(19) Europäisches Patentamt
European Patent Office
Office européen des brevets

(11) EP 2 679 341 A1

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

(43) Date of publication:
01.01.2014 Bulletin 2014/01

(21) Application number: **12763618.1**

(22) Date of filing: **07.03.2012**

(51) Int Cl.:
B24B 29/00 *(2006.01)* ***C22C 9/00*** *(2006.01)*
C22C 9/02 *(2006.01)* ***C22C 9/04*** *(2006.01)*
C22C 9/05 *(2006.01)* ***C22C 9/06*** *(2006.01)*
C22C 9/10 *(2006.01)* ***C22F 1/08*** *(2006.01)*
C22F 1/00 *(2006.01)*

(86) International application number:
PCT/JP2012/055830

(87) International publication number:
WO 2012/132805 (04.10.2012 Gazette 2012/40)

(84) Designated Contracting States:
AL AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HR HU IE IS IT LI LT LU LV MC MK MT NL NO PL PT RO RS SE SI SK SM TR

(30) Priority: **28.03.2011 JP 2011070183**

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(54) **Co-Si-BASED COPPER ALLOY SHEET**

(57) A Co-Si based copper alloy plate, comprising: Co: 0.5 to 3.0% by mass, Si: 0.1 to 1.0% by mass and the balance Cu with inevitable impurities, wherein the Co-Si based copper alloy plate satisfies the relationship {(60 degree specular gloss G(RD) in a rolling direction) - (60 degree specular gloss G(TD) in a direction transverse to rolling direction)} => 90%.

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Description

Field of the Invention

[0001] The present invention relates to a Co-Si based copper alloy plate.

Description of the Related Art

[0002] As small sized electric and electronic equipment such as a connector is needed, a high strength Co-Si based copper alloy (Colson alloy) is developed. Since the Co-Si based Colson alloy is provided by producing a precipitate compound of Co and Si, it requires solution treatment at high temperature and aging. Therefore, a firm oxide film is formed on the surface, which degrades solder wettability. Also, the Colson alloy may be stress relief annealed after final rolling, which may further grow the oxide film. For this reason, acid pickling is conducted after a final heat treatment, and the oxide film is dissolved and further removed by buffing (hereinafter referred to as a "buffing with acid pickling"). In view of the above, a copper alloy material having improved solder wettability by specifying surface roughness Ra of 0.2 μm or less and Rt of 2 μm or less (Patent Literature 1).
In addition, when the above-described buffing with acid pickling is conducted, ridged concave-convex is generated by buffing on the surface, thereby degrading the solder wettability. Therefore, a copper alloy material is developed by conducting acid pickling or degreasing before finish rolling, thereby improving the solder wettability (Patent Literature 2). By conducting acid pickling or degreasing before final rolling, a peak position in a frequency distribution graph representing concave-convex components on the surface will appear at a plus side (at a convex component side) of a mean line for the roughness profile (0 position in the frequency distribution graph), and solder wettability and plating property will be improved.

Prior Art Documents

[Patent Literature]

[0003]

[Patent Literature 1] International Publication WO 2010/13790
[Patent Literature 2] Japanese Patent No. 4413992 (paragraph 0013)

Problems to be solved by the Invention

[0004] However, in the case of the technology described in Patent Literature 1, even if the solder wettability is good, the oxide film on the surface of the material is not completely removed and acid pickling and grinding are conducted before the final rolling. Thus, once foreign matters are pushed by rolling, pin holes (partial areas where solder is not attached) may be generated. When the number of the pin holes increases, soldering may be imperfect. In particular, when the pin holes are generated at a soldered area where terminals are molded using the Colson alloy, soldering may be imperfect.
In the case of the technology described in Patent Literature 2, acid pickling or degreasing is needed before the finish rolling, which makes the process complicated and also makes productivity poor. In addition, the oxide film of the Co-Si based Colson alloy is quite firm, and is therefore not removed easily only by acid pickling. In the technology described in Patent Literature 2, only acid pickling is conducted after a heat treatment and no grinding is conducted, or no acid pickling and no grinding are conduced. It is considered that the oxide film on the surface of the material is not completely removed, and the pin holes may be easily generated.
Accordingly, the present invention is made to solve the above-described problems. An object thereof is to provide a Co-Si based copper alloy plate having excellent solder wettability and less pin holes generated when soldering.

Means for Solving the Problems

[0005] Through intense studies by the present inventors, it is found that the excellent solder wettability is attained and the number of the pin holes decreases by conducting the buffing with acid pickling for a sufficient number of times using a relatively fine textured buff (grinding grains) after the final heat treatment such that the oxide film on the surface of the material and the foreign matters pushed by the rolling are removed and a smooth surface having predetermined anisotropy is provided.
In order to achieve the above-described object, the present invention provides a Co-Si based copper alloy plate, com-

prising: Co: 0.5 to 3.0% by mass, Si: 0.1 to 1.0% by mass and the balance Cu with inevitable impurities, wherein the Co-Si based copper alloy plate satisfies the relationship {(60 degree specular gloss G(RD) in a rolling direction) - (60 degree specular gloss G(TD) in a direction transverse to rolling direction)} => 90%.

[0006] Preferably, a surface roughness Ra(RD) in a rolling direction is <= 0.07 μm. Preferably, a surface roughness Ra(RD) in a rolling direction is <= 0.50 μm.

[0007] Preferably, a peak position in a frequency distribution graph representing concave-convex components on a surface in the direction transverse to rolling direction is at a minus side (a concave component side) of a mean line for the roughness profile.

The Co-Si based copper alloy plate may further comprising a total of 2.0% by mass or less of one or two or more selected from the group consisting of Mn, Fe, Mg, Ni, Cr, V, Nb, Mo, Zr, B, Ag, Be, Zn, Sn ,a misch metal and P.

Effect of the invention

[0008] According to the present invention, there can be provided a Co-Si based copper alloy plate having excellent solder wettability and less pin holes generated when soldering.

Brief Description of Drawing

[0009]

[Fig. 1] A diagram showing an example of a production process of a Co-Si based copper alloy plate according to an embodiment of the present invention.

[Fig. 2] A frequency distribution graph of concave-convex components on the surface in Example 4.

[Fig. 3] A frequency distribution graph of concave-convex components on the surface in Example 18.

Description of the Embodiments

[0010] Hereinafter, a Co-Si based copper alloy plate according to an embodiment of the present invention will be described. The symbol "%" herein refers to % by mass, unless otherwise specified.

In addition, the surface roughness Ra is arithmetic mean roughness specified in JIS-B0601 (2001), and the surface roughness Rz is a maximum height roughness specified in the same JIS.

[0011] Referring to Fig. 1, a technical idea of the present invention will be described. Fig. 1 shows an example of a production process of a Co-Si based copper alloy plate according to the present invention.

First, when a copper alloy plate 2 after final heat treating is placed into a pickling tank 4 and is acid pickled, an oxide film is dissolved and thinned almost uniformly in a rolling direction (RD) and a direction transverse to rolling direction (TD). Therefore, a 60 degree specular gloss G(RD) in a rolling direction and a 60 degree specular gloss G(TD) in a direction transverse to rolling direction are almost same after pickling, and a difference {G(RD) - G(TD)} nearly equals to 0 (see Fig. 1(a)).

[0012] Next, a buff 6 is used to grind the copper alloy plate after acid pickling. Grinding mark flaws by buffing are left on a material. In the rolling direction (RD) that is a rotation direction of the buff 6, as the grinding on a surface of the material proceeds, the oxide film that is not completely dissolved upon acid pickling disappears from the surface of the material, the surface of the material becomes smooth and the G(RD) becomes great. On the other hand, even if grinding of the surface of the material proceeds in the direction transverse to rolling direction (TD), the grinding mark flaws by buffing are formed on the surface of the material in the TD direction. A degree of smooth is not largely changed, and the G(RD) is not largely changed. It results in {G(RD) - G(TD)} > 0. It is found that when {G(RD) - G(TD)} => 90%, the buffing proceeds to sufficiently remove the oxide film, improve the solder wettability and the pin holes generated when soldering are decreased. An upper limit of {G(RD) - G(TD)} is not especially limited, but is practically 400% or less.

The 60 degree specular gloss reflects a state of the surface of the material having a predetermined area. On the other hand, the surface roughness (such as Ra) reflects a state of the surface of the material on a predetermined straight line. It is therefore considered that the 60 degree specular gloss reflects the state of a locally existing oxide film and foreign matters on the surface of the material better than the surface roughness.

The buff 6 is hollow cylindrical, and grinding grains are attached to the surface thereof. By rotating the buff 6 in a forward direction, i.e., a threading direction of the copper alloy plate 2 (from left to right in Fig. 1), the grinding grains of the buff 6 grinds the surface of the copper alloy plate 2. Accordingly, a degree of the oxide film removal by the buffing process can be adjusted by a grain size (count) of respective grinding grains, a threading number of the copper alloy plate 2, a threading speed (line speed), a rotation number of the buff 6 and the like.

[0013] Also, the surface roughness Ra (RD) in the rolling direction is preferably 0.07 μm or less. If the Ra (RD) is less than 0.07 μm, the zero cross time may be decreased.

[0014] According to the present invention, a peak position in the frequency distribution graph of concave-convex components on the surface in the direction transverse to rolling direction can be specified. Here, the frequency distribution graph of the concave-convex components on the surface is identical with that described in Patent Literature 2, and is a plot where a horizontal axis represents a height from a mean line for the roughness profile and a vertical axis represents a frequency (measurement data numbers). According to the present invention, the horizontal axis is at 0.05 μm intervals (increments in between) for the mean line for the roughness profile and the measurement data numbers at the intervals are summed up as the frequency to generate the plot. The "mean line for the roughness profile" is specified in JIS-B0601.

[0015] Specifically, the frequency distribution graph is created as follows: (1) Firstly, "the height from a mean line for the roughness profile" is measured along a direction transverse to rolling direction of a sample. In other words, there are provided data of the height from the mean line for the roughness profile (hereinafter referred to as "measurement data" as appropriate) per surface position. The peak position or the like is determined from the resultant measurement data, and the measurement data is numerically treated to calculate Ra and Rz. (2) The height from the "mean line for the roughness profile" is delimited at 0.05 μm intervals. (3) The measurement data numbers (frequency) are counted at the 0.05 μm intervals.

To provide the measurement data, measurement is made at an evaluation lenghth of 1.25 mm, a cut off value of 25 mm (in accordance with JIS-80601) and a scan speed of 0.1 mm/sec. For the measurement, a surface roughness meter manufactured by Kosaka Laboratory Ltd. (Surfcorder SE3400) is used. The measurement data numbers are 7500 points at an evaluation lenghth of 1.25 mm.

[0016] Also, the method of measuring the peak position is identical with that described in Patent Literature 2. The resultant measurement data is categorized as follows: When the height from "the mean line for the roughness profile" is more than 0, the data is categorized as upper (plus) components. When the height is less than 0, the data is categorized as lower (minus) components. Thus, the frequency distribution is plotted. The height (μm) from "the mean line for the roughness profile" is replotted on the horizontal axis. The measurement data numbers are replotted as the frequency summed up at 0.05 μm intervals on the vertical axis. Thus, Figs. 2 and 3 are provided (corresponding to Fig. 3 in Patent Literature 2). In Figs. 2 and 3, at the height from "the mean line for the roughness profile" of the horizontal axis of 0 μm, a line is drawn to determined that the peak position of the frequency is a concave component (at a minus side), a convex component (at a plus side) or (0).

Here, the "peak position" is determined as follows: Firstly, from the graphs (see Figs. 2 and 3) of a height from "the mean line for a frequency-roughness curve", the frequency having the highest value is denoted as P1 and the frequency having the second highest value is denoted as P2. (1) When P1 and P2 are in the minus side or when P2/P1 < 99% and P1 is in the minus side, the peak position of the frequency is a concave component (at a minus side). (2) When P1 and P2 are in the plus side or when P2/P1 < 99% and P1 is in the plus side, the peak position of the frequency is a convex component (at a plus side). (3) When P2/P1 => 99% (except that both P1 and P2 are in the minus side and both P1 and P2 are in the plus side), the peak position of the frequency is 0.

Here, a line wherein the height from the mean line for the roughness profile being 0 μm is the mean line for the roughness profile.

When the peak positions measured three times may be in plus and minus and the peaks are in the upper (plus) components two times, they are considered as in the convex component side.

[0017] Fig. 2 is a graph replotted by the frequency (%) on the vertical axis and the height (μm) from the mean line for the roughness profile on the horizontal axis about actual measurement data in Example 4 described later.

Fig. 3 is a graph replotted by the frequency (%) on the vertical axis and the height (μm) from the mean line for the roughness profile on the horizontal axis about actual measurement data in Example 18 described later.

In Fig. 3, the peak position in the frequency distribution graph of the concave-convex components on the surface is at the plus side (a convex component side) of the mean line for the roughness profile. In Fig. 2, the peak position is at the minus side (a concave component side) of the mean line for the roughness profile. In other words, according to the present invention (for example, Fig. 2 and Example 4), even when the peak position is in the minus side (the concave component side), a wetting property is good. The wetting property does not depend on the peak position. In Example 18, the peak position is in the plus position because an acid pickling solution is changed upon acid pickling.

[0018] The method of measuring the surface roughness Ra, Rz is identical with that described in Patent Literature 2 and measurement is made at an evaluation length of 1.25 mm, a cut off value of 25 mm (in accordance with JIS-80601) and a scan speed of 0.1 mm/sec. For the measurement, a surface roughness meter manufactured by Kosaka Laboratory Ltd. (Surfcorder SE3400) is used. The measurement data numbers are 7500 points at an evaluation lenghth of 1.25 mm. The surface roughness Ra, Rz is measured three times, which are averaged.

[0019] Next, other definitions and compositions of the Co-Si based copper alloy plate according to the present invention will be described.

<Composition>

[0020] The composition includes Co: 0.5 to 3.0% by mass, Si: 0.1 to 1.0% by mass and the balance Cu with inevitable impurities. If the content of Co and Si is less than the above-defined range, precipitation by Co_2Si is insufficient, and the strength cannot be enhanced. On the other hand, if the content of Co and Si exceeds the above-defined range, an electrical conductivity is degraded, and hot workability is also degraded. The content of Co is preferably 1.5 to 2.5% by mass, more preferably 1.7 to 2.2% by mass. The content of Si is preferably 0.3 to 0.7% by mass, more preferably 0.4 to 0.55% by mass.

A mass ratio of Co/Si is preferably 3.5 to 5.0, more preferably 3.8 to 4.6. Within the range of the mass ratio of Co/Si, Co_2Si can be fully precipitated.

[0021] Preferably, the composition further includes a total of 2.0% by mass or less of one or two or more selected from the group consisting of Mn, Mg, Ag, P, B, Zr, Fe, Ni, Cr, V, Nb, Mo, Be, Zn, Sn ,and a misch metal. If the total amount of the above element exceeds 2.0% by mass, the following advantages are saturated and the productivity is degraded. However, if the total amount of the element is less than 0.001% by mass, less advantages are provided. The total amount of the element is preferably 0.001 to 2.0% by mass, more preferably 0.01 to 2.0% by mass, most preferably 0.04 to 2.0% by mass.

[0022] Here, when a minor amount of Mn, Mg, Ag and P improves product properties such as strength and a stress relaxation property without impairing electric conductivity. The above-described advantage is provided by dissolving the element mainly to a matrix in a solid solution. When the element is contained in second phase particles, further advantages are provided.

Also, the addition of B, Zr and Fe improves the product properties such as strength, electric conductivity, a stress relaxation property and a plating property. The above-described advantage is provided by dissolving the element mainly to a matrix in a solid solution. When the element is contained in second phase particles, further advantages are provided.

Ni, Cr, V, Nb, Mo, Be, Zn, Sn and a misch metal are complemented each other, and improve not only strength and electric conductivity, but also production properties such as a stress relaxation property, bending workability, a plating property, and manufacturability such as a hot workability by refining an ingot tissue.

In addition, elements that are not specifically described in the present specification may be added as long as the alloy of the present invention is not adversely affected.

[0023] Next, an example of a method of producing the Co-Si based cooper alloy plate according to the present invention will be described. Firstly, an ingot including copper, alloy element(s) required, and inevitable impurities is hot rolled, mechanical finished, cold rolled, solution treated, and then aging treated to precipitate Co_2Si. Next, the material is final cold rolled to have a predetermined thickness. If desired, a stress relief annealing may be further conducted. Finally, the material is acid pickled and is promptly buffing. Solution treatment may be conducted at any temperature within 700°C to 1000°C. Aging treatment may be conducted at 400°C to 650°C for 1 to 20 hours. A reduction ratio of the final cold rolling is preferably 5% to 50%, more preferably 20% to 30%. A crystal grain size of the alloy material according to the present invention is not especially limited, but is generally 3 to 20 μm. A grain size of the precipitate is 5 nm to 10 μm.

Examples

[0024] The ingot having the composition shown in Table 1 was casted, was hot rolled at 900°C or more to have a thickness of 10 mm, mechanical finished to remove an oxidized scale on the surface, cold rolled, solution treated at a temperature within 700°C to 1000°C, and then aging treated at 400°C to 650°C for 1 to 20 hours. Next, the material was final cold rolled to have a predetermined thickness at a reduction ratio of 5 to 40%. Further, the material was stress relief annealed at 300 to 600°C for 0.05 to 3 hours. Finally, the material was acid pickled and was promptly buffing under the conditions shown in Table 1. An acid pickling solution used for the acid pickling before the buffing was a solution of dilute sulfuric acid, hydrochloric acid or dilute nitric acid at a concentration of 20 to 30% by mass at pH = 1 or less. An immersion time in the acid pickling was 60 to 180 seconds. A buffing material used for the buffing was alumina grinding grains, and a nylon non-woven cloth containing the alumina. Buff materials having different buff texture roughnesses (counts of grinding grains) were used. The count of the grinding grains represents the grinding grains by the number of mesh per inch, and is specified by JIS R6001. For example, when the count is 1000, an average size of the grinding grains will be 18 to 14.5 μm. Example 18 is similar to other Examples except that a nitric acid solution at a concentration of 40 to 50% by mass at pH = 1 or less was used as the acid pickling solution of the acid pickling buffing.

[0025] Respective samples thus obtained were evaluated for a variety of properties.

(1) Ra and Rz

[0026] Arithmetic mean roughness Ra and a maximum height roughness Rz were measured in accordance with JIS B0601 (2001). Measurement was made in the rolling direction (RD) and the direction transverse to rolling direction (TD).

The measurement was made at an evaluation length of 1.25 mm, a cut off value of 0.25 mm (in accordance with the JIS above described) and a scan speed of 0.1 mm/sec. A surface roughness meter manufactured by Kosaka Laboratory Ltd. (Surfcorder SE3400) was used. The measurement data numbers are 7500 points at an evaluation lenghth of 1.25 mm.

(2) Frequency distribution graph

[0027] The measurement data in the direction transverse to rolling direction obtained in (1) was categorized into upper (plus) components and lower (minus) components from "the mean line for the roughness profile", a frequency distribution was plotted by delimiting the height from the "mean line for the roughness profile" at 0.05 μm intervals. From the measurement data, the frequency (%) was re-plotted on the vertical axis, and the height (μm) from "the mean line for the roughness profile" was replotted on the horizontal axis. Thus, Figs. 2 and 3 were provided. In Figs. 2 and 3, at the height from "the mean line for the roughness profile" of the horizontal axis of 0 μm, a line was drawn to determine that the peak position of the frequency is a concave component (at a minus side), a convex component (at a plus side) or (0).

(3) Gloss

[0028] 60 degree specular gloss was measured by using a gloss meter in accordance with JIS-Z8741 (trade name "PG-1M" manufactured by Nippon Denshoku Industries Co., Ltd.) at an entry angle of 60 degrees in the rolling direction RD and the direction transverse to rolling direction TD.

[0029] Fig. 2 is a graph replotted by the frequency (%) on the vertical axis and the height (μm) from the mean line for the roughness profile on the horizontal axis about actual measurement data in Example 4.
Fig. 3 is a graph replotted by the frequency (%) on the vertical axis and the height (μm) from the mean line for the roughness profile on the horizontal axis about actual measurement data in Example 18 described later.

(3) Solder properties

(3-1) Pin hole number

[0030] A pin hole number refers to the number of the holes through which a base material (copper alloy material) is viewed without solder wetting. When the pin hole number increases, soldering may be imperfect. The pin hole number was tested by acid pickling each sample having a width of 10 mm with a solution including 10% by mass of dilute sulfuric acid, immersing the sample into a solder bath at an immersion depth of 12 mm, an immersion speed of 25 mm/s and an immersion time of 10 sec, and pulling up the sample from the solder bath. Front and back sides of the sample were observed by an optical microscope (50 magnification), and the number of the pin holes through which the base material was visible was counted. If the number was not more than 5, the sample was determined as good.
A solder test was conducted in accordance with JIS-C60068-2-54. The solder bath composition was 60 wt% of tin and 40 wt% of lead. An appropriate amount of a flux (25 wt% of rosin and 75 wt% of ethanol) was added thereto. A solder temperature was 235 ± 3°C.

(3-1) Zero cross time (T2 value)

[0031] A zero cross time (T2 value) refers to a time until a wet stress value becomes zero. The shorter the zero cross time is, the more the solder wets. The test was conducted by acid pickling the sample with a solution including 10% by mass of dilute sulfuric acid, and immersing the sample into the above-described solder bath at an immersion depth of 4 mm, an immersion speed of 25 mm/s, an immersion time of 10 sec and 235 ± 3°C in accordance with JIS-C60068-2-54. The zero cross time was determined by a meniscograph method. When the zero cross time was 2.0 sec or less, the solder wettability was determined as good.

[0032] Tables 1 to 3 show the results obtained. As to "pretreatment before finish rolling" in Tables 1 and 2, methods A and B refer the buffing with acid pickling under the conditions described below. For example, in Example 9, the buffing with acid pickling was conducted before and after the finish rolling. The acid pickling solution used for the buffing with acid pickling before the finish rolling was same as the acid pickling solution used for the buffing with acid pickling after the finish rolling discussed above.
Method A: Number of buffing time of 1, threading speed of 40 m/min, buff texture roughnesses (grinding grains) of 1000 counts, and buff rotating number of 500 rpm
Method B: Number of buffing time of 3, threading speed of 10 m/min, buff texture roughnesses (grinding grains) of 2000 counts, and buff rotating number of 1400 rpm
Some samples were only acid pickled with a 10% sulfuric acid solution for 30 sec before the finish rolling. Some samples were only degreased by immersing into hexane for 30 sec before the finish rolling. The other samples were not treated

before the finish rolling.

[0033]

[Table 1]

No.	Composition (wt%)				Production process			Buffing				
	Co	Si	Other component	Pretreatment before finish rolling	Finish rolling	Stress relief annealing	Acid pickling	Buffing	Threading number	Threading speed (m/min)	Buff texture roughness (counts)	Rotation number (/min)
Example 1	0.50	0.11		-	○	○	○	○	3	10	2000	1400
Example 2	1.00	0.23	-	-	○	○	○	○	3	10	2000	1400
Example 3	1.50	0.40	-	-	○	○	○	○	3	10	2000	1400
Example 4	1.80	0.41	-	-	○	○	○	○	3	10	2000	1400
Example 5	2.50	0.70	-	-	○	○	○	○	3	10	2000	1400
Example 6	3.00	1.00	-	-	○	○	○	○	3	10	2000	1400
Example 7	1.50	0.40	-	-	○	○	○	○	2	10	2000	1400
Example 8	1.50	0.40	-	-	○	○	○	○	4	10	4000	1400
Example 9	1.50	0.40	-	Method A	○	○	○	○	3	10	2000	1400
Example 10	1.50	0.40	-	Method B	○	○	○	○	3	10	2000	1400
Example 11	1.50	0.40	-	Only acid pickling	○	○	○	○	3	10	2000	1400
Example 12	1.50	0.40	-	Only degreasing	○	○	○	○	3	10	2000	1400
Example 13	1.50	0.40	-	-	○	○	○	○	2	10	2000	1200
Example 14	1.50	0.40	Mn:0.1, Fe: 0.2, Mg: 0.05, Ni:1.2	-	○	○	○	○	3	10	2000	1400
Example 15	1.50	0.40	Cr:0.1, V: 0.2,Nb: 0.1,Mo:0.1 , Zr:0.1	-	○	○	○	○	3	10	2000	1400

(continued)

No.	Composition (wt%)			Production process				Buffing				
	Co	Si	Other component	Pretreatment before finish rolling	Finish rolling	Stress relief annealing	Acid pickling	Buffing	Threading number	Threading speed (m/min)	Buff texture roughness (counts)	Rotation number (/min)
Example 16	1.50	0.40	B:0.05,Ag: 0.1,Zn: 0.5,Sn:0.4	-	○	○	○	○	3	10	2000	1400
Example 17	1.50	0.40	Be:0.1, misch metal: 0.1,P0.05	-	○	○	○	○	3	10	2000	1400
Example 18	1.50	0.40	-	-	○	○	○	○	3	10	2000	1400
Example 19	1.50	0.40	-	-	○	○	○	○	6	10	4000	1500

[0034]

[Table 2]

No.	Composition (wt%)				Production process			Buffing				
	Co	Si	Other component	Pretreatment before finish rolling	Finish rolling	Stress relief annealing	Acid pickling	Buffing	Threading number	Threading speed (m/min)	Buff texture roughness (counts)	Rotation number (/min)
Comparative Example 1	1.50	0.40	-	-	○	○	○	○	3	60	2000	1400
Comparative Example 2	1.50	0.40	-	-	○	○	○	○	3	100	2000	1400
Comparative Example 3	1.50	0.40	-	-	○	○	○	○	1	10	2000	1400
Comparative Example 4	1.50	0.40	-	-	○	-	-	-	-	-	-	-
Comparative Example 5	1.50	0.40	-	-	○	○	○	○	1	10	4000	1400
Comparative Example 6	1.50	0.40	-	-	○	○	○	○	2	10	4000	1400
Comparative Example 7	1.50	0.40	-	-	○	○	○	○	3	10	4000	1400
Comparative Example 8	1.50	0.40	-	-	○	○	○	○	1	10	500	1400
Comparative Example 9	1.50	0.40	-	-	○	○	○	○	2	10	500	1400
Comparative Example 10	1.50	0.40	-	-	○	○	○	○	3	10	500	1400
Comparative Example 11	1.50	0.40	-	-	○	○	○	○	3	10	2000	200
Comparative Example 12	1.50	0.40	-	-	○	○	○	○	3	10	2000	500
Comparative Example 13	1.50	0.40	-	-	○	○	○	-	1	10	-	-

(continued)

No.	Composition (wt%)			Production process					Buffing				
	Co	Si	Other component	Pretreatment before finish rolling	Finish rolling	Stress relief annealing	Acid pickling	Buffing	Threading number	Threading speed (m/min)	Buff texture roughness (counts)	Rotation number (/min)
Comparative Example 14	1.50	0.40	-	Method A	○	-	-	-	-	-	-	-
Comparative Example 15	1.50	0.40	-	Method A	○	○	○	○	1	60	2000	500
Comparative Example 16	1.50	0.40	-	Only degreasing	○	-	-	-	-	-	-	-
Comparative Example 17	1.50	0.40	-	Only degreasing	○	○	○	○	1	60	2000	500
Comparative Example 18	1.50	0.40	-	Only acid pickling	○	-	-	-	-	-	-	-
Comparative Example 19	1.50	0.40	-	Only acid pickling	○	○	○	○	1	60	2000	500
Comparative Example 20	1.50	0.40	-	-	○	○	○	○	1	40	1000	500
Comparative Example 21	1.50	0.40	-	-	○	-	-	-	-	-	-	-

[0035]

[Table 3]

No.	Frequency distribution curve peak position	Ra(μm)		Rz(μm)		Gloss G(60°)			Solder properties	
		RD	TD	RD	TD	RD	TD	G (RD) -G (TD)	Pinhole numbers	Zero cross time (sec)
Example 1	-	0.05	0.08	0.42	0.6	299	191	108	0	1.61
Example 2	-	0.06	0.08	0.44	0.68	288	193	95	0	1.73
Example 3	-	0.05	0.08	0.43	0.65	288	192	96	0	1.65
Example 4	-	0.06	0.08	0.43	0.67	288	190	98	0	1.73
Example 5	-	0.05	0.08	0.44	0.66	293	192	101	0	1.62
Example 6	-	0.06	0.08	0.43	0.68	288	192	96	0	1.81
Example 7	-	0.06	0.08	0.54	0.71	288	193	95	4	1.87
Example 8	-	0.04	0.06	0.35	0.53	387	288	99	0	1.59
Example 9	-	0.06	0.08	0.42	0.68	288	189	99	1	1.72
Example 10	-	0.05	0.08	0.43	0.68	297	190	107	0	1.65
Example 11	-	0.06	0.08	0.42	0.68	287	190	97	1	1.82
Example 12	-	0.06	0.08	0.43	0.68	288	193	95	1	1.73
Example 13	-	0.08	0.10	0.52	0.68	274	174	100	4	1.87
Example 14	-	0.06	0.08	0.42	0.66	288	186	102	0	1.70
Example 15	-	0.05	0.08	0.43	0.67	294	188	106	0	1.61
Example 16	-	0.06	0.08	0.42	0.66	288	188	100	0	1.70
Example 17	-	0.06	0.09	0.43	0.67	288	179	109	0	1.71
Example 18	+	0.07	0.1	0.45	0.69	276	168	108	3	1.59
Example 19	-	0.04	0.06	0.23	0.37	384	280	104	0	1.20
Comparative Example 1	-	0.10	0.10	0.72	0.72	184	184	0	7	1.73
Comparative Example 2	-	0.13	0.14	0.76	0.78	180	168	12	8	1.88
Comparative Example 3	-	0.10	0.09	0.71	0.70	186	168	18	7	1.80
Comparative Example 4	-	0.31	0.28	1.54	1.74	123	134	-11	42	2.81
Comparative Example 5	-	0.14	0.15	0.82	0.83	160	153	7	13	1.88
Comparative Example 6	-	0.10	0.12	0.69	0.73	175	170	5	9	1.87
Comparative Example 7	-	0.07	0.08	0.49	0.60	275	190	85	6	1.80
Comparative Example 8	-	0.34	0.38	2.38	2.42	120	100	20	11	2.64

(continued)

No.	Frequency distribution curve peak position	Ra(μm)		Rz(μm)		Gloss G(60°)			Solder properties	
		RD	TD	RD	TD	RD	TD	G (RD) -G (TD)	Pinhole numbers	Zero cross time (sec)
Comparative Example 9	-	0.35	0.38	2.45	2.42	122	102	20	12	2.48
Comparative Example 10	-	0.34	0.38	2.38	2.48	121	100	21	11	2.43
Comparative Example 11	-	0.13	0.13	0.78	0.79	174	158	16	9	1.84
Comparative Example 12	-	0.10	0.11	0.68	0.71	184	175	9	6	1.87
Comparative Example 13	-	0.15	0.15	0.82	0.83	151	158	-7	21	2.50
Comparative Example 14	-	0.30	0.27	1.51	1.74	133	138	-5	20	1.87
Comparative Example 15	-	0.12	0.13	1.42	1.43	169	160	9	8	1.85
Comparative Example 16	+	0.30	0.28	1.52	1.86	130	145	-15	39	2.80
Comparative Example 17	-	0.13	0.13	1.42	1.42	155	155	0	12	1.85
Comparative Example 18	+	0.31	0.28	1.51	1.78	128	133	-5	28	2.45
Comparative Example 19	-	0.12	0.13	1.42	1.43	175	178	-3	10	1.87
Comparative Example 20	-	0.14	0.16	1.01	1.12	150	149	1	9	2.23
Comparative Example 21	-	0.06	0.05	0.4	0.37	261	280	-19	38	2.73

[0036] As apparent from Tables 1 to 3, in each of Examples where the buffing with acid pickling was conducted for a sufficient number of times using a relatively fine textured buff (grinding grains) after a final heat treatment (stress relief annealed), the solder wettability was excellent, and the pin holes are decreased. In each Example, {(60 degree specular gloss G(RD) in a rolling direction) - (60 degree specular gloss G(TD) in a direction transverse to rolling direction)} => 90%. It is considered that the oxide film on the surface of the material and the foreign matters pushed are sufficiently removed and the surface becomes smooth.

The buffing with acid pickling in each Example was conducted under the conditions: grinding grains of 2000 counts or more, threading time of two or more, threading speed of 10 mpm or less, and rotating number of 1200 rpm or more. It should be appreciated that these optimum ranges are changed depending on a production apparatus.

[0037] On the other hand, in each of Comparative Examples where the buffing with acid pickling was conducted insufficiently, the oxide film on the surface of the material and the foreign matters pushed are not sufficiently removed. Therefore, in each Comparative Example, {(60 degree specular gloss G(RD) in a rolling direction) - (60 degree specular gloss G(TD) in a direction transverse to rolling direction)} < 90%. The pin holes are increased, and the solder wettability was degraded when the oxide film was remained largely.

[0038] A cause of degradation may be that when the buffing with acid pickling was conducted in Comparative Examples 1, 2, 15, 17 and 19, the threading speed exceeded 20 mpm.

The cause of degradation may be that in Comparative Examples 3, 5, 8 and 20 the threading time was less than two.

Notably, in Comparative Example 20, the buffing with acid pickling was conducted using the above-described method A after the final rolling.

The cause of degradation may be that in Comparative Example 13 no buffing was conducted although acid pickling was conducted.

In Comparative Examples 6 and 7 where the count of the grinding grains used in the buffing with acid pickling was 4000, the grinding grains were too fine to grind, and it is thus considered that Ra(RD) is not so decreased.

The cause of degradation may be that, in Comparative Examples 11 and 12, the rotating number in the buffing with acid pickling was less than 1200 rpm.

In Comparative Examples 9 and 10, the grinding grains were coarse and the surface after the buffing with acid pickling became roughened, {(60 degree specular gloss G(RD) in a rolling direction) - (60 degree specular gloss G(TD) in a direction transverse to rolling direction)} < 90%, the pin holes are increased and the zero cross time was bad. It is considered that, since the count of the grinding grains used in the buffing with acid pickling was 500, the grinding grains were too coarse.

The cause of degradation may be that, in Comparative Examples 4, 14, 16, 18 and 21 where no buffing with acid pickling was conducted after the final rolling, the oxide film on the surface and the foreign matters pushed were not removed and the rolled surface was left as it is. Comparative Example 21 was similar to each Example except that the roughness of the mill rolls of the final rolling was finer.

[0039] In Comparative Examples 16 and 18, the treatment (acid pickling or degreasing) was conducted before the finish rolling and no buffing with acid pickling was conducted. As a result, the peak position was at the plus side (at the convex component side) of the mean line for the roughness profile (0 position in the frequency distribution graph representing the concave-convex components on the surface). In other words, these Comparative Examples show the copper alloy plate described in Patent Literature 2.

In Comparative Examples 4, 13, 16 and 21, the zero cross time exceeded 2.0 sec and the solder wettability was degraded. It is considered that, since no acid pickling and no buffing were conducted, the oxide film remained on the surface of the metal (Comparative Example 16 corresponds to the conditions described in Patent Literature 2).

Claims

1. A Co-Si based copper alloy plate, comprising:

Co: 0.5 to 3.0% by mass, Si: 0.1 to 1.0% by mass and the balance Cu with inevitable impurities, wherein the Co-Si based copper alloy plate satisfies the relationship {(60 degree specular gloss G(RD) in a rolling direction) - (60 degree specular gloss G(TD) in a direction transverse to rolling direction)} => 90%.

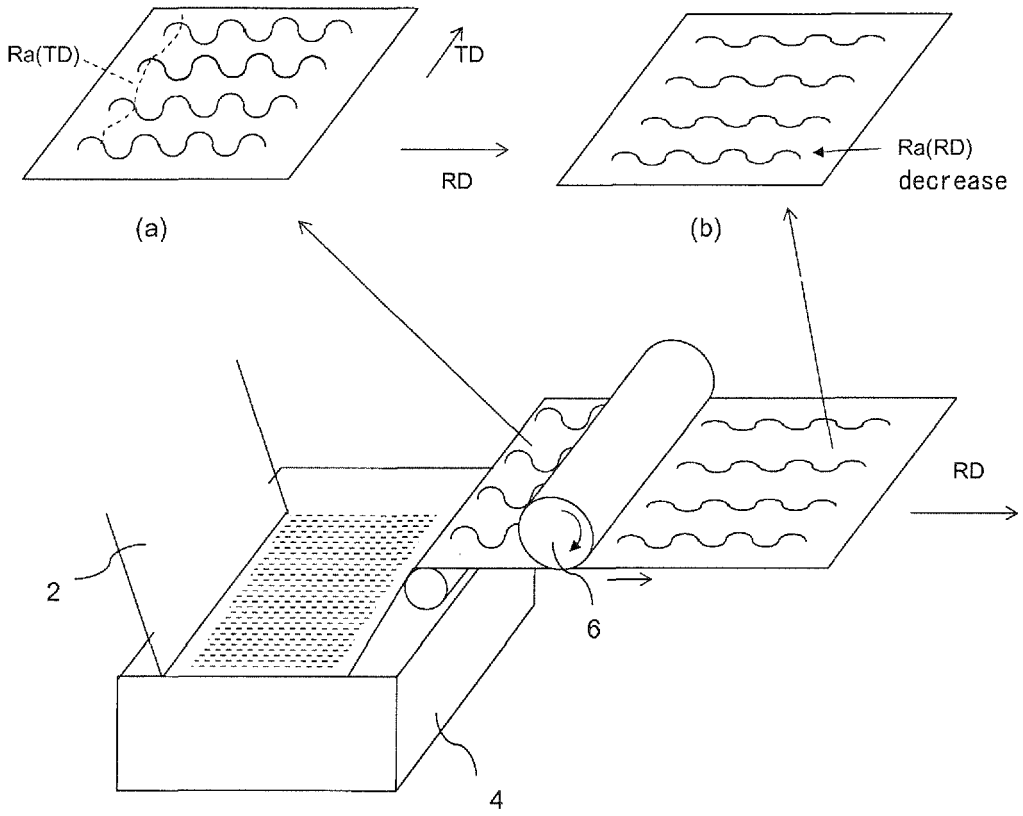
2. The Co-Si based copper alloy plate according to Claim 1, wherein a surface roughness Ra(RD) in a rolling direction is <= 0.07 μm.

3. The Co-Si based copper alloy plate according to Claim 2, wherein a surface roughness Ra(RD) in a rolling direction is <= 0.50 μm.

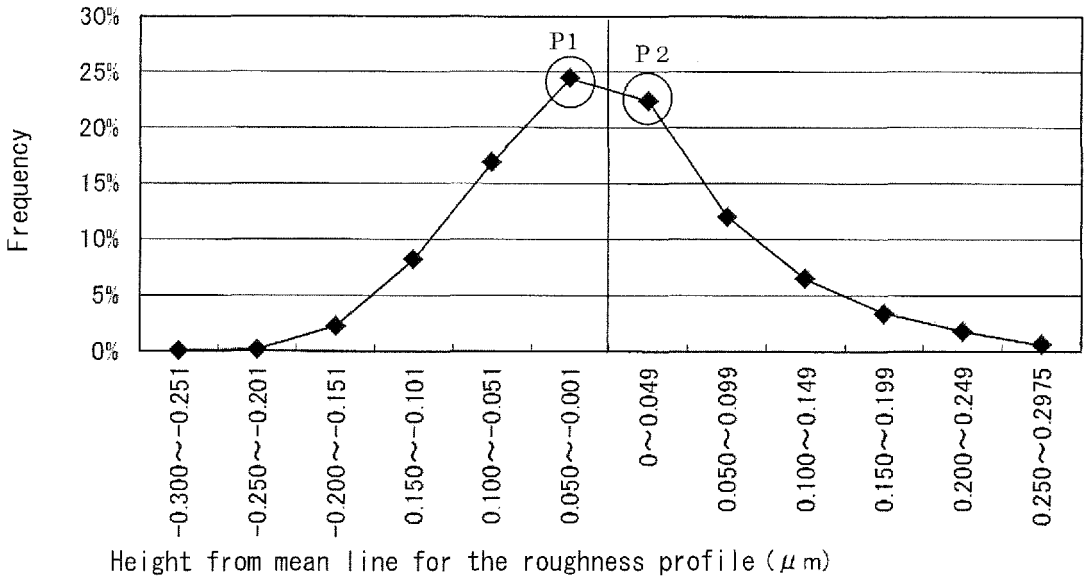
4. The Co-Si based copper alloy plate according to any one of Claims 1 to 3, wherein a peak position in a frequency distribution graph representing concave-convex components on a surface in the direction transverse to rolling direction is at a minus side (a concave component side) of a mean line for the roughness profile.

5. The Co-Si based copper alloy plate according to any one of Claims 1 to 4, further comprising a total of 2.0% by mass or less of one or two or more selected from the group consisting of Mn, Fe, Mg, Ni, Cr, V, Nb, Mo, Zr, B, Ag, Be, Zn, Sn ,a misch metal and P.

[Fig. 1]


Ra(TD)
TD
RD
Ra(RD)
decrease
(a)
(b)
RD
2
6
4

[Fig. 2]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25%
20%
15%
10%
5%
0%
Frequency
P1
P2
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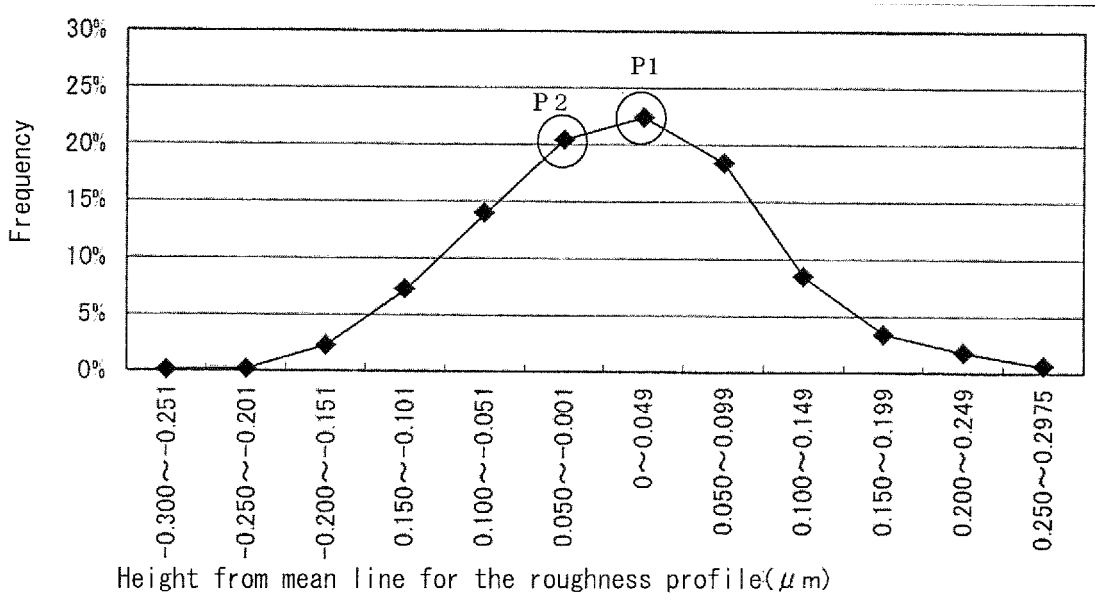
-0.250~-0.201
-0.200~-0.151
-0.150~-0.101
-0.100~-0.051
-0.050~-0.001
0~0.049
0.050~0.099
0.100~0.149
0.150~0.199
0.200~0.249
0.250~0.2975
Height from mean line for the roughness profile (μm)

[Fig. 3]


30%
25%
20%
15%
10%
5%
0%
Frequency
P1
P2
-0.300~-0.251
-0.250~-0.201
-0.200~-0.151
0.150~-0.101
0.100~-0.051
0.050~-0.001
0~0.049
0.050~0.099
0.100~0.149
0.150~0.199
0.200~0.249
0.250~0.2975
Height from mean line for the roughness profile(μm)

INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/055830

A. CLASSIFICATION OF SUBJECT MATTER
B24B29/00(2006.01)i, *C22C9/00*(2006.01)i, *C22C9/02*(2006.01)i, *C22C9/04*(2006.01)i, *C22C9/05*(2006.01)i, *C22C9/06*(2006.01)i, *C22C9/10*(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)
B24B29/00, C22C9/00, C22C9/02, C22C9/04, C22C9/05, C22C9/06, C22C9/10, 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 1996-2012
Kokai Jitsuyo Shinan Koho 1971-2012 Toroku Jitsuyo Shinan Koho 1994-2012

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 4677505 B1 (JX Nippon Mining & Metals Corp.), 04 February 2011 (04.02.2011), entire text; all drawings (Family: none)	1-5
A	JP 2010-227971 A (Nippon Mining & Metals Co., Ltd.), 14 October 2010 (14.10.2010), entire text; all drawings (Family: none)	1-5
A	JP 2008-91040 A (Nippon Mining & Metals Co., Ltd.), 17 April 2008 (17.04.2008), entire text; all drawings (Family: none)	1-5

☒ 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	Date of mailing of the international search report
22 March, 2012 (22.03.12)	03 April, 2012 (03.04.12)
Name and mailing address of the ISA/ Japanese Patent Office Facsimile No.	Authorized officer Telephone No.

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/JP2012/055830

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 1-306162 A (Nippon Steel Corp.), 11 December 1989 (11.12.1989), entire text; all drawings (Family: none)	1-5
A	JP 2006-231451 A (Nitto Shinko Co., Ltd.), 07 September 2006 (07.09.2006), entire text; all drawings (Family: none)	1-5

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Patent documents cited in the description

- WO 201013790 A **[0003]**
- JP 4413992 B **[0003]**