	1 x 10^{6}	50	846	40	1.5	1.0	11
This invention 4-5	Ti=0.5	B= 0.004	Cr=0.3	0.05	4 x 10^{9}	Cr-Ti-B	0.6	4 x 10^{3}	1000000	844	33	1.5	1.0	9
This invention 4-6	O= 0.003	Cr=0.4	Zr= 0.12	0.20	3 x 10^{9}	Zr-Cr-O	0.5	3 x 10^{2}	10000000	841	39	1.5	1.0	13
This invention 4-7	Be= 0.003	Al= 0.01	Hf=0.2	0.05	4x10^{9}	Hf-Be-Al	0.1	8x10^{7}	50	846	41	1.0	1.0	14
This invention 4-8	Cr=0.2	Hf= 0.15	Zr= 0.49	0.04	8 x 10^{10}	Zr-Cr-Hf	0.2	5 x 10^{8}	160	872	37	1.0	1.0	12
This invention 4-9	C= 0.03	Ti= 0.08	S= 0.003	0.06	2 x10^{8}	Ti-C-S	0.6	3 x 10^{3}	67000	847	43	1.5	1.0	13
This invention 4-10	N= 0.008	S= 0.008	O= 0.002	0.04	4 x10^{8}	O-N-S	0.5	4 x 10^{5}	100	838	40	1.0	1.0	13
This invention 4-11	Mn=0.5	Cr=0.1	Zr=0.3	0.01	3x10^{9}	Zr-Mn-Cr	0.3	3x10^{7}	400	852	40	1.0	1.0	15
This invention 4-12	In=0.3	Cr=0.3	Zr=0.3	0.03	8 x 10^{9}	Zr-In-Cr	0.4	4 x 10^{8}	20	862	38	1.0	1.0	13

(continued)

	Component			Precipitate X		Precipitate Y			Number of X/ number of Y	TS	EC	Bending property		SRR
	α	β	γ	Size	Density	Composition	Size	Density				GW	BW	
	mass%	mass%	mass%	μm	/mm^{2}	Compound	μm	/mm^{2}		MPa	%IACS	R/t	R/t	%
This invention 4-13	Al= 0.25	P=0.08	Ti= 0.49	0.04	8x10^{8}	Ti-Al-P	0.4	8x10^{6}	100	849	39	1.0	1.0	12
This invention 4-14	Co=0.1	Cr=0.2	Zr=0.3	0.03	3 x 10^{10}	Co-Mn-Cr	0.3	1 x 10^{8}	300	852	40	1.0	1.0	15
Comparative example 4-1	B= 0.0002	Mn=0.5	P=0.6	0.55	4x10^{6}	Mn-B-P	3.6	3x10^{3}	130	807	42	2.0	1.5	24
Comparative example 4-2	C= 0.008	Ti=0.2	Cr=0.2	0.01	8x10^{9}	Cr-C-Ti	0.009	2 x 10^{8}	40	860	41	2.5	2.0	30
Comparative example 4-3	Cr= 0.25	P=0.3	Al=0.2	0.04	9 x 10^{9}	Al-Cr-P	0.006	8 x 10^{9}	1.1	860	39	2.0	2.0	37
Comparative example 4-4	Zr= 0.24	Fe= 0.12	S= 0.003	0.02	5 x 10^{10}	Fe-Zr-S	0.004	5 x 10^{7}	1000	829	38	2.0	2.0	22

INDUSTRIAL APPLICABILITY

[0062] The copper alloy of the present invention can be preferably applied, for example, to lead frame, connector, or terminal materials for electric and electronic instrument materials, e.g. connector/terminal materials, relays, and switches for electric and electronic instruments, such as on-vehicle/automobile electric and electronic instruments.
Having described our invention as related to the present embodiments, it is our intention that the present invention not be limited by any of the details of the description, unless otherwise specified, but rather be construed broadly within its spirit and scope as set out in the accompanying claims.
This non-provisional application claims priority under 35 U.S.C. § 119 (a) on Patent Application No. 2005-055144 filed in Japan on February 28, 2005, and Patent Application No. 2005-055147 filed in Japan on February 28, 2005, each of which is entirely herein incorporated by reference.

Claims

1. A copper alloy, having: a precipitate Y composed of Ni and/or Si, and at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be; and a precipitate X composed of Ni and Si, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm.

2. The copper alloy according to Claim 1, wherein the grain diameter of the precipitate Y is 0.02 to 0.9 μm.

3. A copper alloy, having: a precipitate X composed of Ni and Si; and at least one precipitate selected from the group consisting of a precipitate Y1 composed of Ni, Si, and Cr, a precipitate Y2 composed of Ni, Si, and Co, a precipitate Y3 composed of Ni, Si, and Zr, and a precipitate Z composed of Ni, Si, and B, wherein a grain diameter of the at least one precipitate selected from the group consisting of the precipitates Y1, Y2, Y3, and Z is 0.1 to 2 μm.

4. A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of Ni, Si, and at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm.

5. A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of Ni, and at least two or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm.

6. A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of Si, and at least two or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm.

7. A copper alloy, comprising: Ni 2.0 to 5.0 mass%, Si 0.3 to 1.5 mass%, at least one or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be each in an amount of 0.005 to 1.0 mass%, with a balance being Cu and inevitable impurities; said copper alloy having a precipitate X composed of Ni and Si; and a precipitate Y composed of at least three or more selected from the group consisting of B, Al, As, Hf, Zr, Cr, Ti, C, Fe, P, In, Sb, Mn, Ta, V, S, O, N, Misch metal (MM), Co, and Be, wherein a grain diameter of the precipitate Y is 0.01 to 2 μm.

8. The copper alloy according to any one of Claims 1 to 7, wherein the melting point of the precipitate Y is higher than a solid solution treatment temperature.

9. The copper alloy according to any one of Claims 1 to 8, wherein the number of precipitates X per mm^2 is 20 to 2,000

times the number of precipitates Y per mm^2.

10. The copper alloy according to any one of Claims 1 to 9, wherein the number of precipitates X is 10^8 to 10^{12} per mm^2, and the number of precipitates Y is 10^4 to 10^8 per mm^2.

11. The copper alloy according to any one of Claims 1 to 10, wherein a composition of the copper alloy further comprises at least one or more selected from Sn 0.1 to 1.0 mass%, Zn 0.1 to 1,0 mass%, and Mg 0.05 to 0.5 mass%.

12. The copper alloy according to any one of Claims 1 to 11, which has a stress relaxation ratio of less than 20%.

13. The copper alloy according to any one of Claims 1 to 12, which is for use as a material of an electric or electronic instrument.

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2006/303738

A. CLASSIFICATION OF SUBJECT MATTER
C22C9/06(2006.01), *C22F1/00*(2006.01), *C22F1/08*(2006.01)

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, C22F1/00-3/02

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	1996-2006
Kokai Jitsuyo Shinan Koho	1971-2006	Toroku Jitsuyo Shinan Koho	1994-2006

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.
X	JP 63-076839 A (The Furukawa Electric Co., Ltd.), 07 April, 1988 (07.04.88), Claims; tables 1, 2 (Family: none)	1-13
X	JP 64-028337 A (The Furukawa Electric Co., Ltd.), 30 January, 1989 (30.01.89), Claims; tables 1, 2 (Family: none)	1-13
P,X	JP 2005-344163 A (The Furukawa Electric Co., Ltd.), 15 December, 2005 (15.12.05), Claims; examples (Family: none)	1-5,8-13

☐ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:
"A" document defining the general state of the art which is not considered to be of particular relevance
"E" earlier application or patent but published on or after the international filing date
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"O" document referring to an oral disclosure, use, exhibition or other means
"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
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"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
"&" document member of the same patent family

Date of the actual completion of the international search 29 May, 2006 (29.05.06)	Date of mailing of the international search report 06 June, 2006 (06.06.06)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

Form PCT/ISA/210 (second sheet) (April 2005)

REFERENCES CITED IN THE DESCRIPTION

Patent documents cited in the description

- JP 11043731 A **[0006]**
- JP 2003082425 A **[0006]**
- JP 2005055144 A **[0062]**
- JP 2005055147 A **[0062]**