

HIGH-STRENGTH COPPER ALLOY PLATE EXCELLENT IN OXIDE FILM ADHESIVENESS

FIELD OF THE INVENTION

The present invention relates to a copper alloy plate of a Cu-Fe-P system having an improved oxide film adhesiveness.

BACKGROUND OF THE INVENTION

The explanations are hereunder made on the basis of the case of using a copper alloy plate for a lead frame that is a semiconductor component as a representative application example of a copper alloy plate according to the present invention.

As a copper alloy for a semiconductor lead frame, a copper alloy of a Cu-Fe-P system containing Fe and P is generally used.

Meanwhile, as a plastic package for a semiconductor device, a package of sealing a semiconductor chip with a thermosetting resin is the mainstream.

There are however the problems of package cracking and peel off caused during implementation and use.

Here, the above problems are caused by poor adhesiveness between a resin and a lead frame. A substance most influencing the adhesiveness is an oxide film of a lead frame base material. An oxide film of several ten to several hundred nanometers in thickness is formed on the surface of a base material during various heating processes for manufacturing a lead frame and a copper alloy and a resin touch each other through the oxide film. The peel off of such an oxide film from a lead frame base material directly leads to the peel off between a resin and the lead frame and the adhesiveness between the lead frame and the resin deteriorates considerably.

The problems of package cracking and peel off therefore depend on the adhesiveness of such an oxide film to a lead frame base material. Consequently, in a copper alloy plate of a Cu-Fe-P system as a lead frame base material, an oxide film formed on a surface through various heating processes is required to have a good adhesiveness.

To cope with the problems, JP-A No. 2008-45204 (hereunder referred to as Patent Literature 1) proposes a method of improving oxide film adhesiveness by controlling a texture and an average crystal grain size

on a copper alloy plate surface in a composition having a reduced Fe content of 0.50 mass % or less. That is, in Patent Literature 1, an orientation distribution density of Brass orientation in a texture measured by a crystal orientation analysis method with an electron backscatter diffraction pattern EBSD of a copper alloy plate surface is 25% or more and an average crystal grain size is 6.0 μm or less.

Meanwhile, JP-A No. 2008-127606 (hereunder referred to as Patent Literature 2) proposes a method of improving oxide film adhesiveness by controlling the roughness and conformation of a copper alloy plate surface in a composition having a reduced Fe content of 0.50 mass % or less likewise. That is, a center line average roughness R_a is 0.2 μm or less, a maximum height R_{max} is 1.5 μm or less, and a kurtosis (degree of sharpness) R_{ku} in a roughness curve is 5.0 or less in surface roughness measurement of a copper alloy plate surface.

With a Cu-Fe-P system copper alloy plate disclosed in Patent Literatures 1 and 2 however, it is impossible to materialize a higher level of oxide film adhesiveness which has been desired in recent years.

SUMMARY OF THE INVENTION

An object of the present invention is to provide a Cu-Fe-P system copper alloy plate having both a higher strength and a higher level of oxide film adhesiveness which has been desired in recent years in a composition substantially having a reduced Fe content of 0.5 mass % or less.

In order to attain the above object, a high-strength copper alloy plate excellent in oxide film adhesiveness according to the present invention is characterized by the copper alloy plate comprising Fe: 0.02–0.5% and P: 0.01–0.25% in mass % with the balance consisting of copper and unavoidable impurities and having the ratio Fe/P of Fe to P in mass % being 2.0 to 5.0, wherein: a ratio of the area of fine crystal grains less than 0.5 μm in equivalent circle diameter to an observation area when a surface is observed by electron backscatter diffraction analysis is 0.90 or less; and the ratio C_{1s}/Cu_{2p} of a peak area of C_{1s} to a peak area of Cu_{2p} on the surface by XPS analysis is 0.35 or less.

In a high-strength copper alloy plate excellent in oxide film adhesiveness stated above, C_{1s}/Cu_{2p} of a surface obtained by XPS analysis means a relative C quantity on a copper alloy plate surface as it will be described later. In order to reduce C_{1s}/Cu_{2p} on a copper alloy plate

surface to 0.35 or less, it is necessary to almost completely remove a C source unremovable by alkali cathode electrolytic cleaning from the surface of the copper alloy plate prior to the alkali cathode electrolytic cleaning that is generally applied as finish of plating pretreatment or the like. In other words, by almost completely removing a C source unremovable by alkali cathode electrolytic cleaning from the surface of a copper alloy plate prior to the alkali cathode electrolytic cleaning, it is possible to obtain a copper alloy plate excellent in oxide film adhesiveness wherein C1s/Cu2p on a surface obtained by XPS analysis is 0.35 or less after the alkali cathode electrolytic cleaning is applied.

A copper alloy plate according to the present invention has a high strength equivalent to a conventional copper alloy plate described in Patent Literatures 1 and 2. Further, by regulating an area ratio of fine crystal grains when the surface of a copper alloy plate according to the present invention is observed by EBSD analysis and C1s/Cu2p of the surface obtained by XPS analysis to 0.35 or less, it is possible to materialize a higher level of oxide film adhesiveness that has been desired in recent years. As a result, the present invention makes it possible to prevent package cracking and peel off and provide a highly-reliable semiconductor device. Alkali cathode electrolytic cleaning is generally applied to a copper alloy plate as finish of plating pretreatment or the like and, as long a C source unremovable by alkali cathode electrolytic cleaning is almost completely removed from the surface of a copper alloy plate prior to the alkali cathode electrolytic cleaning, it is possible to obtain a copper alloy plate excellent in oxide film adhesiveness wherein C1s/Cu2p of the surface obtained by XPS analysis is 0.35 or less after the alkali cathode electrolytic cleaning is applied.

DETAILED DESCRIPTION OF THE PREFERRED EMBODIMENT

The significance of requirements and embodiments in a Cu-Fe-P system copper alloy plate according to the present invention for satisfying characteristics necessary as a material for a semiconductor lead frame or the like are specifically explained hereunder.

[Component composition of copper alloy plate]

In the present invention, in order to attain both a high strength and an excellent oxide film adhesiveness as a material for a semiconductor lead frame or the like, a Cu-Fe-P system copper alloy plate has a basic

composition comprising Fe: 0.02–0.5% and P: 0.01–0.25% in mass % and the ratio Fe/P of Fe to P in mass % being 2.0 to 5.0, with the balance consisting of Cu and unavoidable impurities.

An embodiment further containing one or two kinds of Sn and Zn in the ranges described below in the basic composition may also be allowable. Further, other unavoidable impurity elements are also allowed to be contained within ranges not hindering the characteristics. Here, % representing the contents of alloy elements and unavoidable impurity elements means mass % in all cases.

(Fe)

Fe is a major element that precipitates as Fe or an Fe-base intermetallic compound and improves the strength and heat resistance of a copper alloy. When an Fe content is less than 0.02%, the quantity of precipitated particles is small, the contribution to the improvement of strength is insufficient, and thus strength is insufficient. On the other hand, when an Fe content exceeds 0.5%, coarse crystallized/precipitated particles tend to be generated, etching property (smoothness of an etched face) and plating property (smoothness of Ag plating and the like) deteriorate, and the contribution to the improvement of strength is saturated. Consequently, an Fe content is set in the range of 0.02-0.5%, desirably 0.04-0.4%, and more desirably 0.06-0.35%.

(P)

P has deoxidation function and is a major element that forms a compound with Fe and improves the strength and heat resistance of a copper alloy. When a P content is less than 0.01%, the precipitation of a compound is insufficient and hence a desired strength cannot be obtained. On the other hand, when a P content exceeds 0.25%, hot workability and oxide film adhesiveness deteriorate. Consequently, a P content is set in the range of 0.01-0.25%, desirably 0.015-0.2%, and more desirably 0.02-0.15%.

(Fe/P)

The regulation of Fe/P as a ratio of Fe to P in mass % is a regulation necessary for efficiently precipitating a fine compound of Fe and P contributing to strength. When Fe/P is less than 2.0, the mass % of P is excessively higher than the mass % of Fe, hence the quantity of a generated fine Fe-P compound contributing to strength is insufficient, P in a solid solution state remains abundantly, and strength and the

adhesiveness of an oxide film deteriorate. On the other hand, when Fe/P exceeds 5.0, the mass % of P is excessively lower than the mass % of Fe, hence likewise the quantity of a generated fine Fe-P compound contributing to strength is insufficient, Fe in a solid solution state remains abundantly, and strength and the adhesiveness of an oxide film deteriorate. Consequently, Fe/P is set in the range of 2.0-5.0, desirably 2.2-4.7, and more desirably 2.4-4.4.

(Sn)

Sn contributes to the improvement of the strength of a copper alloy. When an Sn content is less than 0.005%, Sn does not contribute to strengthening. On the other hand, when Sn is excessively contained in excess of 3%, the solid solution quantity of Fe or an Fe-P compound reduces, coarse crystallized/precipitated particles of Fe or an Fe-P compound tend to be generated, the effect of improving strength decreases, and hot workability and oxide film adhesiveness deteriorate. Consequently, a content of Sn selectively contained is selected from the range of 0.005-3%, desirably 0.008-2.7%, and more desirably 0.01-2.4% in accordance with the balance between strength and oxide film adhesiveness required for application.

(Zn)

Zn improves the thermal peel resistance of solder in a copper alloy and Sn plating necessary for a lead frame or the like, further improves oxide film adhesiveness, and contributes to the improvement of the strength of the copper alloy. When a Zn content is less than 0.005%, desired effects are not obtained. On the other hand, when a Zn content exceeds 3%, the solid solution quantity of Fe or an Fe-P compound reduces, coarse crystallized/precipitated particles of Fe or an Fe-P compound tend to be generated, the effect of improving strength decreases, and hot workability deteriorates. Further, the effect of improving oxide film adhesiveness is saturated. Consequently, a content of Zn selectively contained is selected from the range of 0.005-3%, desirably 0.008-2.7%, and more desirably 0.01-2.4% in consideration of strength and oxide film adhesiveness required for application.

(Unavoidable impurities)

Unavoidable impurities referred to in the present invention are elements such as Mn, Mg, Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Ni, Au, and Pt for example. When such an element is contained, coarse

crystallized/precipitated particles tend to be generated and strength deteriorates. Consequently, the total quantity of the elements is desirably set at a least possible amount of 0.2 mass % or less. Further, elements such as Hf, Th, Li, Na, K, Sr, Pd, W, S, Si, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B, and misch metals contained in a copper alloy in minute amounts are also unavoidable impurities. When such an element is contained, coarse crystallized/precipitated particles tend to be generated, hot workability deteriorates, and therefore the total quantity of the elements is desirably controlled to a least possible amount of 0.1 mass % or less. Further, O contained in a copper alloy in a minute amount oxidizes added elements, hence the quantity of effective added elements reduces, strength decreases, and therefore an O content is desirably controlled to a least possible amount of 50 ppm or less in mass. Furthermore, H contained in a copper alloy in a minute amount causes defects (blowholes and blisters) to be generated in the copper alloy and hence an H content is desirably controlled to a least possible amount of 5 ppm or less in mass. [Ratio of the area of fine crystal grains less than 0.5 μm in equivalent circle diameter to an observation area when a surface is observed by EBSD analysis is 0.90 or less]

A ratio of the area of fine crystal grains (less than 0.5 μm in equivalent circle diameter) to an observation area when the surface of a copper alloy plate is observed by EBSD analysis means, so to speak, a ratio of the area occupied by fine crystal grains to a copper alloy plate surface. Here, EBSD analysis means electron backscatter diffraction analysis and is a method of analyzing the distributions of the sizes and orientations of crystal grains. Here, a case where an orientation difference between adjacent measurement points is 5° or more by EBSD analysis is regarded as a grain boundary and a crystal grain referred to here is defined by a region completely surrounded by grain boundaries. An equivalent circle diameter referred to in the present invention is the diameter of a circle having an area identical to a surrounded region. The area ratio does not change between before and after alkali cathode electrolytic cleaning.

The fact that the area ratio of fine crystal grains to a copper alloy plate surface is large means that many fine crystal grains exist and also many crystal grain boundaries exist, defects caused by the crystal grain boundaries are introduced abundantly in an oxide film, and the adhesiveness of the oxide film deteriorates. Consequently, the area ratio

of fine crystal grains to a copper alloy plate surface should be smaller and is set at 0.90 or less, desirably 0.85 or less, and more desirably 0.80 or less. [Ratio C1s/Cu2p of a peak area of C1s to a peak area of Cu2p on a surface by XPS analysis is 0.35 or less]

The ratio C1s/Cu2p of a peak area of C1s to a peak area of Cu2p on a surface by XPS analysis means, so to speak, a relative quantity of C on a copper alloy plate surface. XPS analysis means X-ray photoelectron spectrometry, is also called ESCA (Electron Spectroscopy for Chemical Analysis), and is an analysis method exceling at analyzing the composition and state of a very thin layer on a surface. C detected from the surface of a copper alloy plate is generally derived from various contaminants (organic and inorganic substances) and also derived from an organic antirust film (of benzotriazole, etc.) applied for preventing the discoloration of a copper alloy plate. The quantity of the C sources attaching to a copper alloy plate surface influences the magnitude of C1s/Cu2p on the copper alloy plate surface. When the C sources exist on a copper alloy plate surface, the all C sources adversely affect the adhesiveness of an oxide film. This is presumably because an oxide film having many defects tends to form by introducing defects caused by the C sources into the oxide film. Consequently, a value of C1s/Cu2p should be smaller and is set at 0.35 or less in the present invention, desirably 0.30 or less, and more desirably 0.25 or less.

Meanwhile, a copper alloy plate used for a lead frame of a semiconductor device is, after subjected to pretreatment including alkali cathode electrolytic cleaning, partially subjected to plating treatment such as Ag plating and provided to an assembly process. The adhesiveness of an oxide film formed through the thermal history in the assembly process governs the reliability of a package. Consequently, a matter influencing the adhesiveness of an oxide film is a C quantity after pretreatment including alkali cathode electrolytic cleaning is applied to a copper alloy plate. The fact that a C quantity is large means that C sources unremovable by alkali cathode electrolytic cleaning adhere in quantity to a copper alloy plate surface prior to alkali cathode electrolytic cleaning. Here, an organic antirust film (of benzotriazole, etc.) generally used for preventing the discoloration of a copper alloy plate can be removed easily by alkali cathode electrolytic cleaning.

Here, alkali cathode electrolytic cleaning is a cleaning method of

applying electrolysis with an object as a cathode in an alkaline aqueous solution and enhancing detergency by mechanical stirring function of a hydrogen gas generated from the surface of the object and is a known cleaning method in itself. An alkaline aqueous solution used in the method is generally configured by using alkali salt such as sodium hydroxide, sodium silicate, sodium phosphate, or sodium carbonate as the base and adding an organic substance such as a surfactant or a chelate compound, the electrolysis is carried out with an object as a cathode, hence the surface of a copper alloy plate is neither oxidized nor dissolved, and not a damage is caused. Consequently, by using alkali cathode electrolytic cleaning, organic substances such as rolling oil used when a copper alloy plate is manufactured and an organic antirust film such as benzotriazole can be removed easily. Even by alkali cathode electrolytic cleaning however, organic substances (sticking substances and the like) formed by transforming/degrading the rolling oil or the like by heat or the like cannot be removed. When organic substances or the like unremovable by such alkali cathode electrolytic cleaning adhere to the surface of a copper alloy plate prior to alkali cathode electrolytic cleaning, even after alkali cathode electrolytic cleaning, the organic substances remain on the copper alloy plate surface as C sources, the value of C1s/Cu2p on the copper alloy plate surface increases, the adhesiveness of an oxide film deteriorates, and the reliability of a package also deteriorates. Consequently, it is important to remove C sources unremovable by alkali cathode electrolytic cleaning from the surface of a copper alloy plate beforehand at a stage prior to the alkali cathode electrolytic cleaning.

[Tensile strength in the longitudinal direction is 500 MPa or more and percentage elongation after fracture in the longitudinal direction is 5% or more]

In a copper alloy plate according to the present invention, preferably the tensile strength in the longitudinal direction is 500 MPa or more as a measure of a high-strength material. Further, preferably the percentage elongation after fracture in a tensile test in the longitudinal direction is 5% or more. A copper alloy plate according to the present invention: can maintain an appropriate bending workability required for a lead frame material by having an appropriate percentage elongation after fracture; and hence is a copper alloy plate suitable as a material of an electric/electronic component, in particular a material of a lead frame for a

semiconductor device. In contrast, when a percentage elongation after fracture in a tensile test in the longitudinal direction is less than 5%, an appropriate bending workability required for a lead frame material cannot be maintained and hence such a copper alloy plate is not suitable as a material of an electric/electronic component, in particular a material of a lead frame for a semiconductor device. Here, a percentage elongation after fracture of 5% or more can be obtained easily by a manufacturing method which will be described later as long as a copper alloy composition according to the present invention is adopted. Further, a tensile strength of 500 MPa or more can also be obtained easily by a manufacturing method which will be described later except a region where an alloy element quantity is very small.

(Manufacturing conditions)

Successively, manufacturing conditions desirable for making a copper alloy plate structure into a structure stipulated in the present invention are explained hereunder.

That is, firstly molten copper alloy adjusted to the above component composition is cast. Then after the surface of a cast ingot is ground, the cast ingot is subjected to heating or homogenizing heat treatment and successively hot-rolled, and the hot-rolled plate is water-cooled. Ordinary conditions may be applied in the hot rolling.

Successively, primary cold rolling called intermediate rolling is applied, annealing and cleaning are applied, further thereafter finish (final) cold rolling and low temperature annealing (also called final annealing, finish annealing, or stress relief annealing) are applied, and a copper alloy plate of a product thickness or the like is obtained. The annealing and cold rolling may be repeated. Here, quality requirements for the flatness of a plate and the reduction of internal stress come to be increasingly high in accordance with the finer wiring of a lead frame caused by the downsizing and higher integration of a semiconductor device and the low temperature annealing after finish cold rolling is effective for improving such quality. The thickness of a produced copper alloy plate used for a semiconductor material such as a lead frame is about 0.1 to 0.4 mm.

Here, solution treatment and quenching treatment by water cooling may be applied to a copper alloy plate prior to the primary cold rolling. On this occasion, a solution treatment temperature is selected from the

range of 750°C to 1,000°C for example. The final cold rolling is applied also by an ordinary method.

In order to control a ratio of the area of fine crystal grains (less than 0.5 μm in equivalent circle diameter) to an observation area when a copper alloy plate surface is observed by EBSD analysis to 0.90 or less and the ratio C1s/Cu2p of a peak area of C1s to a peak area of Cu2p on a surface by XPS analysis to 0.35 or less, the following processes may be adopted.

Firstly, in order to control a ratio of the area of fine crystal grains (less than 0.5 μm in equivalent circle diameter) to an observation area when a copper alloy plate surface is observed by EBSD analysis to 0.90 or less, it is important to reduce the grain size of an abrasive and keep the crystal grain size in the surface layer to a largest possible extent by either not applying mechanical polishing after annealing or increasing the grit number in mechanical polishing. Further, even when mechanical polishing is applied, it is also an effective means to remove a fine crystal layer generated in mechanical polishing by chemical dissolution treatment, electrochemical dissolution treatment, or the like after the mechanical polishing. Mechanical polishing has heretofore been applied after annealing in many cases. The reason is that an oxide film formed at annealing is robust and hardly removable only by acid cleaning in some cases. Consequently, in order to reduce the area ratio of fine crystal grains by either not applying mechanical polishing or reducing the load of mechanical polishing, it is important to control an annealing atmosphere sufficiently so as not to form a robust oxide film. Specifically, it is important to adopt a reduction atmosphere (atmosphere containing a reducible component such as H_2 or CO) as an annealing atmosphere and control an oxidizing component (O_2 , H_2O , etc.) to a lowest possible concentration so as not to form a robust oxide film. In a low temperature annealing process as the final process in particular, it is desirable to make an oxide film removable only by acid cleaning and not to apply mechanical polishing by controlling the annealing atmosphere sufficiently so as not to form a robust oxide film.

Successively, in order to control the ratio C1s/Cu2p of a peak area of C1s to a peak area of Cu2p on a copper alloy plate surface by XPS analysis to 0.35 or less, it is important to apply cleaning treatment before and after annealing. Although acid cleaning and polishing are generally applied

after annealing in order to remove an oxide film formed at the annealing and residues caused by rolling oil, it is particularly difficult to effectively remove the residues caused by rolling oil only by cleaning after annealing, the residues remain on a copper alloy plate surface even after alkali cathode electrolytic cleaning as plating pretreatment is applied, the C quantity on the copper alloy plate surface increases, and oxide film adhesiveness deteriorates. Otherwise, if it is intended to sufficiently remove the residues and the like caused by rolling oil only by cleaning after annealing, the drawbacks of prolonging the time for cleaning and reducing the grit number of an abrasive (increasing the grain size of an adhesive) are caused. Here, if the grit number of an abrasive is reduced, fine crystal grains on a copper alloy plate surface increase and coarsen and inversely oxide film adhesiveness is caused to deteriorate. Consequently, in order to effectively remove residues and the like caused by rolling oil, it is effective to apply cleaning treatment not only after annealing but also before annealing, it is particularly essential to apply cleaning treatment before low temperature annealing as the final process and moreover it is effective to apply treatment for removing an oxide film by acid cleaning or the like after low temperature annealing. As such cleaning treatment before annealing, there are various kinds of cleaning treatment such as solvent cleaning, alkali cleaning, and alkali electrolytic cleaning and an appropriate cleaning method is used in accordance with need.

It is possible to reduce a C1s/Cu2p ratio on a surface by XPS analysis to 0.35 or less by further applying alkali cathode electrolytic cleaning to a copper alloy plate (prior to alkali cathode electrolytic cleaning) obtained by the above manufacturing method. The copper alloy plate is used for an electric/electronic component such as a semiconductor lead frame and, on that occasion, a C1s/Cu2p ratio on a plate surface reduces to 0.35 or less and an excellent oxide film adhesiveness can be obtained by applying treatment including alkali cathode electrolytic cleaning as pretreatment of plating.

[Example 1]

Test results of Invention Examples and Comparative Examples for verifying the effects of the present invention are explained hereunder. As a manufacturing method of a copper alloy plate, firstly molten copper alloy is melted in a high-frequency furnace and successively casted into a graphite-made book mold by tilt pouring. Thus ingots 50 mm in thickness,

200 mm in width, and 100 mm in length having the compositions shown in Tables 1 and 2 are obtained.

Successively, a block 50 mm in thickness, 180 mm in width, and 80 mm in length is cut out from each of the ingots, the rolled faces are ground, and the block is heated, retained for 0.5 to 1 hour after the temperature has reached 950°C, hot-rolled until the thickness reaches 16 mm, and water-cooled from a temperature of 700°C or higher. After the surfaces of the rolled plate are ground and oxide scale is removed, cold rolling and annealing are applied, successively final cold rolling is applied, and thus a copper alloy plate 0.2 mm in thickness is obtained. Low temperature annealing is applied after the final cold rolling. In the low temperature annealing, conditions allowing strength not to lower and enabling a braking elongation (percentage elongation after fracture in tensile test in the longitudinal direction) of 5% or more to be secured are selected from the temperature range of about 200°C to 500°C and the time range of about 1 to 300 sec.

Here the annealing and the low temperature annealing are applied in an $N_2 + 10\%H_2$ atmosphere (dew point: -20°C or lower, O_2 concentration: 50 ppm or less) and the cleaning treatment before and after annealing is applied as follows. With regard to the annealing, ultrasonic cleaning (20 kHz, 1 min.) by hexane is applied before the annealing and, after the annealing, sulfuric acid cleaning (10% sulfuric acid, 10 sec.) and successively mechanical polishing (#2400 waterproof abrasive paper) are applied. With regard to the low temperature annealing, ultrasonic cleaning (20 kHz, 1 min.) by hexane is applied before the annealing and, after the low temperature annealing, only sulfuric acid cleaning (10% sulfuric acid, 10 sec.) is applied and mechanical polishing is not applied.

Here, the component other than the described elements in each of the copper alloys shown in Table 1 comprises Cu and, as other impurity elements, the elements such as Mn, Mg, Ca, Zr, Ag, Cr, Cd, Be, Ti, Co, Ni, Au, and Pt are 0.2 mass % or less in total and the elements such as Hf, Th, Li, Na, K, Sr, Pd, W, S, Si, C, Nb, Al, V, Y, Mo, Pb, In, Ga, Ge, As, Sb, Bi, Te, B, and misch metals are 0.1 mass % or less in total.

With regard to each of the copper alloy plates obtained as stated above, a specimen is cut out from a copper alloy plate, characteristics of the specimen such as the surface properties (a $C1s/Cu2p$ ratio and an area ratio of fine crystal grains), mechanical properties (a tensile strength and a

percentage elongation after fracture), and an oxide film adhesiveness retention temperature are evaluated. The results are shown in Tables 1 and 2 respectively. In Table 2, a composition or a component ratio deviating from Claims 1 to 4 according to the present invention is represented by being underlined.

(Area ratio of fine crystal grains)

An area ratio of fine crystal grains is obtained by measuring an observation area when a copper alloy plate surface is observed by EBSD analysis and an area of fine crystal grains (less than 0.5 μm in equivalent circle diameter) and computing an area ratio of the fine crystal grains by the method described earlier.

(C1s/Cu2p ratio)

A C1s/Cu2p ratio is computed by measuring a peak area of Cu2p and a peak area of C1s on a surface by XPS analysis after alkali cathode electrolytic cleaning is applied to a copper alloy plate surface. Here, the alkali cathode electrolytic cleaning is applied with an aqueous solution containing sodium hydroxide by 20 g/L under the conditions of liquid temperature: 60°C, cathode current density: 5 A/dm², and time: 30 sec.

(Mechanical properties)

Mechanical properties are obtained by making a JIS-No. 5 test piece in the longitudinal direction and measuring a tensile strength and a percentage elongation after fracture in tensile test.

(Oxide film adhesiveness retention temperature)

An oxide film adhesiveness retention temperature is obtained by applying alkali cathode electrolytic cleaning to a copper alloy plate surface, further applying water washing, acid washing (10% sulfuric acid), water washing, and then drying in sequence, successively applying heating for 5 and 10 min. at a prescribed temperature in the atmosphere, and successively evaluating by peeling test with an adhesive tape. The alkali cathode electrolytic cleaning is applied under the same conditions as the alkali cathode electrolytic cleaning applied when a C1s/Cu2p ratio is measured. The peeling test with an adhesive tape is carried out by a method of attaching a commercially available tape (mending tape made by Sumitomo 3M Limited) and peeling off the tape. On this occasion, evaluation is carried out by varying the heating temperature at the intervals of 10°C and regarding the maximum temperature at which an oxide film does not peel off as an oxide film adhesiveness retention

temperature.

TABLE 1

	No.	Chemical components					Surface properties		Mechanical properties		Oxide film adhesiveness retention temperature		°C
		Fe Mass %	P Mass %	Sn Mass %	Zn Mass %	Fe/P Ratio	C1s/Cu2 p Ratio	Area ratio of fine crystal grains	Tensile strength MPa	Percentage elongation after fracture %	Heating time 5 min.	Heating time 10 min.	
Invention Example	1	0.03	0.013	-	-	2.3	0.20	0.54	410	7	440	390	
	2	0.05	0.011	-	-	4.6	0.17	0.56	440	7	440	390	
	3	0.06	0.026	-	-	2.3	0.22	0.53	460	6	430	380	
	4	0.10	0.023	-	-	4.4	0.18	0.51	510	7	440	390	
	5	0.10	0.031	-	-	3.2	0.21	0.45	520	8	430	380	
	6	0.11	0.050	-	-	2.2	0.24	0.47	530	7	420	370	
	7	0.17	0.038	-	-	4.5	0.19	0.50	560	7	430	380	
	8	0.23	0.090	-	-	2.6	0.23	0.48	580	8	410	360	
	9	0.30	0.064	-	-	4.7	0.16	0.51	600	7	420	370	
	10	0.30	0.110	-	-	2.7	0.21	0.50	620	8	410	360	
	11	0.32	0.150	-	-	2.1	0.18	0.52	630	8	400	350	
	12	0.45	0.100	-	-	4.5	0.19	0.48	680	7	390	340	
	13	0.46	0.210	-	-	2.2	0.20	0.49	700	8	390	340	
	14	0.10	0.033	0.02	-	3.0	0.25	0.51	540	8	430	380	
	15	0.10	0.035	1.0	-	2.9	0.21	0.53	650	10	410	360	
	16	0.11	0.035	2.5	-	3.1	0.18	0.45	750	11	390	340	
	17	0.11	0.030	-	0.02	3.7	0.19	0.47	520	8	440	390	
	18	0.10	0.031	-	1.0	3.2	0.20	0.48	560	8	460	410	
	19	0.10	0.032	-	2.5	3.1	0.15	0.55	600	9	480	430	
	20	0.11	0.034	1.1	1.0	3.2	0.22	0.47	680	10	440	390	
	21	0.30	0.105	1.0	1.1	2.9	0.23	0.44	750	10	420	370	

TABLE 2

No.	Chemical components					Surface properties		Mechanical properties		Oxide film adhesiveness retention temperature	
	Fe Mass %	P Mass %	Sn Mass %	Zn Mass %	Fe/P Ratio	C1s/Cu2p Ratio	Area ratio of fine crystal grains	Tensile strength MPa	Percentage elongation after fracture %	Heating time 5 min.	Heating time 10 min.
22	0.025	0.015	-	-	1.7	0.17	0.53	400	7	420	370
23	0.03	0.008	-	-	3.8	0.18	0.51	360	6	440	390
24	0.06	0.010	-	-	6.0	0.21	0.50	420	7	430	380
25	0.09	0.016	-	-	5.6	0.20	0.52	460	8	420	370
26	0.11	0.062	-	-	1.8	0.22	0.49	500	8	390	340
27	0.30	0.055	-	-	5.5	0.19	0.48	580	7	400	350
28	0.29	0.160	-	-	1.8	0.17	0.51	610	8	350	300
29	0.45	0.080	-	-	5.6	0.20	0.54	650	7	370	320
30	0.50	0.290	-	-	1.7	0.17	0.47	680	8	310	260
31	0.56	0.160	-	-	3.5	0.23	0.50	670	8	380	330
32	0.10	0.031	4.0	-	3.2	0.22	0.51	770	11	370	320
33	0.11	0.033	-	4.0	3.3	0.18	0.48	580	9	480	430

As shown in Table 1, in the copper alloy plates (Invention Examples 1 to 21) according to the present invention, Invention Examples 1 to 13 satisfy the composition ranges of Claims 1 and 2, Invention Examples 14 to 16 satisfy the composition range of Claim 3, and Invention Examples 17 to 21 satisfy the composition range of Claim 4. Further, Invention Examples

1 to 21 satisfy the surface properties (an area ratio of fine crystal grains and a C1s/Cu2p ratio) stipulated in Claims 1 and 2. In this way, the copper alloy plates of Invention Examples 1 to 21 have good characteristics of the oxide film adhesiveness retention temperatures being 390°C X 5 min. or more and 340°C X 10 min. or more.

Here, whereas the oxide film peel off temperature of Invention Example 9 in Table 1 of Patent Literature 1 (JP-A No. 2008-45204) is 370°C X 5 min. (360°C X 5 min. in terms of oxide film adhesiveness retention temperature), the oxide film adhesiveness retention temperatures of Invention Examples 10 and 11 in Table 1 of the present application having similar compositions are 410°C to 400°C X 5 min. and it is obvious that the oxide film adhesiveness further improves in comparison with Patent Literature 1. Further, whereas the oxide film peel off temperature of Invention Example 6 in Table 2 of Patent Literature 2 (JP-A No. 2008-127606) is 400°C X 5 min. (390°C X 5 min. in terms of oxide film adhesiveness retention temperature), the oxide film adhesiveness retention temperature of Invention Example 10 in Table 1 of the present application having a similar composition is 410°C X 5 min. and it is obvious that the oxide film adhesiveness further improves also in comparison with Patent Literature 2.

On the other hand, in Comparative Examples 22 to 33, the compositions and/or component ratios of Claims 1 to 4 are not satisfied as shown in Table 2. Consequently, as it will be individually explained below, a tensile strength is inferior or an oxide film adhesiveness retention temperature is low in comparison with Invention Examples 1 to 21. In Comparative Example 22, Fe/P is lower than the lower limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, P in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 1.

In Comparative Example 23, the P content is lower than the lower limit value, the quantity of the generated Fe-P compound is insufficient, and hence the tensile strength lowers in comparison with Invention Example 1.

In Comparative Example 24, Fe/P exceeds the upper limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, Fe in a solid solution state increases, and hence the tensile

strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 2.

In Comparative Example 25 too, Fe/P exceeds the upper limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, Fe in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 4.

In Comparative Example 26, Fe/P is lower than the lower limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, P in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 6.

In Comparative Example 27, Fe/P exceeds the upper limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, Fe in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 9.

In Comparative Example 28, Fe/P is lower than the lower limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, P in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 11.

In Comparative Example 29, Fe/P exceeds the upper limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, Fe in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 12.

In Comparative Example 30, P exceeds the upper limit value and Fe/P is lower than the lower limit value, the quantity of the generated fine Fe-P compound contributing to strength is insufficient, P in a solid solution state increases, and hence the tensile strength and the oxide film adhesiveness retention temperature are low in comparison with Invention Example 13.

In Comparative Example 31, the Fe content exceeds the upper limit value, coarse crystallized/precipitated particles tend to be generated, hence the contribution to the improvement of strength is low, and the tensile strength lowers in comparison with Invention Example 13.

In Comparative Example 32, the Sn content exceeds the upper limit value, coarse crystallized/precipitated particles tend to be generated, hence the strength improvement effect is low, and the tensile strength is almost saturated and the oxide film adhesiveness retention temperature lowers in comparison with Invention Example 16.

In Comparative Example 33, the Zn content exceeds the upper limit value, coarse crystallized/precipitated particles tend to be generated, hence the strength improvement effect is low, and the tensile strength lowers and the effect of improving the oxide film adhesiveness retention temperature is saturated in comparison with Invention Example 19.

[Example 2]

Test results on the relationship between surface properties (an area ratio of fine crystal grains and C1s/Cu2p) and an oxide film adhesiveness retention temperature are explained hereunder. In Example 2, copper alloy plates 0.2 mm in thickness are manufactured from the ingots of Invention Examples 5, 10, and 21 in Table 1 through the methods and conditions similar to Example 1.

Here in Example 2, surface properties (an area ratio of fine crystal grains and C1s/Cu2p) of a copper alloy plate are varied by changing cleaning methods before and after annealing. Successively, surface properties (an area ratio of fine crystal grains and C1s/Cu2p) and an oxide film adhesiveness retention temperature are evaluated in the same manner as Example 1.

The cleaning methods of the cases and the evaluation results of the surface properties (an area ratio of fine crystal grains and C1s/Cu2p) and the oxide film adhesiveness retention temperatures are shown in Tables 3 and 4. Copper alloy plates manufactured from the ingots used in Invention Example 5 in Table 1 are used in Invention Examples 5-1 to 5-3 and Comparative Examples 5-4 and 5-5 in Tables 3 and 4, copper alloy plates manufactured from the ingots used in Invention Example 10 in Table 1 are used in Invention Example 10-1 and Comparative Examples 10-2 and 10-3 in Tables 3 and 4, and copper alloy plates manufactured from the ingots used in Invention Example 21 in Table 1 are used in Invention Examples 21-1 to 21-5 and Comparative Examples 21-6 to 21-9 in Tables 3 and 4. In Tables 3 and 4, in the alkali dip cleaning, a typical commercially-available alkali dip cleaning solvent agent containing sodium hydroxide as the main component, phosphoric salt, silicate salt, carbonate,

and a surfactant is used. Further, in the chemical dissolution treatment applied in the post-treatment of annealing, a typical commercially-available aqueous solution containing sulfuric acid and hydrogen peroxide as the main components is used. Here, the items deviating from the scope of Claims in the column of the surface properties in Table 4 are shown by being underlined.

TABLE 3

	No.	Cleaning method before and after annealing				Surface properties		Oxide film adhesiveness retention temperature	
		Before annealing	After annealing	Before low temperature annealing	After low temperature annealing	C1s/Cu2p Ratio	Area ratio of fine crystal grains	Heating time 5 min.	Heating time 10 min.
								°C	
Invention Example	5-1	Hexane, dip	Sulfuric acid →#600 Polishing	Hexane, dip	Sulfuric acid	0.30	0.73	410	360
	5-2	Hexane, ultrasonic wave	Sulfuric acid →#2400 Polishing	Hexane, ultrasonic wave	Sulfuric acid	0.21	0.45	430	380
	5-3	Hexane, ultrasonic wave	Sulfuric acid →#2400 Polishing →Chemical dissolution	Hexane, ultrasonic wave →Alkali dip	Sulfuric acid	0.09	0.12	450	400
	10-1	Hexane, ultrasonic wave	Sulfuric acid →#2400 Polishing	Hexane, ultrasonic wave	Sulfuric acid	0.21	0.50	410	360
	21-1	Hexane, dip	Sulfuric acid →#600 Polishing	Hexane, dip	Sulfuric acid	0.31	0.72	400	350
	21-2	Hexane, ultrasonic wave	Sulfuric acid →#2400 Polishing	Hexane, ultrasonic wave	Sulfuric acid	0.23	0.44	420	370
	21-3	Hexane, ultrasonic wave	Sulfuric acid →#2400 Polishing →Chemical dissolution	Hexane, ultrasonic wave →Alkali dip	Sulfuric acid	0.10	0.11	440	390
	21-4	Hexane, ultrasonic wave	Sulfuric acid →#600 Polishing	Hexane, ultrasonic wave →Alkali dip	Sulfuric acid	0.12	0.68	420	370
	21-5	Hexane, dip	Sulfuric acid →#2400 Polishing →Chemical dissolution	Hexane, dip	Sulfuric acid	0.29	0.10	420	370

TABLE 4

Oxide film adhesiveness
retention temperature

No.	Cleaning method before and after annealing				Surface properties		°C	
	Before annealing	After annealing	Before low temperature annealing	After low temperature annealing	C1s/Cu2p Ratio	Area ratio of fine crystal grains	Heating time 5 min.	Heating time 10 min.
5-4	Ethanol, dip	Sulfuric acid → #600 Polishing	Ethanol, dip	Sulfuric acid	<u>0.46</u>	0.73	390	340
5-5	Ethanol, dip	Sulfuric acid → #600 Polishing	Ethanol, dip	Sulfuric acid → #600 Polishing	<u>0.48</u>	<u>0.98</u>	370	320
10-2	Ethanol, dip	Sulfuric acid → #600 Polishing	Ethanol, dip	Sulfuric acid	<u>0.45</u>	0.72	370	320
10-3	Ethanol, dip	Sulfuric acid → #600 Polishing	Ethanol, dip	Sulfuric acid → #600 Polishing	<u>0.46</u>	<u>0.96</u>	350	300
21-6	Ethanol, dip	Sulfuric acid → #600 Polishing	Ethanol, dip	Sulfuric acid	<u>0.43</u>	0.75	380	330
21-7	Ethanol, dip	Sulfuric acid → #600 Polishing	Ethanol, dip	Sulfuric acid → #600 Polishing	<u>0.45</u>	<u>0.97</u>	360	310
21-8	Hexane, dip	Sulfuric acid → #600 Polishing	Hexane, dip	Sulfuric acid → #600 Polishing	0.30	<u>0.97</u>	380	330
21-9	Ethanol, dip	Sulfuric acid → #120 Polishing	Ethanol, dip	Sulfuric acid	<u>0.44</u>	<u>0.92</u>	370	320
Comparative Example								

As shown in Table 3, in the copper alloy plates (Invention Examples 5-1 to 5-3, 10-1, and 21-1 to 21-5) according to the present invention, appropriate cleaning treatment is applied before and after both the respective annealing and low temperature annealing, hence C1s/Cu2p on a surface by XPS analysis after alkali cathode electrolytic cleaning is applied to the surface of a copper alloy plate is as good as 0.35 or less, and the area ratio of fine crystal grains (less than 0.5 μm in equivalent circle diameter) to an observation area by EBSD analysis on a copper alloy plate surface is also as good as 0.90 or less. Here, Invention Example 5-2 is identical to

Invention Example 5 in Table 1, Invention Example 10-1 is identical to Invention Example 10 in Table 1, and Invention Example 21-2 is identical to Invention Example 21 in Table 1.

As a result, the oxide film adhesiveness retention temperatures of the copper alloy plates (Invention Examples 5-1 to 5-3, 10-1, and 21-1 to 21-5) according to the present invention are 400°C X 5 min. or more and 350°C X 10 min. or more and show good characteristics. Further, when compositions are identical, as C1s/Cu2p and the area ratio of fine crystal grains reduce, the oxide film adhesiveness retention temperature improves further.

In Comparative Example 5-4, ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value and the oxide film adhesiveness retention temperature is low in comparison with Invention Example 5-1.

In Comparative Example 5-5, likewise ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value. Further, since polishing is applied after the low temperature annealing, the area ratio of the fine crystal grains also exceeds the upper limit value and the oxide film adhesiveness retention temperature is further low in comparison with Invention Example 5-1.

In Comparative Example 10-2, ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value and the oxide film adhesiveness retention temperature is low in comparison with Invention Example 10-1.

In Comparative Example 10-3, likewise ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value. Further, since polishing is applied after the low temperature annealing, the area ratio of the fine crystal grains also exceeds the upper limit value and the oxide film adhesiveness retention temperature is further low in

comparison with Invention Example 10-1.

In Comparative Example 21-6, ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value and the oxide film adhesiveness retention temperature is low in comparison with Invention Example 21-1.

In Comparative Example 21-7, likewise ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value. Further, since polishing is applied after low temperature annealing, the area ratio of the fine crystal grains also exceeds the upper limit value and the oxide film adhesiveness retention temperature is further low in comparison with Invention Example 21-1.

In Comparative Example 21-8, although hexane is applied at the cleaning treatment before both the annealing and the low temperature annealing and C1s/Cu2p satisfies the stipulation of Claims, polishing is applied after the low temperature annealing, hence the area ratio of the fine crystal grains exceeds the upper limit value, and the oxide film adhesiveness retention temperature is further low in comparison with Invention Example 21-1.

In Comparative Example 21-9, ethanol showing a weak detergency to rolling oil and the like is used and also only dip cleaning is applied at the cleaning treatment before both the annealing and the low temperature annealing, and hence C1s/Cu2p exceeds the upper limit value. Further, even though polishing is not applied after the low temperature annealing, an abrasive paper of a small grit number (a large grain size of an abrasive) is used for the polishing after the annealing, hence the area ratio of the fine crystal grains exceeds the upper limit value, and the oxide film adhesiveness retention temperature is low in comparison with Invention Example 21-1.

A copper alloy plate according to the present invention has an excellent oxide film adhesiveness. Further, a copper alloy plate according to the present invention has a high strength and an appropriate bending workability necessary for a material for a lead frame. Consequently, a copper alloy plate according to the present invention is preferably used as a

material for a lead frame. Moreover, a copper alloy plate according to the present invention is preferably used for not only a lead frame in a semiconductor device but also various electric/electronic components such as other semiconductor components, electric/electronic component materials such as a printed circuit board, and mechanism components such as switch parts, a bus bar, and a terminal/connector.

WHAT IS CLAIMED IS:

1. A high-strength copper alloy plate excellent in oxide film adhesiveness, the copper alloy plate comprising Fe: 0.02–0.5% and P: 0.01–0.25% in mass % with the balance consisting of copper and unavoidable impurities and having the ratio Fe/P of Fe to P in mass % being 2.0 to 5.0, wherein: a ratio of the area of fine crystal grains less than 0.5 μm in equivalent circle diameter to an observation area when a surface is observed by electron backscatter diffraction analysis is 0.90 or less; and the ratio C1s/Cu2p of a peak area of C1s to a peak area of Cu2p on the surface by XPS analysis is 0.35 or less.

2. The high-strength copper alloy plate excellent in oxide film adhesiveness according to Claim 1, the copper alloy plate further comprising Sn: 0.005-3% in mass %.

3. The high-strength copper alloy plate excellent in oxide film adhesiveness according to Claim 1 or 2, the copper alloy plate further comprising Zn: 0.005-3% in mass %.

4. The high-strength copper alloy plate excellent in oxide film adhesiveness according to any one of Claims 1 to 3, wherein: a tensile strength in the longitudinal direction of the copper alloy plate is 500 MPa or more; and a percentage elongation after fracture in the longitudinal direction is 5% or more.

5. The high-strength copper alloy plate excellent in oxide film adhesiveness according to Claim 1, wherein the XPS analysis is carried out after alkali cathode electrolytic cleaning is applied.

6. The high-strength copper alloy plate excellent in oxide film adhesiveness according to Claim 5, the copper alloy plate further comprising Sn: 0.005-3% in mass %.

7. The high-strength copper alloy plate excellent in oxide film adhesiveness according to Claim 5 or 6, the copper alloy plate further comprising Zn: 0.005-3% in mass %.

8. The high-strength copper alloy plate excellent in oxide film adhesiveness according to any one of Claims 5 to 7, wherein: a tensile strength in the longitudinal direction of the copper alloy plate is 500 MPa or more; and a percentage elongation after fracture in the longitudinal direction is 5% or more.