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(54) **CU-NI-SI-BASED ALLOY FOR ELECTRONIC MATERIAL**

(57) An object of the present invention is to provide a Corson alloy having significantly improved characteristics, i.e. high strength and high electrical conductivity, by enhancing the effect of addition of Cr to a Cu-Ni-Si system alloy. There is provided a copper alloy for electronic materials comprising 1.0-4.5% by mass Ni, 0.50-1.2% by mass Si, 0.003-0.3% by mass Cr wherein the weight ratio of Ni to Si satisfies the expression: $3 \leq \text{Ni}/$

$\text{Si} \leq 5.5$, and the balance being Cu and incidental impurities, wherein particles of Cr-Si compounds having a size of 0.1 μm to 5 μm are dispersed in the alloy and the dispersed particles having an atomic concentration ratio of Cr to Si of 1 to 5 and a dispersion density of no more than $1 \times 10^6/\text{mm}^2$.

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Description**FIELD OF THE INVENTION**

[0001] The present invention relates to precipitation hardening copper alloys, and in particular, to Cu-Ni-Si-Cr system alloys suitable for use in components for various electronic devices.

BACKGROUND OF THE INVENTION

[0002] Copper alloys for electronic materials used in components for various electronic devices such as lead frames, connectors, pins, terminals, relays, and switches must satisfy both high strength and high electrical conductivity (or high thermal conductivity) as basic characteristics. Recent rapid advances of high integration and reductions in size and thickness of electronic components have accelerated requirements for higher performances of copper alloys used in components for electronic devices.

[0003] In recent years, in consideration of high strength and high electrical conductivity of copper alloys for electronic materials, the use of precipitation hardening copper alloys has increased, in place of traditional solid solution strengthened copper alloys such as phosphor bronze and brass. In the precipitation hardening copper alloys, age hardening of supersaturated solid solution after solution treatment facilitates uniform dispersion of fine precipitates and thus an increase in strength of the alloys. It also leads to a decrease in amount of solute elements in copper matrix and thus an improvement in electrical conductivity. The resulting materials have superior mechanical properties such as strength and spring properties, as well as high electrical and thermal conductivities.

[0004] Among precipitation hardening copper alloys, Cu-Ni-Si copper alloys known as Corson alloys are typical copper alloys having compatibility of relatively high electrical conductivity and strength, proper stress relaxation, and excellent bendability. Corson alloys are now being actively developed in the industry. In such copper alloys, fine particles of a NiSi intermetallic compound are precipitated in a copper matrix, thereby improving strength and electrical conductivity.

[0005] The precipitation of a NiSi intermetallic compound generally has a stoichiometric composition. For example, Japanese Unexamined Patent Application Publication No. 2001-207229 discloses that satisfactory electrical conductivity is achieved by bringing the mass ratio Ni/Si in an alloy close to the mass composition ratio of the intermetallic compound Ni_2Si $[(\text{Ni atomic weight}) \times 2 / (\text{Si atomic weight}) \times 1]$, i.e. a weight concentration ratio of Ni/Si in the range of 3 to 7.

[0006] Although characteristics may be improved by bringing the mass ratio Ni/Si close to the mass composition ratio of the intermetallic compound Ni_2Si $[(\text{Ni atomic weight}) \times 2 / (\text{Si atomic weight}) \times 1]$ as mentioned in Japanese Unexamined Patent Application Publication No. 2001-207229, the presence of an excess amount of Si leads to some reductions in electrical conductivity. A possible countermeasure to increase the electrical conductivity is addition of elements that form compounds with excess Si. Cr is one of these elements, and forms Cr-containing Cu-Ni-Si system alloys.

[0007] Examples of the Cu-Ni-Si system alloys containing Cr as an alloy element are disclosed in Japanese Patent Nos. 2862942 and 3049137. Japanese Patent No. 2862942 discloses a method of heat treatment of a Corson alloy containing 1.5-4.0% by weight of Ni, 0.35-1.0% by weight of Si, optionally 0.05-1.0% by weight of at least one metal selected from the group consisting of Zr, Cr, and Sn, and the balance being Cu and incidental impurities, wherein the Corson alloy is heated (or cooled) in the temperature range of 400 to 800°C, so as to reduce the tensile thermal strain of the Corson alloy to a level not exceeding 1×10^{-4} . The patent states that the method can prevent an ingot from cracking during the heat treatment.

[0008] Japanese Patent No. 3049137 discloses a high strength copper alloy containing 2-5% by weight of Ni, 0.5-1.5% by weight of Si, 0.1-2% by weight of Zn, 0.01-0.1% by weight of Mn, 0.001-0.1% by weight of Cr, 0.001-0.15% by weight of Al, 0.05-2% by weight of Co, not more than 15 ppm of S as an impurity, and the balance being Cu and incidental impurities. This copper alloy exhibits excellent bendability. This patent states that Cr is an element which reinforces grain boundaries in an ingot and leads to an improvement in hot workability. It also states that a Cr content exceeding 0.1% by weight causes oxidation of molten metal and poor casting performance. In addition, it states that the copper alloy is covered with charcoal in a crytol furnace to be melted and cast in the atmosphere.

[0009] A compound of Cr and Si is disclosed in Japanese Unexamined Patent Application Publication No. 2005-113180. This patent refers to the hot working temperature and heat treatment temperature for age hardening of an ingot of a copper alloy having excellent etching and punching workability for electronic devices. The copper alloy contains 0.1-0.25% by weight of Cr, 0.005-0.1% by weight of Si, 0.1-0.5% by weight of Zn, 0.05-0.5% by weight of Sn, and the balance being Cu and incidental impurities, wherein the weight ratio Cr/Si is in the range of 3 to 25, particles of Cr-Si compounds having a size of 0.05 μm to 10 μm are present in a number density of 1×10^3 to $5 \times 10^5/\text{mm}^2$ in the copper matrix while particles of Cr compounds (other than the Cr-Si compound) having a size greater than 10 μm are not present. According to this method, both etching and punching workability are preferably available.

SUMMARY OF THE INVENTION

[0010] Rapid advances of high integration and reductions in size and thickness of electronic components in recent years have also placed a requirement on Cr-containing Cu-Ni-Si system alloys to have significantly improved performance. In Japanese Unexamined Patent Application Publication No. 2001-207229, Cr is not added and the excess Ni and Si actually reduce electrical conductivity in some degree. This means the significant progress in performance is unfulfilled yet. Although Cr is added in Cu-Ni-Si system alloys in Japanese Patent Nos. 2862942 and 3049137, it is added for solid solution hardening in Japanese Patent No. 2862942 and for an improvement in hot workability in Japanese Patent No. 3049137. No description of Cr-Si compounds, which is a key component of the present invention, is found in these documents. Accordingly, these patent documents do not suggest the solution achieved by the present invention.

[0011] Although Japanese Unexamined Patent Application Publication No. 2005-113180 discloses that etching and punching workabilities are improved by controlling the number density and size of the Cr-Si compounds, consideration is focused on the conditions for the formation of the Cr-Si compounds and no consideration is paid for the formation of NiSi compounds because no Ni is added. Accordingly, Japanese Unexamined Patent Application Publication No. 2005-113180 also does not suggest the solution achieved by the present invention.

[0012] An object of the present invention is to provide a Corson alloy having significantly improved characteristics, i.e. high strength and high electrical conductivity, by enhancing the effect of Cr contained in a Cu-Ni-Si system alloy.

[0013] Through extensive research for solving the problem, the inventors have accomplished an invention as described below. In a Cu-Ni-Si system alloy, the Si content is in excess of the Ni content so that nickel silicide is surely precipitated from the contained Ni in order to improve the strength, while the excess Si is combined with the contained Cr to achieve high conductivity of the alloy. The essence of the present invention is to control the excess growth of particles of Cr-Si compounds so as to prevent a shortage of Si, which combines with Ni. In particular, the inventors have found that the control of the temperature and cooling rate of the heat treatment can enhance such effects, through investigation on the preferred composition, size, and number density of particles of the Cr-Si compounds.

[0014] The present invention includes the following Aspects:

(1) A copper alloy for electronic materials, comprising 1.0-4.5% by mass Ni, 0.50-1.2% by mass Si, 0.003-0.3% by mass Cr (wherein the weight ratio of Ni to Si satisfies the expression: $3 \leq \text{Ni/Si} \leq 5.5$), and the balance being Cu and incidental impurities, wherein particles of Cr-Si compounds having a size of 0.1 μm to 5 μm are dispersed in the alloy, the dispersed particles having an atomic concentration ratio of Cr to Si of 1 to 5 and a dispersion density of no more than $1 \times 10^6/\text{mm}^2$.

(2) The copper alloy for electronic materials according to Aspect (1), wherein the dispersion density of the particles of the Cr-Si compounds having a size of 0.1 μm to 5 μm is higher than $1 \times 10^4/\text{mm}^2$.

(3) The copper alloy for electronic materials according to Aspect (1) or (2), further comprising 0.05-2.0% by mass of at least one element selected from Sn and Zn.

(4) The copper alloy for electronic materials according to any one of Aspects (1) to (3), further comprising 0.001-2.0% by mass of at least one element selected from Mg, Mn, Ag, P, As, Sb, Be, B, Ti, Zr, Al, Co and Fe.

(5) A wrought copper product comprising the copper alloy according to any one of Aspects (1) to (4).

(6) A component for electronic devices, comprising the copper alloy according to any one of Aspects (1) to (4).

[0015] The present invention can provide the Corson copper alloy having significantly improved strength and electrical conductivity suitable for electronic materials due to the positive effect of Cr, which is an element contained in the alloy.

DESCRIPTION OF THE PREFERRED EMBODIMENTS**Amounts of Ni and Si to be added**

[0016] Ni and Si form nickel silicides (e.g. Ni_2Si) as an intermetallic compound through suitable heat treatment, resulting in high strength without a decrease in conductivity. The mass ratio of Ni to Si is preferably close to the stoichiometric ratio as described above, i.e. $3 \leq \text{Ni/Si} \leq 5.5$, more preferably $3.5 \leq \text{Ni/Si} \leq 5.0$.

[0017] However, even if the ratio Ni/Si is within the range, desired strength is not achieved at a Si content of less than 0.5% by mass. Furthermore, a Si content of more than 1.2% by mass is not preferred because of significantly reduced conductivity and poor hot workability due to formation of a liquid phase in a segregation region, despite enhanced strength. As a result, the preferred Si content is in the range of 0.5% to 1.2% by mass, preferably 0.5% to 0.8% by mass. The amount of Ni to be added may be determined so as to satisfy the preferable ratio described above. In view of balance with the Si content, the suitable Ni content is in the range of 2.5% to 4.5% by mass, preferably 3.2% to 4.2% by mass, more preferably 3.5% to 4.0% by mass.

Amount of Cr to be added

[0018] In general Cu-Ni-Si system alloys, increased concentrations of Ni and Si raise the total number of precipitated particles, and thus enhance strength through precipitation strengthening. Such increased concentrations, however, are accompanied by an increased amount of solid solution that does not contribute to precipitation. This causes a reduction in conductivity at a maximum strength, regardless of an increase in the maximum strength after age precipitation. In this regard, when 0.003% to 0.3% by mass of, preferably 0.01 % to 0.1 % by mass of Cr is added to the Cu-Ni-Si system alloy, higher conductivity can be achieved without a reduction in strength compared to a Cu-Ni-Si system alloy having the same Ni-Si concentrations. Furthermore, a higher yield can be achieved due to improved hot workability,.

[0019] Regarding the composition of particles precipitated in the Cr-containing Cu-Ni-Si system alloy, particles primarily composed of elemental Cr having a bcc structure are readily precipitated as well as particles of Cr-Si compounds. Since Cr can easily precipitate chromium silicides (e.g. Cr_3Si) in the copper matrix through proper heat treatment, the dissolved Si component, which has not precipitated in the form such as Ni_2Si during a combined process of solution treatment, cold rolling and aging, can be precipitated as Cr-Si compounds. This process can suppress a reduction in conductivity caused by the dissolved Si and thus achieve high conductivity without a reduction in strength.

[0020] A low concentration of Si in Cr particles leads to residual Si in the matrix, resulting in a reduction in conductivity. On the other hand, a high concentration of Si in Cr particles causes a decreased concentration of Si contributing to precipitation of particles of a NiSi compound, resulting in a reduction in strength. Furthermore, a high concentration of Si in Cr particles accelerates formation of coarse Cr-Si particles, resulting in decreases in bendability and fatigue strength. Moreover, a lower cooling rate after solution treatment and excess heating treatment for aging cause coarsening of particles of the Cr-Si compounds. This causes a decrease in Si concentration necessary for formation of a NiSi compound and thus precludes the formation of a NiSi compound contributing to strength. This is because diffusion rates in Cu of Si and Cr are higher than that of Ni, which accelerates coarsening of particles of the Cr-Si compounds. The precipitation rate of Cr-Si compounds is thus higher than that of NiSi compounds.

[0021] The composition, size and density of particles of the Cr-Si compounds can, therefore, be controlled by regulating the cooling rate after solution treatment and avoiding severer aging conditions such as higher temperature and longer time than the optimum conditions for maximum strength. Consequently, the Cr concentration should be 0.003% by mass to 0.3% by mass, and the atomic ratio of Cr to Si in Cr-Si compounds should be in the range of 1 to 5.

[0022] Since Cr is preferentially precipitated at crystal grain boundaries in the cooling process after melting and casting, it can strengthen the grain boundaries. As a result, cracking during hot working can be reduced, and thus a high yield can be achieved. Although Cr precipitated at grain boundaries after melting and casting is redissolved during the solution treatment, it forms silicides during the subsequent age precipitation process. In general Cu-Ni-Si system alloys, part of the added Si does not contribute to age precipitation and remains dissolved in the matrix, obstructing an increase in conductivity. Since the addition of Cr, which is an element to form silicides, leads to further precipitation of silicides and a reduction in dissolved Si, the conductivity can be increased without a reduction in strength, compared to conventional Cu-Ni-Si system alloys.

Size and dispersion density of particles of Cr-Si compounds

[0023] The size of particles of the Cr-Si compounds has an effect on bendability and fatigue strength. When the particles of the Cr-Si compounds have a size of greater than $5\text{ }\mu\text{m}$ or when the dispersion density of particles of the Cr-Si compounds having a size in the range of $0.1\text{ }\mu\text{m}$ to $5\text{ }\mu\text{m}$ exceeds $1 \times 10^6/\text{mm}^2$, the bendability and the fatigue strength are significantly reduced. Furthermore, since the number density has an effect on the excess and deficiency of the concentration of Si in the matrix, the presence of large particles dispersed in large quantities will become an obstacle to the desired strength. Consequently, the upper limit of the dispersion density is $1 \times 10^6/\text{mm}^2$, preferably $5 \times 10^5/\text{mm}^2$, more preferably $1 \times 10^5/\text{mm}^2$. In addition, it is preferred that the density be more than $1 \times 10^4/\text{mm}^2$, in order to achieve the significant effect of the addition of Cr.

Sn and Zn

[0024] Addition of at least one element selected from Sn and Zn in a total amount of 0.05-2.0% by mass to the Cu-Ni-Si system alloy of the present invention can improve stress relaxation and other characteristics without significant reductions in strength and conductivity. An amount of less than 0.05% by mass leads to insufficient effect of addition. On the other hand, an amount of more than 2.0% by mass causes poor production characteristics such as castability and hot workability and low conductivity of the products. It is therefore preferred that the amount of these elements should be added from 0.05% by mass to 2.0% by mass.

Other elements to be added

[0025] Addition of appropriate amounts of Mg, Mn, Ag, P, As, Sb, Be, B, Ti, Zr, Al, Co and Fe brings about various effects that are complementary to each other, for example, enhanced strength and conductivity, and improved production characteristics such as bendability, plating property, and hot workability of an ingot due to the formation of a fine micro-structure. Accordingly, at least one element selected from these elements may be added as necessary in a total amount of 2.0% by mass or less to the Cu-Ni-Si system alloy of the present invention, to meet required properties. An amount of less than 0.001 % by mass cannot achieve the desired effects. On the other hand, an amount of more than 2.0% by mass causes a significant decrease in conductivity and poor production characteristics. Accordingly, the total amount of the elements to be added is preferably 0.001 to 2.0% by mass, more preferably 0.01 to 1.0% by mass. Incidentally, elements not specified in this specification may be added in a range causing no negative effect on the characteristics of the Cu-Ni-Si system alloy of the present invention.

[0026] The method of producing alloys of the present invention is described below. The Cu-Ni-Si system alloy of the present invention can be produced by any conventional method, except for conditions of solution treatment and aging treatment for control of Ni-Si compounds and Cr-Si compounds. Although no specific explanation would be necessary for those skilled in the art who can select an optimal method depending on the composition and required properties, a typical method is described below for illustrative purposes.

[0027] First, raw materials such as electrolytic copper, Ni, Si, and Cr are melted in a melting furnace in atmosphere to obtain molten metal having a desired composition. Next, this molten metal is cast into an ingot. Through subsequent hot-rolling and repeated processes of cold-rolling and heat treatment, strips and foils having a desired thickness and properties are formed. The heat treatment includes solution treatment and aging treatment. In the solution treatment, the Ni-Si compounds and the Cr-Si compounds are dissolved into the copper matrix while the copper matrix is recrystallized at the same time, during heating at a high temperature of 700 to 1000°C. The hot rolling may combine with the solution treatment.

[0028] The important factors in the solution treatment are a heating temperature and a cooling rate. In conventional methods, the cooling rate after heating was not controlled, and water-cooling using a water tank provided at a furnace outlet or air-cooling in the atmosphere was employed. In that case, the cooling rate easily varied depending on the set heating temperature. The conventional cooling rate varied in a wide range of 1°C/s or less to 10°C/s or more. Consequently, in the conventional cooling, it was difficult to control properties of alloys, such as an alloy of the present invention.

[0029] Preferably the cooling rate is in the range of 1°C/s to 10°C/s. In aging treatment, the Ni-Si compounds and the Cr-Si compounds dissolved during the solution treatment are precipitated as fine particles by heating at a temperature in the range of 350 to 550°C for at least 1 hour, typically for 3 to 24 hours. The strength and conductivity increases through the aging treatment. Before and/or after the aging, cold-rolling may be employed for higher strength. When the cold-rolling is performed after the aging treatment, stress relief annealing (annealing at low temperature) may be performed after the cold-rolling.

[0030] In one embodiment, the Cu-Ni-Si copper alloy of the present invention may have a 0.2% yield strength of not less than 780 MPa and a conductivity of not less than 45% IACS; may further have a 0.2% yield strength of not less than 860 MPa and a conductivity of not less than 43% IACS; or may still further have a 0.2% yield strength of not less than 890 MPa and a conductivity of not less than 40% IACS.

[0031] The Cu-Ni-Si system alloy of the present invention can be shaped into various wrought copper products such as strips, ribbons, pipes, rods and bars. Furthermore, the Cu-Ni-Si system alloy of the present invention can be used in components for electronic devices such as lead frames, connectors, pins, terminals, relays, switches and foils for secondary batteries, which require both high strength and high electrical conductivity (or thermal conductivity).

EXAMPLES

[0032] The following examples are merely illustrative for further understanding of the present invention and its advantages, and not limiting to the disclosure in any way.

[0033] The copper alloys used in Examples of the present invention are copper alloys containing various amounts of Ni, Si and Cr and further containing optional Sn, Zn, Mg, Mn, Co and Ag, as shown in Table 1. The copper alloys used in Comparative Examples are Cu-Ni-Si copper alloys having parameters out of the range of the present invention.

[0034] The copper alloys having various compositions described in Table 1 were melted in a high-frequency melting furnace at 1300°C and each alloy was cast into an ingot having a thickness of 30 mm. Next, this ingot was heated to 1000°C, then was hot-rolled into a plate having a thickness of 10 mm, and was cooled immediately. After the plate was planed for removal of scales to a thickness of 8 mm, it was cold-rolled into a thickness of 0.2 mm. Subsequently, solution treatment was conducted in argon gas atmosphere at a temperature of 800 to 900°C for 120 seconds, depending on the addition amount of Ni and Cr, followed by cooling down to room temperature at various cooling rates. The cooling rate was controlled by varying the flow rate of gas blowing against the sample. The cooling rate was determined by the

measurement of the time required for the sample to be cooled from its attained maximum temperature to 400°C. The cooling rate of the furnace without gas blow was 5°C/s, and the lower cooling rate was set at 1°C/s in the case of cooling along with controlled heating output. After this, the plate was cold-rolled into a thickness of 0.1 mm, and was finally aged in inert atmosphere at 400 to 550°C for 1 to 12 hours depending on the amount of added elements, thereby samples were produced.

[0035] The strength and conductivity of each alloy produced as described above were evaluated. The strength was evaluated by 0.2% yield strength (YS; MPa) measured by a tensile test in the direction of rolling. The electric conductivity (EC; %IACS) was determined from the volume electrical resistivity measured by double bridges. The bendability was evaluated by W bend test using a W-shaped mold at a ratio of the bending radius to the thickness of the sample plate of 1. The evaluation was performed through observation of the bent surface with an optical microscope. For samples where no crack was observed, Rank A was given indicating a satisfactory level in practical use. For samples any crack was observed, Rank F was given. In a fatigue test, symmetrically reversed stress load according to JIS Z 2273 was loaded to determine the fatigue strength (MPa) where the alloy was broken at 10^7 cycles.

[0036] For observation of particles of the Cr-Si compounds by FE-AES, a plate surface of the samples was electropolished. Particles having a size of not smaller than 0.1 μm were observed at many places. Adsorbed elements (C and O) on the surface layer were removed by Ar^+ sputtering. Auger spectra of individual particles were measured and the weight concentrations of detected elements were determined by semiquantitative analysis using sensitivity coefficients. Particles containing the detected Cr and Si were extracted as objects. The composition (Cr/Si), size, and dispersion density of particles of the Cr-Si compounds were respectively defined as the average Cr/Si ratio, the minimum inside diameter, and the average number in each observation view for the particles of the Cr-Si compounds having a size of 0.1 to 5 μm analyzed at many places by FE-AES observation. The results are shown in Tables 1 and 2.

Table 1

		Ni	Si	Cr	Sn	Zn	Mg, Mn, Ag, P, As, Sb, Be, B, Ti, Zr, Al, Co, Fe	Solution treatment temperature (°C×120s)	Cooling rate (°C/s)	Aging temperature (°C)	Aging time (h)	Dispersion density of CrSi particles (×10 ⁵ /mm ²)	Composition of CrSi particles (Cr/Si)	Yield Strength	Electrical Conductivity	Bendability	Fatigue Strength
Examples	1	2.7	0.6	0.005				800	1	450	6	0.3	4	760	48	A	275
	2	2.7	0.6	0.05				800	2	450	6	0.5	3	765	48	A	280
	3	2.7	0.6	0.05				800	4	450	6	0.4	3	765	48	A	280
	4	2.7	0.6	0.05				800	8	450	6	0.2	3	765	47	A	280
	5	2.7	0.6	0.05				800	2	400	12	0.5	3	770	47	A	280
	6	2.7	0.6	0.05				800	2	500	2	0.5	3	770	47	A	280
	7	2.7	0.6	0.1				800	4	450	6	1	2	770	46	A	285
	8-1	2.7	0.6	0.05			0.1Mg	800	4	450	6	0.5	3	785	46	A	285
	8-2	2.7	0.6	0.05			1.0Co	800	4	450	6	0.5	3	790	48	A	285
	8-3	2.7	0.6	0.05			1.0Co 0.1Mg	800	4	450	6	0.5	3	800	47	A	285
	9	2.7	0.6	0.05			0.1Mn	800	4	450	6	0.5	3	785	46	A	285
	10	2.7	0.6	0.05	0.3			800	4	450	6	0.5	3	785	46	A	285
	11	2.7	0.6	0.05	0.3		0.1Ag	800	4	450	6	0.5	3	785	46	A	285
	12	2.7	0.6	0.05	0.3	0.5		800	4	450	6	0.5	3	785	45	A	285
	13	2.7	0.6	0.05	0.3	0.5	0.1Mg	800	4	450	6	0.5	3	800	45	A	285
	14	4.0	0.9	0.005				900	2	450	4	0.7	4	860	44	A	300
	15	4.0	0.9	0.05				900	3	450	4	1.1	3	870	43	A	300
	16	4.0	0.9	0.05				900	6	450	4	0.8	3	870	43	A	300
	17	4.0	0.9	0.05				900	9	450	4	0.4	3	870	43	A	300
	18	4.0	0.9	0.05				900	3	400	10	1.1	3	870	43	A	300
	19	4.0	0.9	0.05				900	3	500	2	1.1	3	870	43	A	300
	20	4.0	0.9	0.1				900	6	450	4	2.2	2	870	44	A	300
	21	4.0	0.9	0.17				900	7	450	4	5.6	2	875	43	A	300
	22	4.0	0.9	0.05			0.2Mg	900	3	450	4	1.1	3	890	41	A	325
	23	4.0	0.9	0.05			0.1Mn	900	3	450	4	1.1	3	890	41	A	325
24	4.0	0.9	0.05	0.3			900	3	450	4	1.1	3	890	41	A	325	
25	4.0	0.9	0.05	0.3		0.1Ag	900	3	450	4	1.1	3	890	41	A	325	

Composition: % by mass

Table 2

	Ni	Si	Cr	Sn	Zn	Mg, Mn, Ag, P, As, Sb, Be, B, Ti, Zr, Al, Co, Fe	Solution treatment temperature (°C×120s)	Cooling rate (°C/s)	Aging tem- perature (°C)	Aging time (h)	Dispersion density of CrSi particles ($\times 10^9/\text{mm}^2$)	Composi- tion of CrSi particles (Cr/Si)	Yield Strength	Electric al Conductivity	Bendability	Fatigue Strength
1	2.7	0.6	0.05				800	0.5	450	6	15	3	700	51	F	225
2	2.7	0.6	0.1				800	0.5	450	6	20	3	720	49	F	230
3	4.0	0.9	0.05				900	0.5	450	6	25	3	820	43	F	270
4	2.7	0.6	0.05				800	15	450	6	0.05	20	740	43	A	240
5	2.7	0.6	0.1				800	15	450	6	0.1	25	750	43	A	240
6	2.7	0.6	0.05				800	4	600	6	20	7	680	53	F	200
7	4.0	0.9	0.05				900	5	600	6	25	8	780	44	F	250
8	2.7	0.6	0.5				800	4	450	6	14	3	710	51	F	230
9	4.0	0.9	0.5				900	6	450	4	18	3	810	44	F	270

Composition: % by mass

[0037] Examples 1 to 25 of the present invention show satisfactory properties, since particles of Cr-Si compounds have a dispersion density of no more than 1×10^6 and a Cr/Si ratio in the range of 1 to 5 due to a proper cooling rate. In contrast, Comparative Examples 1 to 3 show insufficient strength and poor bendability due to excess grow of particles of Cr-Si compounds caused by a slow cooling rate. Comparative Examples 4 and 5 show poor strength and conductivity due to insufficient grow of the particles and excess Si dissolved in the alloy caused by a rapid cooling rate. Comparative Examples 6 and 7 show insufficient strength and poor bendability due to excess grow of particles of Cr-Si compounds caused by a high aging temperature. Comparative Examples 8 and 9 show poor strength and poor bendability due to excess grow of particles of Cr-Si compounds caused by an excess concentration of Cr.

Claims

1. A copper alloy for electronic materials, comprising 1.0-4.5% by mass Ni, 0.50-1.2% by mass Si, 0.003-0.3% by mass Cr wherein the weight ratio of Ni to Si satisfies the expression: $3 \leq \text{Ni/Si} \leq 5.5$, and the balance being Cu and incidental impurities, wherein particles of Cr-Si compounds having a size of 0.1 μm to 5 μm are dispersed in the alloy, the dispersed particles having an atomic concentration ratio of Cr to Si in the range of 1 to 5 and a dispersion density of no more than $1 \times 10^6/\text{mm}^2$.
2. The copper alloy for electronic materials according to Claim 1, wherein the dispersion density of the particles of the Cr-Si compounds having a size of 0.1 μm to 5 μm is higher than $1 \times 10^4/\text{mm}^2$.
3. The copper alloy for electronic materials according to Claim 1 or 2, further comprising 0.05-2.0% by mass of at least one element selected from Sn and Zn.
4. The copper alloy for electronic materials according to any one of Claims 1 to 3, further comprising 0.001-2.0% by mass of at least one element selected from Mg, Mn, Ag, P, As, Sb, Be, B, Ti, Zr, Al, Co and Fe.
5. A wrought copper product comprising the copper alloy according to any one of Claims 1 to 4.
6. A component for electronic devices, comprising the copper alloy according to any one of Claims 1 to 4.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/056138

A. CLASSIFICATION OF SUBJECT MATTER C22C9/06(2006.01)i, C22C9/00(2006.01)i, C22C9/01(2006.01)i, C22C9/02(2006.01)i, C22C9/04(2006.01)i, C22C9/05(2006.01)i, C22C9/10(2006.01)i, C22F1/08(2006.01)i, H01B1/02(2006.01)i, H01B5/02(2006.01)i, 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) C22C1/00-49/14, C22F1/00-3/02, H01B1/02, H01B5/02 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 1996-2008 Kokai Jitsuyo Shinan Koho 1971-2008 Toroku Jitsuyo Shinan Koho 1994-2008 Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2005-350696 A (Hitachi Cable, Ltd.), 22 December, 2005 (22.12.05), Full text (Family: none)	1-6
A	JP 7-18356 A (Mitsubishi Electric Corp.), 20 January, 1995 (20.01.95), Full text (Family: none)	1-6
☐ 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 “L” document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) “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 “X” document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone “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 28 May, 2008 (28.05.08)		Date of mailing of the international search report 10 June, 2008 (10.06.08)
Name and mailing address of the ISA/ Japanese Patent Office		Authorized officer
Facsimile No.		Telephone No.

INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/056138

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

C22F1/00(2006.01)n, C22F1/02(2006.01)n

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

REFERENCES CITED IN THE DESCRIPTION

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