

(19)



(11)

EP 2 221 391 A1

(12)

EUROPEAN PATENT APPLICATION published in accordance with Art. 153(4) EPC

(43) Date of publication:

25.08.2010 Bulletin 2010/34

(51) Int Cl.:

C22C 9/06 (2006.01)**B21B 3/00** (2006.01)**C22C 9/04** (2006.01)**C22F 1/08** (2006.01)**C22F 1/00** (2006.01)(21) Application number: **08847798.9**(22) Date of filing: **05.11.2008**

(86) International application number:

PCT/JP2008/070139

(87) International publication number:

WO 2009/060873 (14.05.2009 Gazette 2009/20)

(84) Designated Contracting States:

**AT BE BG CH CY CZ DE DK EE ES FI FR GB GR
HR HU IE IS IT LI LT LU LV MC MT NL NO PL PT
RO SE SI SK TR**

Designated Extension States:

AL BA MK RS

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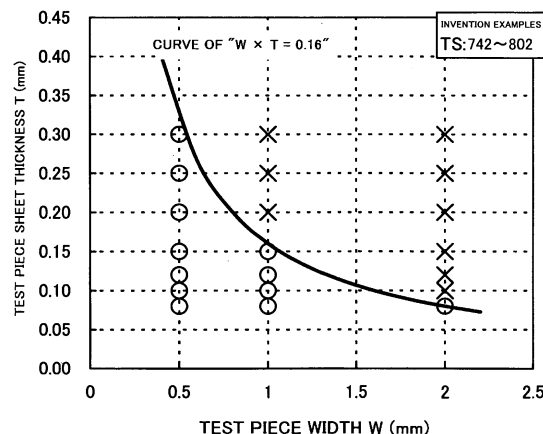
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(54) **COPPER ALLOY SHEET MATERIAL**

(57) A copper alloy sheet material which has a tensile strength of 730-820 MPa and contains at least nickel (Ni) and silicon (Si), with the remainder being copper (Cu) and inevitable impurities. When the sheet material has a shape capable of 180° tight bending and the width and thickness of this sheet material are expressed by W (unit: mm) and T (unit: mm) respectively, then the product of W and T is 0.16 or less. Preferably, the sheet material is

constituted of an alloy containing nickel at 1.8-3.3 mass%, silicon at 0.4 mass%, and chromium (Cr) at 0.01-0.5 mass%, with the remainder being copper and inevitable impurities. The sheet material may further contain one or more of: at least one member selected among tin (Sn), magnesium (Mg), silver (Ag), manganese (Mn), titanium (Ti), iron (Fe), and phosphorus (P) in a total amount of 0.01-1 mass%; zinc (Zn) at 0.01-10 mass%, cobalt (Co) at and 0.01-1.5 mass%.

FIG. 2



Description

Technical Field

[0001] The present invention relates to a copper alloy sheet material.

Background Art

[0002] Characteristics that are required for copper alloy sheet material that is used for electrical / electronic equipment include for example, constant electrical conductivity, constant tensile strength, constant bending workability, and constant stress relaxation resistance. In recent years, as electrical / electronic equipment have become more compact, more lightweight, more highly functional and more densely packaged, and as the operating temperature has increased, the level of these required characteristics has also increased.

[0003] Conventionally, in addition to iron-based materials, copper-based materials such as phosphor bronze, red brass and brass have typically been used as materials for electrical / electronic equipment. Through a combination of solid solution strengthening using Sn or Zn, and work hardening by cold working such as rolling or drawing, the strength of these alloys has been improved. However, alloys that are obtained through these strengthening methods have insufficient electrical conductivity for the recent required level, and since high strength is obtained by adding a high cold working rate, the bending workability and stress relaxation resistance are also insufficient.

As an alternative strengthening method, precipitation strengthening causes microscopic secondary-phase particles on a nanometer order to precipitate into a material. In addition to increasing strength, this strengthening method has the merit of simultaneously improving the electrical conductivity, so it is used in many alloy systems. Of these, Cu-Ni-Si system alloys that are strengthened by precipitating microscopic Ni and Si compounds into Cu (for example, CDA70250, which is a registered alloy of the CDA (Copper Development Association); refer to patent documents 1 and 2) are increasingly being used in the market.

[0004]

Patent document 1: JP-A-1999-43731

Patent document 2: JP-T-2005-532477

Disclosure of the Invention

[0005] Generally, in the case of precipitation-hardened alloys, before aging precipitation heat treatment for obtaining a microscopic precipitation state, solution heat treatment is employed as an intermediate process for solidifying the solution of solute atoms. The temperature of this process differs depending on the alloy system and the solute concentration, however, is a high temperature of about 750 °C. Since the temperature of this solution heat treatment is a high temperature, there is a problem in that the grain size of the material becomes coarse. When the grain size is coarse, problems occur such as cracking due to the promotion of localized deformation during bending, concentration of electric current when bent sections are used as contacts due to large creases on the surface of the bent sections, or cracking of plating that is coated on the surface of the material. Moreover, when the temperature of the solution heat treatment is lowered in order to prevent the grain size from becoming coarse, problems occur in that the amount of atoms that enter into solid solution decreases, the density of microscopic precipitate in the aging treatment decreases, the amount of age hardening decreases and the material strength decreases.

Therefore in solution heat treatment at a temperature at which solute Ni and Si atoms can sufficiently enter into solid solution, there is a demand for technology by which the grain size can be kept small and material having high strength and good bending workability can be obtained.

[0006] Taking the aforementioned problems into consideration, it is the object of the present invention to provide a copper alloy sheet material for use in electrical / electronic equipment that has excellent bending workability and strength.

[0007] The inventors performed research of copper alloys suitable for use in electrical / electronic equipment, and by focusing their attention on methods of dispersing second-phase particles in order to greatly improve the bending workability and strength of Cu-Ni-Si series copper alloys, developed the present invention after much dedicated study. In addition, the inventors found the best modes of the present invention by discovering added elements that function to improve the strength and stress relaxation resistance characteristics without impairing electrical conductivity. The second-phase particles referred to here are precipitates and crystallized matter.

[0008] The following means are provided with the present invention:

(1) A copper alloy sheet material having a tensile strength of 730 to 820 MPa, and comprising at least Ni and Si in addition to copper and inevitable impurities, wherein when the material is capable of 180° tight bending and the

sheet width is taken to be W (unit: mm) and the sheet thickness is taken to be T (unit: mm), the product of W and T (unit: mm²) is 0.16 or less.

(2) The copper alloy sheet material of item (1) wherein second-phase particles existing on a grain boundary exist at a density of 10^4 to 10^8 particles/mm², and the average grain size is 10 μm or less.

(3) The copper alloy sheet material of item (1) wherein the value of the ratio r/f of the particle size r (unit: μm) of second-phase particles inside the grain and on the grain boundary and the volume fraction f of the particles is at least 1 and not more than 100, and the average grain size is 10 μm or less.

(4) The copper alloy sheet material of item (2) or item (3) wherein of the second-phase particles, the ratio of particles comprising Cr as a constituent element is 50% or more.

(5) The copper alloy sheet material of any one of the items 1 to 4 wherein the alloy composition includes Ni at 1.8 to 3.3 mass%, Si at 0.4 to 1.1 mass% and Cr at 0.01 to 0.5 mass%, with the remaining being Cu and inevitable impurities.

(6) The copper alloy sheet material of any one of the items 1 to 5 comprising one kind or two kinds or more elements from among at least one of Sn, Mg, Ag, Mn, Ti, Fe and P at 0.01 to 1 mass%, Zn at 0.01 to 10 mass% and Co at 0.01 to 1.5 mass%.

(7) The copper alloy sheet material of any one of the items 1 to 6 wherein when the material is maintained at 165 °C for 3000 hours, the stress relaxation rate is 30% or less.

[0009] The above and other features and advantages of the present invention will become better understood from the following detailed description with reference to the accompanying drawings.

Brief Description of the Drawings

[0010]

FIG. 1 is a drawing explaining a method for testing stress relaxation resistance, where (a) of FIG. 1 shows before heat treatment and (b) of FIG. 1 shows after heat treatment.

FIG. 2 is a graph showing the results of whether or not cracking occurs when the sheet width W (mm) and sheet thickness T (mm) of a test specimen are varied in examples and comparative examples.

Best Mode for Carrying Out the Invention

[0011] The preferred embodiment of the copper alloy sheet material of the present invention is explained in detail.

[0012] The tensile strength of the copper alloy sheet material of the present invention is 730 to 820 MPa. More preferably, it is 740 to 800 MPa. The bending workability is such that under rigid conditions such as when the product of the material sheet width W (mm) and the material sheet thickness T (mm) is 0.16 (mm²) or less, 180° tight bending is possible. It is preferred that this product of width W and thickness T be 0.14 or less. The minimum value of this product of width W and thickness T is not especially limited, however is normally 0.01 or greater.

Moreover, an electrical conductivity of 30% IACS is preferred, and it is also preferred for the stress relaxation resistance that when the material is maintained for 3000 hours or more at 165 °C, the stress relaxation rate be 30% or less.

Suitable dispersion of second-phase particles is effective against grain coarsening during solutionization that causes bending workability to worsen. This is because it is considered that when grain is grown, a gain in energy occurs at the interface between the dispersed particles and grain boundary when the grain boundary passes the second-phase particles and suppresses grain boundary migration.

The obtained grain size is preferably 10 μm or less, and more preferably 8 μm or less, and yet even more preferably 6 μm or less. The minimum value of grain size is not particularly limited, however, normally is 2 μm or more. The grain size is measured according to the Japanese Industrial Standard JIS H 0501 (cutting method).

[0013] Regulating the preferred dispersion state of the present invention in order to fully demonstrate the effect of obtaining this controlled grain size can be performed by the following two methods.

First, the second-phase particles that exist on the grain boundary should exist at a density of 10^4 to 10^8 particles/mm². In this case, it is further preferred that the density be 5×10^5 to 5×10^7 particles/mm².

Second, the value of the ratio r/f of the particle size r (unit: μm) of all of the second-phase particles inside the grain and on the grain boundary and the volume fraction f of the particles should be 1 to 100. The particle size r of the second-phase particles is the arithmetic mean value of the particle size of all of the measured particles. The notation $f = 0.005$ for the volume fraction f indicates 0.5 vol%.

[0014] The inventors discovered that these kinds of second-phase particles possessed the preferred function of improving the stress relaxation resistance. The stress relaxation phenomenon is considered to be caused by dislocations inside the grain moving to the grain boundary, or by grain boundary slippage occurring in part of the grain boundary,

with the strain inside the elastic limit changing to permanent strain. In the case of the aforementioned preferred second-phase particles of the present invention, the particles existing inside the grain function to suppress moving of dislocations, and the particles existing at the grain boundary suppress slipping movement of the grain boundary.

Of all these second-phase particles, it is further preferred that the percentage of particles that include Cr as a constituent element be 50% or greater. This is because when Cr is included, the particles can exist as stable compounds without entering the solid solution of Cu even at high temperature. This contributes to a higher density of second-phase particles and increases the effect of suppressing the growth of grain. It is even more preferable that this percentage be 70% or greater. The maximum value of this percentage is not particularly limited, however normally is 90% or less.

[0015] By controlling the composition amounts of the main solute components Ni and Si, favorable characteristics can be obtained as follows. It is preferred that the contained amount of Ni be 1.8 to 3.3 mass%, and more preferably 2.0 to 3.0 mass%, and the contained amount of Si be 0.4 to 1.1 mass%, and more preferably 0.5 to 1.0 mass%. Too large of an amount of these elements leads to a drop in electrical conductivity, and causes cracking at the grain boundary by the precipitation at the grain boundary during bending. However, too small of an amount of these elements leads to the insufficient strength.

[0016] Cr precipitates as the second-phase particle with Ni or Si, and is effective in controlling the grain size. Furthermore, Cr per se performs precipitation hardening. It is preferred that the contained amount of Cr be 0.01 to 0.5 mass%, and more preferably 0.03 to 0.4 mass%. When the amount is too small, the effect is not obtained, and when the amount is too large, adverse effects occur in that the Cr crystallizes out as coarse crystallized matter during solidification, which causes the plating characteristics to worsen, and promotes starting points for cracking as well as the propagation of cracking during plastic working.

[0017] In addition, at least one kind of element that is selected from among (1) at least one of Sn, Mg, Ag, Mn, Ti, Fe and P for a total of 0.01 to 1 mass%, (2) Zn at 0.01 to 10 mass %, and (3) Co at 0.01 to 1.5 mass% can be added in order to improve the alloy characteristics.

These elements improve the strength and the stress relaxation resistance characteristic, and especially Sn and Mg are very effective for that. Zn and Sn function to improve solder joinability, Co functions to improve electrical conductivity, and Mn functions to improve hot workability. When the contained amount when added is too small, the effect is not sufficient, and too large of an amount leads to a drop in electrical conductivity.

[0018] In the case of the stress relaxation resistance characteristics, it is preferred that the stress relaxation rate be 30% or less when the material is kept at 165 °C for 3000 hours, and more preferably 25% or less.

[0019] The preferred method for manufacturing the copper alloy sheet material of the present invention is explained below. The copper alloy sheet material of the present invention can, for example, be manufactured by a method comprising the steps of casting, (homogenization) heat treatment, hot working (for example, hot rolling) and cold working (for example, cold rolling) (1), solution heat treatment, cold working (for example, cold rolling) (2), (aging precipitation) heat treatment, cold working (for example cold rolling) (3) and (strain relief) annealing. Here, it is preferred that rapid cooling and facing be performed after heat treatment and before cold working (1).

First, the copper alloy material is prepared by combining all of the elements so that the specified alloy constituent composition is achieved, with the remaining part being Cu and inevitable impurities, and this is melted using a high-frequency melting furnace. Casting is performed at a preferable cooling rate of 0.1 to 100 °C/sec (more preferably, 0.5 to 50 °C/sec) to obtain an ingot. Heat treatment (homogenization) is performed by preferably maintaining the ingot at 900 to 1050 °C for 0.5 to 10 hours (more preferably, for 0.8 to 8 hours). Hot working (hot rolling) is preferably performed at a reduction percentage (rolling reduction) of 50% or greater (more preferably, 60 to 98%), and a processing temperature of 600 °C or greater (more preferably, 620 to 1000 °C) to form a sheet. Rapid cooling (for example, water cooling) is preferably performed by cooling this sheet at a cooling rate of 10 °C/sec or greater (more preferably, 15 to 300 °C/sec). This hot rolled sheet can be faced according to a conventional method. Cold working (cold rolling) (1) is preferably performed with a reduction percentage of 90% or greater (more preferably, 92 to 99%). Solution heat treatment is preferably performed by maintaining the material at 720 to 860 °C for 3 sec to 2 hours (more preferably 5 sec to 0.5 hours). In the solution heat treatment, it is preferred that treatment be performed within a range of rising temperature from 400 °C to 700 °C and a rate of temperature increase of 0.1 °C/sec to 200 °C/sec (more preferably, 0.5 to 100 °C/sec). Cold working (cold rolling) (2) is preferably performed with a reduction percentage of 5 to 50% (more preferably, 7 to 45%). Aging precipitation heat treatment is preferably performed by maintaining the material at 400 °C to 540 °C for 5 min to 10 hours (more preferably, at 410 to 520 °C for 10 min to 8 hours). Cold working (cold rolling) (3) is preferably performed with a reduction percentage of 10% or less (meaning greater than 0% but not exceeding 10%). Strain relief annealing is preferably performed by maintaining the material at 200 °C to 600 °C for 15 sec to 10 hours (more preferably, 250 to 570 °C for 20 sec to 8 hours).

When there is sufficient strength after aging precipitation heat treatment, cold working (3) and strain relief annealing do not need to be performed after that and can be omitted.

[0020] By performing at least one process of the aforementioned processes under the aforementioned preferable conditions, and particularly by preferably performing all of the processes under the preferable conditions, the specified

preferred metallic structure for the copper alloy sheet material of the present invention can be obtained. For example, by adjusting the casting speed (cooling speed during casting), it is possible to prevent crystallization of Cr series compounds from occurring excessively. In addition, by adjusting the temperature range and time during which the material is maintained at that temperature during hot rolling, it is possible to suppress coarse precipitation during hot rolling, and suitable precipitation can be performed in a later process. Moreover, the second-phase particles that suppress coarsening of the grain mainly precipitate out during the temperature rise of the solution heat treatment, however, in order to effectively induce that precipitation, it is preferred that processing be performed such that both the processing rate of the cold working (1) process, which is the process prior to the solution heat treatment process, and the rate of temperature rise during the solution heat treatment be within the aforementioned preferred conditions. Furthermore, by employing the cold working (2) process before the aging precipitation heat treatment process, it is possible to induce higher density of microscopic precipitate that contributes to precipitation hardening, and suppress the coarsening of second-phase particles that remain at the time of solutionization during aging precipitation heat treatment.

[0021] The copper alloy sheet material of the present invention has excellent strength and bending workability, and is suitable for use in electrical / electronic equipment. The preferred copper alloy sheet material of this present invention also has excellent electrical conductivity and stress relaxation resistance. With the characteristics described above, the copper alloy sheet of the present invention can also be suitably used in lead frames, connectors, and terminals of electrical / electronic equipment, and is particularly suitable for use in connectors, terminals, relays, switches and sockets that are used in automobiles.

There never before has been material having high strength and high bending workability such as that of the present invention, and this material will improve freedom when designing parts for cutting-edge uses in the future, as well as have a large effect on high functionality of electronic equipment. In addition, by having increased strength makes it possible to make the copper alloy material thinner, thus contributing to a reduction in the amount of global resources used.

Examples

[0022] The present invention will be explained in further detail below based on examples; however, the present invention is not limited to these examples.

(Examples 1)

[0023] An alloy comprising elements that were combined so that their composition was as shown in the table, with the remaining part being Cu and inevitable impurities, was melted in a high-frequency melting furnace, and then cast at a cooling rate of 0.1 to 100 °C/sec to obtain an ingot. After maintaining this ingot at 900 to 1050 °C for 0.5 to 10 hours, a sheet was formed by hot working with the percentage of reduction being 50% or greater and the processing temperature being 600 °C or greater, then the sheet was water cooled at a cooling rate of 10 °C/sec or greater. The hot rolled sheet was then faced, and cold working (1) was performed at a reduction percentage of 90% or greater. Solution heat treatment was then performed by maintaining the sheet at 720 to 860 °C for 3 sec to 2 hours. Solution heat treatment was performed such that the rate of temperature rise during a temperature rise at 400 °C to 700 °C was in the range of 0.1 °C/sec to 200 °C/sec. After that, cold working (2) was performed at a reduction percentage of 5 to 50%, aging precipitation heat treatment was performed by maintaining the material at 400 °C to 540 °C for 5 min to 10 hours, cold working (3) was performed at a reduction percentage of 10% or less, and strain relief annealing was performed by maintaining the material at 200 °C to 600 °C for 15 sec to 10 hours to obtain material to be used as test material. In the case where there was sufficient strength after aging precipitation heat treatment, the cold working (3) and strain relief annealing after that aging precipitation heat treatment were not performed.

[0024] The comparative examples given below that are presented with the examples were made outside the range of these manufacturing conditions in order to be separated from the range of examples of the present invention. Details of the comparative examples are given below.

Comparative example 1-1 is an example in which the cooling rate during the casting process was too low.

Comparative example 1-2 is an example in which the temperature during the homogenization process was too low.

Comparative example 1-3 is an example in which the temperature during the aging precipitation heat treatment process was too high.

Comparative example 1-4 is an example in which the temperature during the homogenization process was too low.

In each of the tables, for example, in the case of the test results of invention example 1-1 as the ID number in Table 1, in regards to the evaluation of the bending workability, judgment results for bending work conditions outside the range of the invention $W \times T > 0.16$ are also displayed on the same line as the judgment results for the bending work conditions within the range of the invention, however, this is done for convenience of listing the ID number. This will be the same

for all of the test examples given in each of the tables below.

[0025] The characteristics presented below were investigated for these test materials.

a. Electrical conductivity [EC]

[0026] The electrical conductivity (% IACS) was calculated by using the four-terminal method to measure the specific resistance of the material in an isothermal bath that was maintained at 20 °C (± 0.5 °C). The spacing between terminals was 100 mm.

b. Tensile strength [TS]

[0027] Three test pieces that were cut out from the direction parallel to the rolling direction according to JIS Z2201-13B were measured according to JIS Z2241, and the average value (MPa) is given.

c. 180° tight bending workability

[0028] Bending work was performed according to JIS Z2248. After preliminary bending was performed using a 0.4 mm R 90° bending die, tight bending was performed using a compression testing machine. The bending location was observed by using a 50x optical microscope to visually inspect whether or not there was cracking on the outside of the bent section. The sheet width W and sheet thickness T conditions of the test piece are indicated in mm. In the table "GW (Good way)" indicates testing in the case where the bending axis is perpendicular to the rolling direction, and "BW (Bad way)" indicates testing in the case where the bending axis is parallel to the rolling direction. In the table, the observation results are indicated as "O (Good)" when no cracking occurred, and as "X (Bad)" when cracking occurred.

d. Particle size [r], distribution density [ρ] and volume fraction [f] of the second-phase particles

[0029] Observation test pieces were formed by punching the test material into 3 mm diameter pieces, and polishing the pieces to a thin film by using a twin-jet polishing method. Using a transmission electron microscope having an accelerating voltage of 300 kV, 5000x photographs were taken arbitrarily every ten fields of view, and the particle size r (μm) and distribution density ρ (particles/ mm^2) were measured on the photographs. The particle size r of the second-phase particles was found by first, finding the particle size of each particle, then, for all of the measured particles, finding the calculated average value of the particle sizes of all of the particles. The particle size of each particle was taken to be the calculated average value of the long diameter and short diameter of the particle. Moreover, the thickness of an observed test piece was measured from the thickness contours, and of the total volume of an observed field of view, the percentage of the volume occupied by the second-phase particles was taken to be the volume fraction f.

e. Identification of second-phase constituent atoms [C]

[0030] An EDX spectrometer that was attached to the TEM was used. Analysis was performed for 20 second-phase particles, and the percentage of the total number measured comprising Cr was calculated.

f. Stress relaxation resistance [SR]

[0031] The stress relaxation resistance was measured according to the Japan Electronics and Information Technology Industries Association standards EMAS-3003 under conditions of 165 °C for 3000 hours. An initial stress that was 80% the offset yield strength (proof stress) was applied by the cantilever method.

[0032] FIG. 1 is a drawing explaining the method for testing the stress relaxation, where (a) of FIG. 1 shows the state before heat treatment, and (b) of FIG. 1 shows the state after heat treatment. The stress relaxation rate (%) was calculated as $(H_t - H_1)/\delta_0 \times 100$.

g. Average grain size [GS]

[0033] The average grain size was measured according to JIS H 0501 (cutting method). Measurement was performed for a cross-section that is parallel to the rolling direction, and a cross-section that is perpendicular to the rolling direction, and the average of both was taken. Observation of the metallic structure was done by chemically edging a mirror polished material surface and performing SEM reflection electron imaging.

[0034] [Table 1]

TABLE 1

ID Number	Alloy composition			ρ	T	Bending workability (Cracking Y/N) (W unit: mm)						TS	% of particles comprising Cr	GS	EC	SR
	Ni	Si	Cr			GW			BW							
						W=0.5	W=1	W=2	W=0.5	W=1	W=2					
	mass%	mass%	mass%	Particles/mm ²	mm	W=0.5	W=1	W=2	W=0.5	W=1	W=2	MPa	%	μm	%IACS	%
Invention example 1-1	1.81	0.50	-	6 × 10 ⁴	0.30	○	×	×	○	×	×	742	0	5.2	42.1	28.2
Invention example 1-2	2.32	0.65	-	9 × 10 ⁴	0.25	○	×	×	○	×	×	770	0	4.3	40.2	27.4
Invention example 1-3	2.81	0.79	-	7 × 10 ⁵	0.20	○	×	×	○	×	×	784	0	6.8	39.5	28.1
Invention example 1-4	3.28	0.94	-	2 × 10 ⁶	0.15	○	○	×	○	○	×	792	0	7.0	38.6	26.7
Invention example 1-5	1.83	0.50	0.21	2 × 10 ⁵	0.08	○	○	○	○	○	○	755	85	4.8	43.2	28.6
Invention example 1-6	2.36	0.65	0.15	3 × 10 ⁶	0.15	○	○	×	○	○	×	769	75	5.5	39.5	28.3
Invention example 1-7	2.84	0.79	0.11	2 × 10 ⁷	0.12	○	○	×	○	○	×	785	95	4.2	38.2	27.5
Invention example 1-8	3.24	0.94	0.25	8 × 10 ⁷	0.08	○	○	○	○	○	○	805	90	6.2	36.1	26.8
Comparative example 1-1	2.34	0.66	-	3 × 10 ³	0.25	×	×	×	×	×	×	725	0	13.5	39.2	28.2
Comparative example 1-2	2.82	0.77	-	7 × 10 ³	0.20	×	×	×	×	×	×	762	0	18.2	38.2	29.3
Comparative example 1-3	2.35	0.62	0.15	2 × 10 ⁹	0.30	×	×	×	×	×	×	719	65	12.9	39.5	28.0
Comparative example 1-4	2.81	0.75	0.21	5 × 10 ³	0.15	×	×	×	×	×	×	758	45	17.5	37.5	27.9

[0035] As can be clearly seen from Table 1, invention examples 1-1 to 1-8 have excellent strength, electrical conductivity, bending workability and stress relaxation resistance characteristics. However, when some of the elements of the present invention are not satisfied, some characteristics may become inferior. For example, comparative examples 1-1 to 1-4 are all examples in which the bending workability is inferior. In comparative examples 1-1, 1-2 and 1-4, the density of precipitate on the grain boundary is low, and the grain size becomes coarse. Moreover, in comparative example 1-3, the density of precipitate on the grain boundary is high, and it was observed that cracking occurred at the grain boundary.

(Examples 2)

[0036] The same investigation as was performed for examples 1 was performed for a copper alloy comprising the composition shown in Table 2 with the remaining part being Cu and inevitable impurities. The manufacturing method and measurement method were the same as for examples 1.

The comparative examples given below that are presented with the examples were made outside the range of these manufacturing conditions in order to be separated from the range of examples of the present invention. Details of the comparative examples are given below.

Comparative example 2-1 is an example in which the processing rate during cold working (cold rolling) was too low.

Comparative example 2-2 is an example in which the temperature during the homogenization process was too low.

Comparative example 2-3 is an example in which the cooling rate during the casting process was too low.

Comparative example 2-4 is an example in which the temperature during the homogenization process was too low.

[0037] [Table 2]

TABLE 2

ID Number	Alloy composition			r/f	T	Bending workability (Cracking Y/N) (W unit: mm)						TS	% of particles comprising Cr	GS	EC	SR
	Ni	Si	Cr			GW			BW							
						W=0.5	W=1	W=2	W=0.5	W=1	W=2					
Invention example 2-1	1.91	0.55	-	45.1	0.30	○	×	×	○	×	×	MPa	%	μm	%IACS	%
Invention example 2-2	2.41	0.68	-	15.4	0.25	○	×	×	○	×	×	772	0	5.8	40.6	26.7
Invention example 2-3	2.72	0.75	-	17.2	0.20	○	×	×	○	×	×	789	0	6.2	39.8	28.2
Invention example 2-4	3.11	0.89	-	10.4	0.15	○	○	×	○	○	×	790	0	4.7	38.2	27.6
Invention example 2-5	1.93	0.55	0.21	25.2	0.25	○	×	×	○	×	×	751	90	5.6	43.1	26.3
Invention example 2-6	2.45	0.68	0.15	12.1	0.15	○	○	×	○	○	×	773	80	6.3	39.6	28.5
Invention example 2-7	2.76	0.75	0.11	5.4	0.10	○	○	×	○	○	×	783	85	4.5	38.3	27.4
Invention example 2-8	3.18	0.89	0.25	72.3	0.08	○	○	○	○	○	○	802	75	7.4	36.6	26.8
Comparative example 2-1	2.44	0.66	-	24.5	0.15	○	×	×	○	×	×	680	0	5.2	42.1	29.5
Comparative example 2-2	2.74	0.76	-	145.7	0.30	×	×	×	×	×	×	771	0	19.3	39.5	30.2
Comparative example 2-3	2.41	0.65	0.15	0.71	0.12	×	×	×	×	×	×	765	45	18.2	39.1	29.2
Comparative example 2-4	2.72	0.73	0.15	120.2	0.25	×	×	×	×	×	×	761	75	16.2	37.5	27.8

[0038] As can be clearly seen from Table 2, invention examples 2-1 to 2-8 have excellent strength, electrical conductivity, bending workability and stress relaxation resistance characteristics. However, when some of the elements of the present invention are not satisfied, some characteristics may become inferior. For example, comparative example 2-1 is an example in which the tensile strength became inferior. In this comparative example 2-1, the solutionization temperature was lowered and grain size was made small, however, precipitation hardening was thought to be insufficient and there was not enough strength. Comparative examples 2-2 and 2-4 are examples in which the bending workability became inferior. In these comparative examples 2-2 and 2-4, it was found that the precipitation fraction was small, so the r/f value became large and the grain size became coarse. Comparative example 2-3 is an example in which bending workability was inferior. In this comparative example 2-3, it was found that the size of the second-phase particles was small, so the r/f value became small, and because the grain could not be effectively controlled, the grain size became coarse.

(Examples 3)

[0039] The same investigation as was performed for examples 1 was performed for a copper alloy comprising the composition shown in Table 3 with the remaining part being Cu and inevitable impurities. The manufacturing method and measurement method were the same as for examples 1.

[0040] The comparative examples below that are presented with the examples in Table 3 were made with the contained amounts of Ni and Si outside the preferred range of the present invention.

[0041] [Table 3]

TABLE 3

ID Number	Alloy composition			Other added elements	ρ	T	Bending workability (Cracking Y/N) (W unit: mm)								TS	% of particles comprising Cr	GS	EC	SR
	Ni	Si	Cr				GW			BW									
							W=0.5	W=1	W=2	W=0.5	W=1	W=2							
	mass%	mass%	mass%	mass%	Particles/mm ²	mm	W=0.5	W=1	W=2	W=0.5	W=1	W=2	MPa	%	μm	%IACS	%		
Invention example 3-1	1.81	0.51	0.15	0.1Mn, 0.05P	6×10^4	0.20	○	×	×	○	×	×	748	85	5.2	38.2	26.2		
Invention example 3-2	2.31	0.65	0.18	0.1Mg, 0.15Sn, 0.5Zn	9×10^4	0.25	○	×	×	○	×	×	765	75	4.8	39.1	23.6		
Invention example 3-3	2.81	0.77	0.21	0.3Ag, 0.1Ti	8×10^5	0.15	○	○	×	○	○	×	772	80	6.2	37.2	27.3		
Invention example 3-4	3.26	0.92	0.19	0.2Co, 0.1Fe	7×10^5	0.10	○	○	×	○	○	×	790	90	7.1	37.2	26.1		
Comparative example 3-1	1.61	0.31	0.15	0.2Sn, 0.15Mg	6×10^5	0.20	○	×	×	○	×	×	710	85	8.2	41.2	31.2		
Comparative example 3-2	3.51	1.21	0.12	0.3Mn	2×10^6	0.15	○	×	×	○	×	×	795	85	8.9	32.5	26.0		

[0042] As can be clearly seen from Table 3, invention examples 3-1 to 3-4, in which the contained amounts of Ni and Si are especially within the preferred range, have excellent strength, electrical conductivity, bending workability, and stress relaxation resistance characteristics. However, when the added amounts of Ni and Si are not especially within the preferred range, some characteristics may become inferior. For example, comparative example 3-1 is an example in which the amounts of Ni and Si were inadequate, so there was insufficient strength. Comparative example 3-2 is an example in which the amounts of Ni and Si were large, so precipitation occurred at the grain boundary, causing the bending workability to become somewhat inferior. Of course it is not necessary for the contained amounts of Ni and Si to be especially within the preferred range, however, when outside this range, examples are seen in which characteristics become inferior, so it is preferred that when possible, the amount of Ni be within the range 1.8 to 3.3 mass%, and that the amount of Si be within the range 0.4 to 1.1 mass%.

(Examples 4)

[0043] The same investigation as was performed for examples 1 was performed for a copper alloy comprising the composition shown in Table 4 with the remaining part being Cu and inevitable impurities. The manufacturing method and measurement method were the same as for examples 1.

The comparative examples below that are presented with the examples in Table 4 were made with the contained amounts of other added elements outside the preferred range of the present invention.

[0044] [Table 4]

TABLE 4

ID Number	Alloy composition			Other added elements	r/f	T	Bending workability (Cracking Y/N) (W unit mm)						TS	% of particles comprising Cr	GS	EC	SR
	Ni	Si	Cr				GW			BW							
							W=0.5	W=1	W=2	W=0.5	W=1	W=2					
	mass%	mass%	mass%	mass%	23.2	0.20	○	×	×	○	×	W=2	MPa	%	μm	%IACS	%
Invention example 4-1	1.91	0.57	0.15	0.2Co, 0.2Mn	23.2	0.20	○	×	×	○	×	×	751	70	6.8	38.3	27.2
Invention example 4-2	2.42	0.60	0.22	0.2Fe, 0.03P	44.2	0.15	○	○	×	○	×	×	765	75	7.8	39.6	27.8
Invention example 4-3	2.74	0.71	0.1	0.2Ag, 0.3Ti	35.2	0.12	○	○	×	○	×	×	780	80	7.2	37.6	25.6
Invention example 4-4	3.18	0.60	0.2	0.4Sn, 1.0Zn, 0.1Mg	7.8	0.08	○	○	○	○	○	○	802	85	5.1	38.0	24.2
Comparative example 4-1	2.46	0.62	0.15	1.2Sn, 1.2Mg	125.4	0.15	○	×	×	×	×	×	785	40	12.2	28.0	33.2
Comparative example 4-2	2.77	0.70	0.17	1.5Fe	144.2	0.12	○	○	○	○	○	○	669	35	13.1	25.2	40.2

[0045] As is clearly shown in Table 4, invention examples 4-1 to 4-4, in which the contained amounts of other added elements (secondary added elements) other than Ni and Si were especially within the preferred range, have excellent electrical conductivity, bending workability and stress relaxation resistance characteristics. However, when the contained amounts of those other added elements are not especially within the preferred range, some of the characteristics may become inferior. For example, comparative example 4-1 is an example in which the bending workability became inferior. In this comparative example 4-1, it is thought that because the contained amount of the secondary added elements was too large, the grain boundary became fragile. Comparative example 4-2 is an example in which the mechanical strength became inferior. In this comparative example 4-2, it is thought that because the contained amount of the secondary added elements was too large, compounds other than Ni-Si series compounds that contribute to precipitation hardening were formed. Of course, it is not necessary that the contained amounts of secondary added elements be especially within the preferred range, however, by being outside of this range, examples were seen in which characteristics become inferior, so when adding other added elements, it is preferred when possible that one or two or more kinds of elements be included from among at least one of Sn, Mg, Ag, Mn, Ti, Fe and P at a total of 0.01 to 1 mass%, Zn at 0.01 to 10 mass%, and Co at 0.01 to 1.5 mass%.

[0046] The results of examples 1 to 4 above are shown in FIG. 2. It can be seen that with the examples of the invention, under the conditions of 180° tight bending and material dimensions where the product of the test piece thickness T and the test piece width W is 0.16 or less, processing was possible with no cracking; however, for the comparative examples, processing was not possible.

Industrial Applicability

[0047] The copper alloy sheet material of the present invention can be suitably applied for use in lead frames, connectors and terminal materials for electrical / electronic equipment, for example, connectors, terminal materials, relays, switches and sockets for use in automobiles.

[0048] The present invention and examples thereof were explained, however, unless specifically indicated, the invention is not limited by any of the details of the explanation and should be widely interpreted within the spirit and scope of the invention as given in the accompanying claims.

[0049] This application claims priority from a Japanese patent application serial No. 2007-287066 filed on November 5, 2007, the entire content of which is incorporated herein by reference.

Claims

1. A copper alloy sheet material having a tensile strength of 730 to 820 MPa, and comprising at least Ni and Si in addition to copper and inevitable impurities, wherein when the material is capable of 180° tight bending and the sheet width is taken to be W (unit: mm) and the sheet thickness is taken to be T (unit: mm), the product of W and T (unit: mm²) is 0.16 or less.
2. The copper alloy sheet material of claim 1 wherein second-phase particles existing on a grain boundary exist at a density of 10⁴ to 10⁸ particles/mm², and the average grain size is 10 μm or less.
3. The copper alloy sheet material of claim 1 wherein the value of ratio r/f of the particle size r (unit: μm) of second-phase particles inside the grain and on the grain boundary and the volume fraction f of the particles is at least 1 and not more than 100, and the average grain size is 10 μm or less.
4. The copper alloy sheet material of claim 2 or claim 3 wherein of said second-phase particles, the ratio of particles comprising Cr as a constituent element is 50% or more.
5. The copper alloy sheet material of any one of the claims 1 to 4 wherein the alloy composition includes Ni at 1.8 to 3.3 mass%, Si at 0.4 to 1.1 mass% and Cr at 0.01 to 0.5 mass%, with the remaining being Cu and inevitable impurities.
6. The copper alloy sheet material of any one of the claims 1 to 5 comprising one kind or two kinds or more elements from among at least one of Sn, Mg, Ag, Mn, Ti, Fe and P at 0.01 to 1 mass%, Zn at 0.01 to 10 mass% and Co at 0.01 to 1.5 mass%.
7. The copper alloy sheet material of any one of the claims 1 to 6 wherein when the material is maintained at 165 °C for 3000 hours, the stress relaxation rate is 30% or less.

FIG. 1

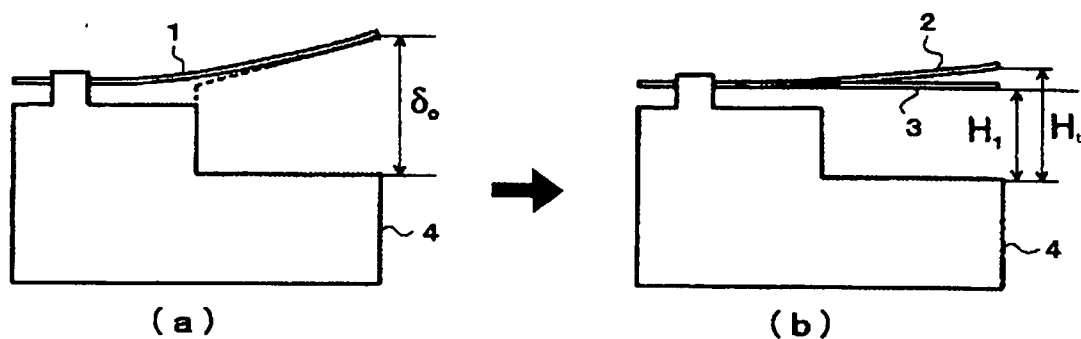
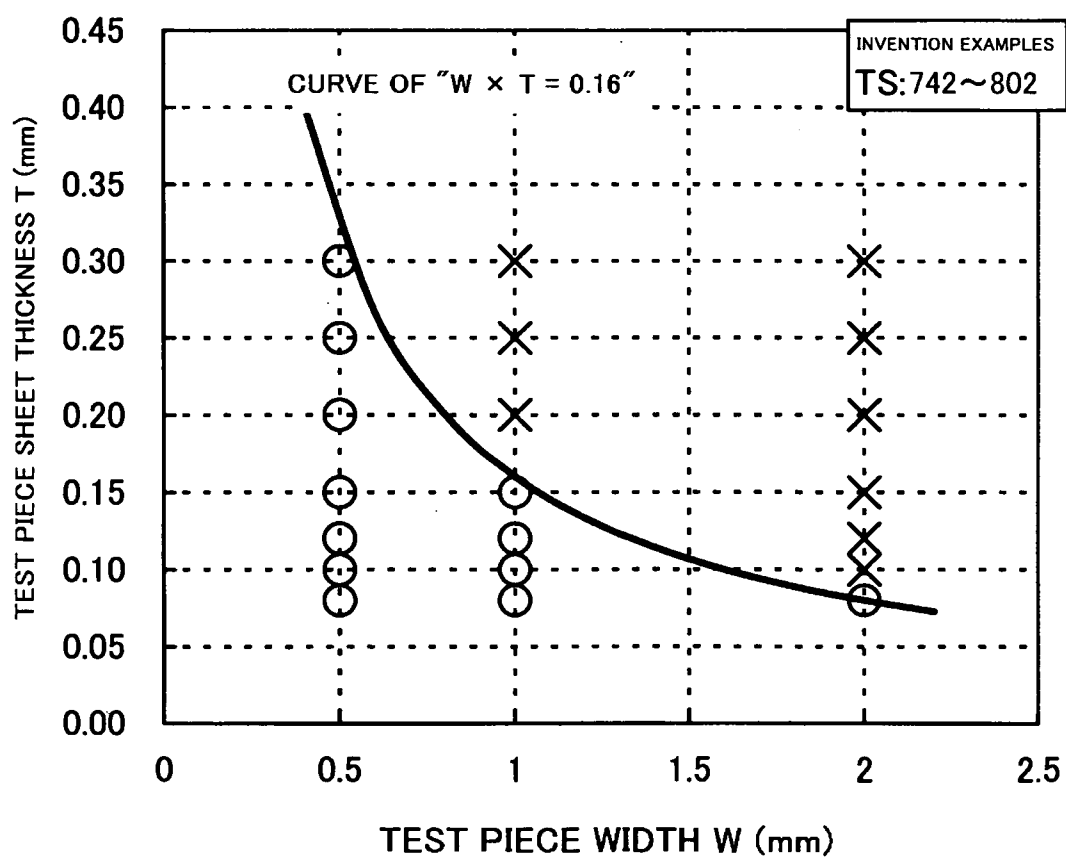


FIG. 2



INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2008/070139

A. CLASSIFICATION OF SUBJECT MATTER

C22C9/06(2006.01)i, B21B3/00(2006.01)i, C22C9/04(2006.01)i, C22F1/08
(2006.01)i, C22F1/00(2006.01)n

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
C22C9/06, B21B3/00, C22C9/04, C22F1/08, C22F1/00

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Jitsuyo Shinan Koho	1922-1996	Jitsuyo Shinan Toroku Koho	1996-2009
Kokai Jitsuyo Shinan Koho	1971-2009	Toroku Jitsuyo Shinan Koho	1994-2009

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 A	JP 2006-265731 A (The Furukawa Electric Co., Ltd.), 05 October, 2006 (05.10.06), Claims 1 to 13; Par. Nos. [0019], [0023] to [0028] & WO 2006/093140 A1 & US 2008/0047634 A1 & EP 1873266 A1 & CN 1166840 A	1, 5, 6 2-4, 7
X A	JP 2006-161148 A (The Furukawa Electric Co., Ltd.), 22 June, 2006 (22.06.06), Claims 1 to 10; Par. Nos. [0018] to [0020] & WO 2005/083137 A1 & US 2005/0236074 A1 & KR 10-2006-0130183 A & CN 1926253 A	1, 5, 6 2-4, 7

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

☐ See patent family annex.

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Date of the actual completion of the international search
21 January, 2009 (21.01.09)

Date of mailing of the international search report
03 February, 2009 (03.02.09)

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International application No.

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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	JP 2002-180165 A (Dowa Mining Co., Ltd.), 26 June, 2002 (26.06.02), Par. Nos. [0024] to [0028] & US 2002/0108685 A1	1-7
A	JP 2002-266042 A (Kobe Steel, Ltd.), 18 September, 2002 (18.09.02), Par. Nos. [0012] to [0015] (Family: none)	1-7
A	JP 2006-152392 A (Kobe Steel, Ltd.), 15 June, 2006 (15.06.06), Claims 1 to 3 (Family: none)	1-7
A	JP 2006-283059 A (Kobe Steel, Ltd.), 19 October, 2006 (19.10.06), Claims 1 to 5 (Family: none)	1-7
A	JP 5-156392 A (The Furukawa Electric Co., Ltd.), 22 June, 1993 (22.06.93), Claims 1 to 4; Par. Nos. [0012] to [0015] (Family: none)	1-7
A	JP 3-236432 A (The Furukawa Electric Co., Ltd.), 22 October, 1991 (22.10.91), Claims; page 2, lower right column, line 19 to page 3, lower right column, line 7 (Family: none)	1-7

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REFERENCES CITED IN THE DESCRIPTION

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Patent documents cited in the description

- JP 11043731 A [0004]
- JP 2007287066 A [0049]
- JP 2005532477 T [0004]