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(54) TITLE: ELECTROLYTIC COPPER FOIL AND METHOD FOR PRODUCING SAME

(54) TITLE OF THE INVENTION: ELECTROLYTIC COPPER FOIL AND METHOD FOR PRODUCING SAME

(57) Abstract: [Problem] To provide an electrolytic copper foil having high mechanical strength under normal conditions, and resistant to thermal deterioration even when heated to about 300°C. [Solution] An electrolytic copper foil containing a metal that exists in the form of an oxide in a liquid at pH 4 or below, or an oxide thereof, and containing chlorine at a level of more than 10 ppm but less than 50 ppm; and a method for producing the same.

(57) Abstract:
PROBLEM
To provide an electrolytic copper alloy foil having high mechanical strength under normal conditions and low thermal degradation even when heated to about 300°C.

RESOLUTION MEANS
An electrolytic copper foil containing a metal existing as an oxide in a solution with a pH of 4 or less and containing

chlorine in an amount exceeding 10 ppm but less than 50 ppm, as well as a manufacturing method thereof.

TRANSLATOR'S CERTIFICATE OF TRANSLATION

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To whom it may concern:

I, Michael Fletcher, a translator fluent in the Japanese and English languages, on behalf of Questel, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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Signed this 5th day of August, 2024



Signature

Michael Fletcher

Name

SPECIFICATION

TITLE OF THE INVENTION: ELECTROLYTIC COPPER FOIL AND MANUFACTURING METHOD THEREOF

TECHNICAL FIELD

[0001] The present invention relates to an electrolytic copper alloy foil (hereinafter also referred to as electrodeposited copper foil), such as copper (Cu)-tungsten (W) copper alloys, and production methods thereof.

BACKGROUND ART

[0002] Electrolytic copper foil has conventionally been used in various fields, including rigid printed circuit boards, flexible printed circuit boards, and electromagnetic wave shielding materials.

[0003] Among these fields, in the field of flexible printed circuit boards (hereinafter referred to as “FPCs”) laminated with a polyimide film, there is a demand to improve the strength of the copper foil as a suspension material for hard disk drives (hereinafter referred to as “HDDs”) or for a tape-automated bonding (hereinafter referred to as “TAB”) material.

[0004] As HDDs continue to increase in capacity, the majority of HDD suspensions are being replaced by wiring-integrated suspensions that provide stable buoyancy and positioning accuracy of the flying head in relation to the disk, which is the storage medium.

[0005] There are three types of wiring-integrated suspensions.

(1) A type where a flexible printed circuit board is processed and laminated using an adhesive, using a method known as the FSA (Flex Suspension Assembly) method.

(2) A type where amic acid, a precursor of polyimide resin, is formed and then processed into polyimide, and wiring is formed by plating on the resulting polyimide, using a method known as the CIS (Circuit Integrated Suspension) method.

(3) A type where a three-layer laminate containing stainless steel foil, polyimide resin, and copper foil is processed into a specified shape by etching, using a method known as the TSA (Trace Suspension Assembly) method.

[0006] Of these, a TSA method suspension can easily form a flying lead by laminating high-strength stainless steel foil with copper foil, and is widely used because of the high degree of freedom in shape processing, relatively low cost, and good dimensional accuracy.

[0007] With suspensions formed by this method, laminates are manufactured using materials with a stainless steel foil thickness of 12 to 30 μm, a polyimide resin layer thickness of 5 to 20 μm, and a copper foil thickness of 7 to 14 μm.

[0008] The laminate is produced by first applying a solution containing a polyimide resin precursor to the stainless steel foil that will serve as the substrate. After coating, solvent is removed by preheating, followed by further heating and performing polyimidization, and a copper foil is overlaid on the polyimidized polyimide resin layer and laminated by heat and pressure bonding at a temperature of about 300°C to produce a laminate containing a stainless steel layer/polyimide resin layer/copper layer.

[0009] The stainless steel foil exhibits little dimensional change after heating to about 300°C. However, when conventional electrolytic copper foil is used, the electrolytic copper foil is annealed at a temperature of about 300°C, which causes recrystallization and softening, resulting in dimensional changes. As a result, the laminate warps after lamination, which interferes with the dimensional accuracy of the product.

[0010] To prevent warpage of the laminate after lamination, the copper foil is required to have the smallest possible dimensional change during heating, usually less than 0.1%.

Rolled copper alloy foils are conventionally used as copper foils to meet these requirements. Rolled copper alloy foil is not easily annealed at temperatures around 300°C, and dimensional changes during heating are small, as are mechanical strength changes.

However, rolled copper foil is more expensive than electrolytic copper foil, and satisfying the width and thickness requirements is difficult.

[0011] Rolled copper alloy foil is foil made by rolling a copper alloy containing at least one or more elements other than copper, such as tin, zinc, iron, nickel, chromium, phosphorus, zirconium, magnesium, or silicon, as a main constituent, using a rolling process. Depending on the type and combination of elements, some of these rolled copper alloy foils are not easily annealed by heating to about 300°C, and the tensile strength, 0.2% proof stress, elongation, and the like do not change significantly.

For example, rolled copper alloy foils such as Cu-0.2mass% Cr-0.1mass% Zr-0.2mass% Zn (Cu-2000ppm Cr-1000ppm Zr-2000ppm Zn) are suitable for HDD suspension materials as well as TSA method suspension.

[0012] Furthermore, even TAB materials require higher strength of the copper foil, similar to the TSA method suspension and HDD suspension materials.

With TAB products, multiple terminals of an IC chip are bonded directly to inner leads (flying leads) that are placed in device holes located almost in the center of the product.

Bonding at this time is performed using a bonding device (bonder) that instantaneously energizes and heats while applying a certain bonding pressure. In this case, there is a problem that the inner lead obtained by etching and forming the electrolytic copper foil is excessively stretched by the bonding pressure.

[0013] High-strength electrolytic copper foil makes the inner leads less prone to sagging and breaking. Therefore, if the strength of the electrolytic copper foil is too small, sagging occurs in the inner lead due to plastic deformation, and in significant cases, the foil breaks.

[0014] Applications use a two-layer FPC where a copper foil and a polyimide resin layer are laminated together, or a three-layer FPC where a copper foil, a polyimide resin layer, and an adhesive layer are laminated together. When laminating polyimide to copper foil in a 3-layer FPC, an epoxy adhesive is used and laminated at a temperature of around 180°C. In a two-layer FPC using a polyimide adhesive, lamination is performed at a temperature of around 300°C.

[0015] Even if the copper foil has high mechanical strength under normal conditions, this is meaningless if the copper foil softens when bonded to the polyimide resin. Conventional high-strength electrolytic copper foil has great mechanical strength in the normal state and the mechanical strength hardly changes when heated to around 180°C. However, when heated to around 300°C, the foil is annealed and recrystallized, resulting in rapid softening and a significant decrease in mechanical strength.

[0016] Furthermore, copper foil is also used as a current collector for batteries such as lithium-ion secondary batteries. A lithium-ion secondary battery basically includes a positive electrode, a negative electrode, and an electrolyte. The negative electrode is formed by coating a negative electrode active material layer on a surface of a copper foil used as a current collector. A common method of forming the negative electrode includes dissolving a negative electrode active material and a binder resin (added for bonding the active material and copper foil substrate) in a solvent to make a slurry, applying the slurry on the copper foil substrate, drying the slurry at a temperature higher than the curing temperature of the binder resin, and compressing.

[0017] Polyvinylidene fluoride and styrene-butadiene rubber (SBR) are widely used as the binder resins.

Conventionally, active materials made of silicon, tin, germanium alloy materials which have high theoretical capacity, and the like, which have been the focus of attention in recent years as batteries achieve higher capacity, have a very large coefficient of volume expansion due to insertion and desorption of lithium during charging and discharging, and the binder resins described above do not provide sufficient strength. Therefore, polyimide resins with high adhesion strength to copper substrates have been preferably used. However, unlike the binder resins mentioned above, polyimide resins have a very high curing temperature of about 300°C, and an anode current collector (copper foil) that can withstand this heating condition is required.

[0018] Thus, in both the FPC and secondary battery fields, polyimide resins with very high curing temperatures of around 300°C are increasingly used as binders, and copper foils that can withstand these heating conditions are required.

[0019] On the other hand, various studies have been conducted on electrolytic copper foils with excellent mechanical strength on the lamination surface of the copper foil and the polyimide resin substrate, as shown below.

[0020] For example, Patent Document 1 describes an electrolytic copper foil with an elongation ratio of 10.0% or higher at 180°C as a copper foil suitable for printed circuit board applications and an anode current collector for lithium secondary batteries.

The above electrolytic copper foil is obtained by using an aqueous sulfuric acid-copper sulfate solution as the electrolyte, and by using polyethyleneimine or a derivative thereof, a sulfonate of an active organic sulfur compound, chlorine ions (chloride ions) at a concentration of 20 to 120 mg/L, and an oxyethylene surfactant at a predetermined concentration.

[0021] In addition, Patent Document 2 describes an electrolytic copper foil having a tensile strength at 25°C of 820 MPa or more when measured within 20 minutes from the completion of electrodeposition, and the rate of decrease in tensile strength at 25°C measured at 300 minutes from completion of electrodeposition relative to the tensile strength at 25°C measured within 20 minutes from completion of electrodeposition is less than 10%.
The above electrolytic copper foil is then obtained using an aqueous solution of sulfuric acid and copper sulfate solution as the electrolyte in the presence of hydroxyethylcellulose, polyethyleneimine, sulfonate of an active organic sulfur compound, acetylene glycol, and chloride ions at a concentration of 20 to 120 mg/L.

[0022] Furthermore, Patent Document 3 describes a controlled electrodeposited copper foil with a particle structure that is essentially free of cylindrical particles and twin boundaries, and has an average particle size up to 10 μm, wherein the particle structure is substantially uniform and randomly oriented.
The electrodeposited copper foil has a maximum tensile strength in a range of 87,000 to 120,000 psi (600 MPa to 827 MPa) at 23°C, and 25,000 to 35,000 psi (172 MPa to 241 MPa) at 180°C.

[0023] Therefore, the present inventors attempted to develop an electrolytic copper foil with excellent mechanical strength by adding tungsten to the copper foil to improve the heat resistance of the copper foil, and to develop an electrolytic copper alloy foil suitable for applications using polyimide resin as a binder resin. However, tungsten is a metal that is very difficult to incorporate into electrolytic copper foil.

[0024] Incidentally, electrolytic solutions containing copper sulfate and sulfuric acid are used for electrolytic copper foils, and various additives are added to the plating bath to brighten and smooth the copper foil surface and to reduce stress on the copper foil. Conventionally, additives have generally been very important because when not used, the surface morphology, mechanical properties, and

the like required of the copper foil cannot be obtained. In particular, copper sulfate plating baths are simple acidic baths that are inferior for uniform electrodeposition, and producing a desirable electrolytic copper foil without additives is difficult. Chlorine ions, polyoxyethylene surfactants, smoothing agents, brightening agents such as organosulfides, glue, gelatin, and the like have been proposed and used as additives for copper sulfate plating baths.

[0025] If chlorine or additives are not added to the copper sulfate plating bath, the plating concentrates in high current areas where electricity flows easily (areas close to the anode, the edge of the cathode, the tip of a pointed object, and the like), resulting in what is commonly referred to as a “burned” condition (plated surface is more uneven). Therefore, in normal copper sulfate plating, about 20 to 100 mg/L of chloride ions are added. When the amount of chlorine ions is less than 20 mg/L, burns are more likely to occur for the above reasons, and conversely, when the amount of chlorine ions exceeds 80 mg/L, the leveling action is excessive, and “fogging” occurs in low-current areas (such as in small holes).

[0026] However, the presence of chlorine ions in the electrolyte impedes changing the properties of the copper foil by adding certain metals to the copper foil. In other words, in the absence of chlorine ions in the electrolyte, it is possible to mix other metals into the copper foil and the properties of the copper foil can be changed by adding (alloying) other metals. However, when chlorine ions are present in the electrolyte, adding other metals into the copper foil is difficult, so changing the copper foil properties using other metals is extremely difficult.

[0027] For example, Patent Document 4 and Patent Document 5 relate to copper foils for printing circuits, and disclose the addition of tungsten to the electrolytic solution used to produce the electrolytic copper foil.
Patent Document 4 and Patent Document 5 describe a method for producing electrolytic copper foils with tungsten or tungsten compounds in an electrolyte containing tungsten or tungsten compounds, and in an acidic

copper sulfate electrolyte containing glue and 20 to 100 mg/L of chloride ions. The effect is that hot elongation at 180°C is more than 3%, and copper foils with fewer pinholes can be produced.

Therefore, the present inventors repeatedly conducted tests in which tungsten or tungsten compounds are added to sulfuric acid and copper sulfate electrolytes, and then electrodeposited using an electrolyte containing glue and 20 to 100 mg/L of chloride ions. This confirmed that Patent Document 4 and Patent Document 5 were able to produce copper foil with a desired hot elongation ratio at 180°C of 3% or more with minimal pinhole formation. However, when this copper foil was heat-treated at 300°C x 1 hour, it was found that the mechanical strength could not be retained. Analysis of the copper foil also revealed that there was no tungsten co-deposited in the electrolytic copper foil. In other words, electrolytic copper alloy foils (copper-tungsten copper alloy foils) could not be obtained (see Comparative Example 7 below). Therefore, the methods described in Patent Document 4 and Patent Document 5 cannot produce electrolytic copper alloy foils that have high mechanical strength under normal conditions and do not easily lose mechanical strength when heated to high temperatures.

Opinions on the cause and the like are discussed below.

[0028] Furthermore, Patent Document 7 describes a dispersion strengthened electrolytic copper foil in which copper is present as fine crystal grains and SnO_2 is dispersed as ultrafine particles.

Patent Document 7 describes that copper, sulfate, and tin ions are included in the acidic copper sulfate electrolyte, and organic additives such as polyethylene glycol are bubbled with an oxygen-containing gas to form SnO_2 ultrafine particles in the electrolyte, and that this electrolyte is used to obtain the dispersion-enhanced electrolytic copper foil.

[0029] Furthermore, Patent Document 8 describes an electrolytic copper foil containing silver (Ag).

Patent document 8 describes obtaining this electrolytic copper foil using a sulfuric acid and copper sulfate electrolyte to which a silver salt has been added to provide a predetermined concentration of silver ions. The silver is thought to be co-deposited in the electrolytic copper foil.

[0030] However, in the case of the electrolytic copper foils described in the aforementioned Patent Documents 1 to 4, 7, and 8, although they all have high mechanical strength under normal conditions, the mechanical strength is significantly reduced when heated to high temperatures such as about 300°C.

[0031] All of the electrolytic copper foils described in the aforementioned Patent Documents 1 to 4 and 7 used a sulfuric acid and copper sulfate electrolyte, and although the type of additive agent differed between Patent Documents 1 to 4 and 7, all used an organic compound as an additive agent (in this document, this is referred to as an organic additive).
Organic additives usually have the effect of inhibiting crystal growth and are thought to be incorporated into the grain boundaries. In this case, the mechanical strength tends to increase with the amount of organic additives incorporated into the grain boundary (see Patent Document 6 and Non-Patent Document 1).
All of the electrolytic copper foils described in Patent Documents 1 to 4 and 7 where organic additives are incorporated into the grain boundaries were found to have high mechanical strength under normal conditions, but the mechanical strength was reduced significantly when heated to a high temperature such as about 300°C. This is thought to be because the organic additives incorporated into the grain boundaries decompose when heated to a high temperature such as about 300°C, resulting in a decrease in mechanical strength.

[0032] On the other hand, it was found that the electrolytic copper foil described in Patent Document 8, which does not use an organic additive, also exhibited a marked decrease in mechanical strength when heated to a high temperature of about 300°C, similar to the electrolytic copper foils containing the aforementioned organic additive.

RELATED ART DOCUMENTS

Patent Documents

[0033] Patent Document 1: Japanese Patent No. 4120806
Patent Document 2: Japanese Patent No. 4273309
Patent Document 3: Japanese Patent No. 3270637
Patent Document 4: Japanese Patent No. 3238278
Patent Document 5: Japanese Unexamined Patent Application Publication H9-67693
Patent Document 6: Japanese Unexamined Patent Application Publication 2009-221592
Patent Document 7: Japanese Unexamined Patent Application Publication 2000-17476
Patent Document 8: Japanese Patent No. 3943214

Non-Patent Documents

[0034] Non-Patent Document 1: SHIGA Shoji, Metal Surface Technology, Vol.31, No. 10, p573 (1980)

SUMMARY OF THE INVENTION

PROBLEM TO BE SOLVED BY THE INVENTION

[0035] Therefore, an object of the present invention is to provide an electrolytic copper alloy foil that has a high mechanical strength under normal conditions, and that is resistant to thermal degradation of mechanical properties even when heated, for example, to the aforementioned high temperature of about 300°C. Furthermore, another object of the present invention is to provide an electrolytic copper alloy foil with high conductivity, high tensile strength, and excellent heat

resistance by incorporating into the electrolytic copper alloy foil a metal that was conventionally metallurgically impossible to form an alloy with copper.

MEANS FOR SOLVING THE PROBLEM

[0036] As a result of diligent research, the present inventors have found that electrolytic deposition (also called electrodepositing or electrolytic deposition) from an electrolyte solution with or without a prescribed organic additive and with the chloride ion concentration adjusted to a prescribed low concentration produces an electrolytic copper alloy foil with high mechanical strength in the normal state and low thermal degradation of mechanical strength even after heating at about 300°C.

The present inventors have also discovered that an electrolytic copper alloy foil with high conductivity, high tensile strength, and excellent heat resistance can be obtained by incorporating ultrafine particles of an oxide of a metal and ultrafine particles of the partially reduced metal into the electrolytic copper foil through the foil making process using an electrolytic solution obtained by mixing an aqueous solution of a metal salt of a metal that exists as an oxide in a solution of pH 4 or lower and an aqueous copper sulfate solution, without or with a prescribed organic additive, and where the chloride ion concentration has been adjusted to a prescribed low concentration.

The present invention was achieved based on these findings.

[0037] In other words, the present invention provides the following means.

(1) An electrolytic copper foil containing a metal oxide or metal existing as an oxide in a solution with a pH of 4 or less and containing chlorine in an amount exceeding 10 ppm but less than 50 ppm.

(2) The electrolytic copper foil according to (1), wherein the metal existing as an oxide in a solution of pH 4 or less is at least one of W, Mo, Ti, or Te.

(3) The electrolytic copper foil according to (1) or (2), containing a metal oxide or a metal existing as an oxide in a solution with a pH of 4 or less and containing chlorine in an amount exceeding 50 ppm but less than 2200 ppm.

(4) The electrolytic copper foil according to any one of (1) to (3), wherein the copper of the base material exists as fine crystal grains, and the metal oxide of the metal is dispersed in the base material as ultrafine particles.

(5) The electrolytic copper foil according to any one of (1) to (4), wherein the electrical conductivity is 65% IACS or higher.

(6) The electrolytic copper foil according to any one of (1) to (5), wherein the value of tensile strength in a normal state is 500 MPa or higher, and the ratio of the value of tensile strength measured at room temperature after heat treatment at 300°C to the value of tensile strength in normal state is 80% or higher.

(7) The electrolytic copper foil according to any one of (1) to (6), produced using an electrolytic solution containing an aqueous copper sulfate solution, an aqueous solution of a metal salt of the aforementioned metal, and chloride ions at 15 mg/L or less.

(8) A method of producing the electrolytic copper foil according to any one of (1) to (7), wherein an electrolytic solution is prepared by adding hydrochloric acid or a water-soluble chlorine-containing compound to a mixture of an aqueous copper sulfate solution and an aqueous solution of a metal salt of the aforementioned metal to obtain a chloride ion concentration of 15 mg/L or less, and electrolytic copper foil is produced by electrodeposition using the electrolytic solution.

(9) The method of producing the electrolytic copper foil according to (8), wherein the electrolyte contains at least one organic additive selected from the group consisting of thiourea compounds, 3-mercaptopropyl sulfonate, hydroxyethyl cellulose and peptides in an amount of 1 ppm to 20 ppm.

(10) An electrolytic copper foil containing tungsten and chlorine in an amount exceeding 10 ppm but less than 50 ppm, the remainder being copper and unavoidable impurities.

(11) The electrolytic copper foil according to (10), containing 50 to 2200 ppm of tungsten.

(12). The method of producing the electrolytic copper foil according to (10) or (11), wherein an aqueous solution of tungsten salt is blended with a sulfuric acid and copper sulfate electrolyte with a chloride ion concentration of 15

mg/L or less to obtain an electrolyte, and electrolyzed copper foil is produced from this electrolyte by electrodeposition.

(13) The method of producing the electrolytic copper foil according to (12), wherein the electrolyte contains at least one organic additive selected from the group consisting of thiourea compounds, 3-mercaptopropyl sulfonate, hydroxyethyl cellulose and peptides in an amount of 1 ppm to 20 ppm.

EFFECT OF THE INVENTION

[0038] The electrolytic copper foil of the present invention (hereinafter also referred to as electrolytic copper alloy foil) is an electrolytic foil of a copper alloy, such as Cu-W alloy, for example, and thus has high mechanical strength under normal conditions and low thermal degradation of mechanical strength even when heated to a high temperature of about 300°C.

It should be noted that mechanical strength here refers to tensile strength (tensile strength), 0.2% proof stress, and the like.

The normal state refers to the state in which the electrolytic copper foil is placed at normal temperature and pressure (25°C, 1 atm) after fabrication, either before or after heat treatment.

The electrolytic copper alloy foil of the present invention is provided high conductivity, high tensile strength, and excellent heat resistance by incorporating metals such as W, Mo, Ti, and Te into the electrolytic copper alloy foil as ultrafine particles of oxides of those metals, which have been difficult to alloy with copper in the past from a metallurgical perspective. Here, a small portion of the metal oxide may be reduced to metal and incorporated into the electrolytic copper alloy foil of the present invention as metallic ultrafine particles. In the present invention, these ultrafine particles of metal oxide and ultrafine particles of metal present in the electrolytic copper alloy foil are collectively referred to as the metal incorporated in the electrolytic copper alloy foil.

Therefore, the electrolytic copper alloy foil of the present invention can be suitably used for various applications such as flexible printed circuit boards (FPCs) and negative electrode current collectors for lithium-ion secondary batteries.

Furthermore, the method of producing electrolytic copper alloy foil of the present invention is also preferable as a method for producing the electrolytic copper alloy foil by simple means.

The above and other features and advantages of the present invention will become more apparent from the following description.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

[0039] (Composition of electrolytic copper alloy foil)

The electrolytic copper alloy foil of the present invention contains metal that exists as an oxide in liquids with a pH of 4 or less, either as ultrafine particles of the oxide or as ultrafine particles of the reduced metal. The electrolytic copper alloy foil of the present invention contains chlorine in an amount exceeding 10 ppm and less than 50 ppm.

First, the metal present as an oxide in the aforementioned liquid of pH 4 or less, preferably a sulfuric acid solution, is preferably at least one of W, Mo, Ti, or Te. More preferably, one type of these metals is included.

The content (incorporated amount) of these metals in the electrolytic copper alloy foil is preferably 50 to 2200 ppm, calculated as the metal, more preferably 200 to 2200 ppm, even more preferably 330 to 1510 ppm, and particularly preferably 630 to 1200 ppm. If the amount is too low, the effect of improving heat resistance is significantly reduced, and the ratio of tensile strength measured at room temperature after heating at 300°C, for example, will degrade to less than 80% as compared to tensile strength under normal conditions. On the other hand, if the amount is excessively high, the aforementioned effect of increasing tensile strength will be saturated and no further improvement is seen, but this is also undesirable because of high cost.

Next, the chlorine content (incorporated amount) in the electrolytic copper alloy foil is greater than 10 ppm and less than 50 ppm. Excessively low chlorine content in the electrolytic copper alloy foil is undesirable because the selection of copper raw materials for use in manufacturing the copper foil by electrolysis will be

stricter, and too many restrictions will be imposed on the manufacturing equipment. On the other hand, an excessively high chlorine content in the electrolytic copper alloy foil is undesirable because the amount of metal incorporated into the foil decreases, resulting in lower initial strength and strength after heating.

By increasing the amount of metal salts such as tungsten added to the electrolyte, it is possible to obtain the electrodeposited copper foil of the present invention that achieves excellent tensile strength and heat resistance, and the like without excessively reducing the chlorine content.

Therefore, from the viewpoint of properties and cost, the chlorine content in the electrolytic copper alloy foil is preferably more than 10 ppm and less than 50 ppm.

[0040] (Crystal grains and dispersed particles in electrolytic copper alloy foil)

In the electrolytic copper alloy foil of the present invention, the copper of the base material exists as fine crystal grains, and the metal oxide of the metal is dispersed in the base material as ultrafine particles.

The particle size (GS) of the fine crystalline grains of the base material copper is preferably 5 to 500 nm, more preferably 5 to 50 nm.

On the other hand, the particle size of the metal oxide ultrafine particles containing the metal is preferably 0.5 to 20 nm, and more preferably 0.5 to 2 nm. Furthermore, when the metal is present as ultrafine particles, the particle size is preferably 0.5 to 20 nm, more preferably 0.5 to 2 nm.

[0041] (Method of producing electrolytic copper alloy foil)

The electrolytic copper alloy foil of the present invention can be produced by the following manufacturing process.

First, an electrolytic solution is prepared by adding hydrochloric acid or a water-soluble chlorine-containing compound to a mixture of an aqueous copper sulfate solution and an aqueous solution of a metal salt of the aforementioned metal to

obtain a chloride ion concentration of 15 mg/L or less, and an electrolytic copper alloy foil is produced by electrodeposition using the electrolytic solution.

1. Electrolyte composition

The basic electrolyte composition is an aqueous solution containing copper sulfate prepared to a copper ion concentration of 50 to 120 g/L (preferably 50 to 90 g/L), a free sulfate ion concentration of 30 to 150 g/L (preferably 40 to 70 g/L), and a chloride ion concentration of 15 mg/L or less.

The copper ions and free sulfate ions can be obtained by adjusting the copper sulfate solution to provide each of the above ion concentrations. Alternatively, the concentration of these ions may be adjusted by adding additional sulfuric acid to the copper sulfate solution that provides the prescribed copper ion concentration.

Chloride ions can be provided by hydrochloric acid or a water-soluble chlorine-containing compound. For example, sodium chloride, potassium chloride, and ammonium chloride can be used as the water-soluble chlorine-containing compound.

2. Addition of metal salt

Ultrafine particles of metal oxides can be dispersed in the electrolytic solution by adding an aqueous solution of a metal salt containing a dissolved metal salt to an electrolytic solution with a pH of 4 or less, preferably a sulfuric acid acidified electrolyte, and then incorporated into the copper foil during electrolytic deposition.

There is no restriction on the type of metal salt, so long as the salt is ionized in water (pH higher than pH 4 and lower than pH 9), alkali (pH 9 or higher), hot concentrated sulfuric acid, or other solvents, and becomes an oxide at pH 4 or lower. Examples of these metal salts include the oxides of W and Mo if the metal is W or Mo, respectively, and sulfates of Ti if the metal is Ti. For example, tungstates such as sodium tungstate, potassium tungstate, and ammonium

tungstate, molybdates such as sodium molybdate, potassium molybdate, and ammonium molybdate, and titanium salts such as titanium sulfate can be used.

Furthermore, although not strictly applicable to metal salts, the salt can be ionized in a solvent to form an oxide at pH 4 or lower. For example, tellurium oxide can be used in the present invention because it ionizes in hot concentrated sulfuric acid.

The concentration of the metal salt solution is preferably 1 mg/L to 1000 mg/L (calculated as the metal), and 100 mg/L to 800 mg/L (calculated as the metal) is even more preferable. If the concentration is too low, fully incorporating the metal into the copper foil will be difficult. On the other hand, if the concentration is too high, the metal may be excessively incorporated into the copper foil, resulting in a decrease in electrical conductivity or, conversely, a decrease in tensile strength after heating due to saturation of the heat resistance enhancing effect.

In the present invention, the water used to prepare the electrolyte and the metal salt aqueous solution preferably is as free of chloride ions as possible in order to adjust to the aforementioned predetermined chloride concentration. In this regard, the aqueous metal salt solution is preferably prepared by dissolving the metal salt in pure water. The pure water is preferably water that contains as few metal ions and chloride ions as possible. Specifically, water with a chloride ion concentration of 15 mg/L or less is preferred.

3. Manufacturing conditions

The conditions during electrolytic deposition are as follows.

Current density 30 to 100 A/dm^2 (preferably 40 to 70 A/dm^2)

Temperature 30 to 70°C (preferably 40 to 60°C)

Under the above conditions, electrolytic copper alloy foil with a foil thickness of, for example, 12 μm can be produced.

[0042] (Presumed mechanism)

The mechanism by which the metal is incorporated into the copper foil in the present invention is presumed to be as follows.

The reason for adding a metal salt solution to the electrolyte is to keep the metal to be incorporated into the copper foil present in the aqueous solution as ions, which are then introduced to the electrolyte. This form of introducing forms ultrafine particles of metal oxides when the metal ions are converted to oxides in electrolyte solutions with a pH of 4 or less. In contrast, if metal salts are directly provided into the electrolyte, no ultrafine particles of metal oxide are formed, and thus no effect on tensile strength and heat resistance is obtained.

Chloride ions in the electrolytic solution are kept at a low concentration of 15 mg/L or less to prevent the specific adsorption of chlorine on the copper surface during deposition of metal oxide ultrafine particles. If the concentration of chloride ions is higher than 15 mg/L, metal incorporation into the electrolytic copper alloy foil will decrease and the effect of improving tensile strength and heat resistance will decrease rapidly.

[0043] (Dislocation inhibiting effect)

Metallic materials, including copper foils, recrystallize and the crystal grains coarsen when heated above the recrystallization temperature, resulting in reduced strength. Here, the starting point of the recrystallization process is the migration of dislocations (unstable states such as lattice defects). In the electrolytic copper alloy foil of the present invention, the metal oxide ultrafine particles are dispersed in the matrix phase, which inhibits the migration of dislocations around the particles. Therefore, softening does not occur unless heated to higher temperatures, resulting in high heat resistance.

In this document, this is referred to as “dislocation inhibiting effect is high”.

[0044] (Electrolytic copper alloy foil thickness)

There are no restrictions on the foil thickness of the electrolytic copper alloy foil of the present invention, which should be adjusted according to the foil

thickness required for the intended use. For example, for flexible printed circuit boards (FPCs), the thickness should be 3 to 20 μm. On the other hand, the thickness of the negative electrode current collector for lithium-ion secondary batteries should be 5 to 30 μm.

[0045] (Electrolytic copper alloy foil properties)

The electrolytic copper alloy foil of the present invention preferably has a conductivity of 65% IACS or higher, more preferably 70% IACS or higher, and even more preferably 75% IACS or higher. There is no limit to the upper limit of conductivity, which may exceed 100% IACS.

The electrolytic copper alloy foil of the present invention preferably has a tensile strength value of 500 MPa or higher under normal conditions, and even more preferably 550 MPa or higher. There is no limit to the upper limit of tensile strength under normal conditions, which is usually 1100 MPa or less.

With the electrolytic copper alloy foil of the present invention, the ratio of the tensile strength value measured at room temperature after heat treatment to 300°C to the tensile strength value under normal conditions is preferably at least 80%, the ratio is even more preferably at least 85%, and the ratio is especially preferably at least 90%. There is no limit to the upper limit of this ratio, which may exceed 100% (or in other words, tensile strength measured at room temperature after heat treatment is higher than the tensile strength measured at room temperature before heating).

[0046] One embodiment of the electrolytic copper foil (electrolytic copper alloy foil) of the present invention is an electrolytic copper alloy foil containing tungsten, and chlorine in an amount exceeding 10 ppm and less than 50 ppm, with the remainder being copper and unavoidable impurities. The description of the amount of chlorine contained in the electrolytic copper foil in this embodiment is the same as above.

The term “containing tungsten” means that tungsten is present as ultrafine particles of tungsten oxide dispersed in the base material. However, a small

portion of the tungsten oxide may be reduced to metallic tungsten during the process of incorporating tungsten into the base material. In the present invention, the term tungsten-containing electrolytic copper alloy foil includes the case where ultrafine particles of tungsten oxide are dispersed and present in the base material, as well as the case where metallic tungsten ultrafine particles are dispersed and present in the base metal.

In this document, these ultrafine particles of tungsten oxide and ultrafine particles of metallic tungsten are collectively referred to as tungsten in the electrolytic copper alloy foil.

The amount of tungsten in the electrolytic copper alloy foil is preferably in a range of 50 to 2200 ppm, more preferably 200 to 1580 ppm. The amount of tungsten contained in the electrolytic copper alloy foil is the amount of tungsten component including ultrafine particles of tungsten oxide and metallic tungsten, calculated as metallic tungsten. If the tungsten content is too small, the effect of addition will be insignificant. On the other hand, if excessive tungsten is added, the effect of the adding is saturated, and even though the cost is high, no improvement in physical properties will be seen.

[0047] In other words, in electrolytic copper alloy foils containing tungsten in an amount of less than 50 ppm, the mechanical strength measured at room temperature after heating at 300°C for 1 hour (hereinafter abbreviated as “300°C x 1H”) will be significantly reduced almost to the degree of the case without tungsten.

As the amount of tungsten added increases, the decrease in strength measured at room temperature after heating to 300°C x 1H becomes smaller, but the effect saturates as the amount increases to a certain level. The upper limit of effective addition is about 2200 ppm.

Note that the unit “ppm” used to indicate the content of a component refers to “mg/kg”. Furthermore, 0.0001 mass% = 1 ppm.

[0048] The electrolytic copper alloy foil of the present invention is obtained by electrolyzing a copper sulfate-based electrolyte with a pH of 4 or less containing copper ions and tungsten oxides formed from tungsten salts at pH 4 or less.
The tungsten salt contained in the electrolyte can be any salt that dissolves in a copper sulfate solution, such as sodium tungstate, ammonium tungstate, and potassium tungstate.

[0049] In the electrolytic copper alloy foil of the present invention, it is thought that tungsten oxides ions produced from tungsten salts are converted to tungsten oxides in the electrolyte with a pH of 4 or lower and are incorporated in the electrolytic copper foil as tungsten oxide (WO_3, W_2O_5, WO_2, and the like) or reduced metallic tungsten by electrolysis with the tungsten salt in the electrolytic solution having a low chloride ion concentration. Herein, these tungsten oxides (WO_3, W_2O_5, WO_2, and the like) or metallic tungsten are present as the ultrafine particles dispersed in the base material.
In other words, the electrolytic copper alloy foil of the present invention is formed by electrodeposition from an electrolytic solution of sulfuric acid and copper sulfate with low chloride ion concentration and containing tungsten oxide. In the sulfuric acid-copper sulfate electrolyte containing tungsten oxide, the tungsten oxide is thought to be formed as ultrafine particles from the tungsten salt via tungstic acid ions (WO_4^{2-} or WO_5^{2-}, and the like). Here, “low chloride ion concentration” means that the amount of chloride ion in the electrolyte is 15 mg/L or less, as in the previous embodiment.

[0050] When copper electrodeposition is performed using a sulfuric acid and copper sulfate electrolyte containing tungsten oxide with low chloride ion concentrations to form the electrolytic copper alloy foil, the tungsten oxides (WO_3, W_2O_5, WO_2, or the like) or ultrafine particles of tungsten metal are adsorbed on the grain boundaries, the growth of crystal nuclei is suppressed, crystal grains are refined (low profile), and an electrolytic copper alloy foil with high mechanical strength under normal conditions is formed.

[0051] The tungsten oxide (WO_3, W_2O_5, WO_2, and the like) or metallic tungsten ultrafine particles that exist at the grain boundaries of the electrolytic copper alloy foil are not bound to or absorbed by the bulk copper crystal. Therefore, the tungsten oxide (WO_3, W_2O_5, WO_2, and the like) and tungsten metal ultrafine particles remain at the grain boundary.

[0052] Even when electrolytic copper alloy foil containing tungsten oxide or tungsten are heated to about 300°C, the ultrafine particles of tungsten oxide (WO_3, W_2O_5, WO_2, and the like) and tungsten metal remain at the grain boundary, thereby preventing recrystallization of the copper fine crystals due to heat and thus the crystal grains are prevented from becoming larger.

[0053] Therefore, the electrolytic copper alloy foil of the present invention has high mechanical strength under normal conditions and a small decrease in mechanical strength when measured at room temperature after heating to a high temperature of about 300°C. This is an excellent feature not seen in conventional electrolytic copper foils produced by a sulfuric acid and copper sulfate-based electrolyte containing an organic additive.

[0054] Conventionally, the electrolytic copper foil of the present invention can be manufactured by electrodepositing copper and co-deposited metallic components from the aforementioned sulfuric acid and copper sulfate electrolyte with a low chloride ion concentration on a rotating titanium drum, which is then pulled off and continuously rolled.

[0055] As mentioned above, organic additives added to conventional sulfuric acid and copper sulfate electrolytes are thought to form compounds or complexes with metal elements and chlorine in the electrolyte. In this case, the metallic element is copper. Thus, a compound or complex of copper, organic additive, and chlorine is formed in the sulfuric acid and copper sulfate electrolyte. When electrolytic copper foil is formed by copper electrodeposition using this electrolyte, a compound or complex of copper, organic additives,

and chlorine is adsorbed on the grain boundaries, inhibiting the growth of crystal nuclei and refining the crystal grains to form an electrolytic copper foil with high mechanical strength under normal conditions.

[0056] However, with this copper foil, the substance present at the grain boundary is a compound or complex of copper, organic additive, and chlorine, so the copper is combined with or absorbed by bulk copper crystals, and the only substances present at the grain boundary will be organic additives and chlorine. These organic additives and chlorine decompose when exposed to temperatures as high as 300°C, which will result in a decrease in mechanical strength.

[0057] The reason for the significant decrease in tensile strength when measured at room temperature after heating to a high temperature of about 300°C is thought to be that the compound present at the grain boundary is an organic compound (organic additive), as described above, and the organic compound is easily decomposed by heating to about 300°C, thus lowering the mechanical strength.

[0058] Although the techniques described in Patent Documents 1 to 4 and 7 use different organic compounds to produce electrolytic copper foils, they are all produced from sulfuric acid and copper sulfate electrolytes containing organic additives and chlorine, and it is the organic compound component that is adsorbed on the grain boundaries of the electrolytic copper foil. The reason why the mechanical strength of the electrolytic copper foil is significantly reduced when measured at room temperature after exposure to a high temperature of about 300°C is thought to be because the compounds adsorbed on the grain boundaries are all organic compounds that decompose easily when heated to a high temperature of about 300°C.

[0059] In contrast, the electrolytic copper alloy foil of the present invention is an electrolytic copper alloy foil formed by electrodeposition from an electrolytic solution of sulfuric acid and copper sulfate with low chloride ion concentration and that contains tungsten oxide and the like.

As mentioned above, the tungsten component is thought to form tungsten oxide (WO_3, W_2O_5, WO_2, and the like) or metallic tungsten ultrafine particles via tungstic acid ions (WO_4^{2-} or WO_5^{2-}, and the like) in the sulfuric acid and copper sulfate electrolyte. When the copper alloy foil is formed by copper electrodeposition with this electrolyte, the ultrafine particles of tungsten oxide (WO_3, W_2O_5, WO_2, and the like) and tungsten metal are adsorbed on the grain boundaries in an ultrafine particle form. As a result, the growth of crystal nuclei is suppressed, crystal grains are refined, and an electrolytic copper alloy foil with high mechanical strength under normal conditions is formed.

[0060] Therefore, in the electrolytic copper alloy foil of the present invention, since the ultrafine particles of tungsten oxide (WO_3, W_2O_5, WO_2, and the like) and tungsten metal exist at the grain boundary, unlike the case of compounds or complexes of copper, organic compound, and chlorine, the tungsten is not bound or absorbed by the bulk copper crystal, but remains at the grain boundary as tungsten oxide (WO_3, W_2O_5, WO_2, and the like) or tungsten metal ultrafine particles.

[0061] Thus, even when exposed to temperatures as high as 300°C, the ultrafine particles of tungsten oxide (WO_3, W_2O_5, WO_2, and the like) and tungsten metal remain at the grain boundaries and prevent the copper microcrystals from recrystallizing due to heat, which causes crystal coarsening. Therefore, the mechanical strength under normal conditions will be high, and even when measured at room temperature after heating to a high temperature of about 300°C, the decrease in mechanical strength will be small, which is an excellent feature not seen in conventional electrolytic copper foils produced by a sulfuric acid and copper sulfate electrolyte containing organic additives.

[0062] The electrolytic copper alloy foil of the present invention can be preferably used for flexible printed circuit boards (FPCs) and negative electrode current collectors for lithium-ion secondary batteries.

As mentioned above, FPCs require a certain level of strength after the polyimide resin is cast or heat-laminated.

When a polyimide resin is used as a binder in the negative electrode current collector for lithium-ion secondary batteries, a heat treatment is performed on the negative electrode to cure the polyimide resin. If the copper foil softens after this heating and the strength decreases excessively, the stress of expansion and contraction of the active material will be applied to the copper foil during charging and discharging, which may cause deformation of the copper foil. In more extreme cases, the copper foil may break. Therefore, the copper foil for negative electrode current collectors must have a certain level of strength after heating.

Thus, in the case of both flexible printed circuit boards (FPCs) and negative electrode current collectors for lithium-ion secondary batteries, the polyimide resin is heated to a temperature of about 300°C for heat curing. Therefore, the copper foil must have a certain level of strength after heat treatment at about 300°C x 1H and then returned to room temperature.

In the electrolytic copper alloy foil of the present invention, the standard acceptable level of these mechanical properties is as follows for each item. Tensile strength (tensile strength) under normal conditions is TS ≥ 500 MPa. Tensile strength measured at room temperature after heating to 300°C x 1H is TS ≥ 280 MPa. The ratio (%) of tensile strength measured at room temperature after heating to tensile strength under normal conditions (300°C x 1H) is 80% or more.

[0063] Another embodiment of the electrolytic copper alloy foil of the present invention may use a predetermined organic additive such as a thiourea compound (hereinafter also referred to as thiourea compound, and the like) as an additive during the production of any of the above electrolytic copper alloy foils.

[0064] The inclusion of the aforementioned organic additive may further improve the strength, surface smoothness, and elongation of the copper foil.

[0065] In this case, a thiourea compound or the like is preferably included in the electrolyte at 1 to 20 ppm.

[0066] The thiourea compound, which is the organic additive, is an organic compound with the following structure.

>N-C(=S)-N<

Examples of thiourea compounds are thiourea (TU), N,N-dimethylthiourea (DMTU), N,N-diethylthiourea (DETU), tetramethylthiourea (TMTU) and ethylthiourea (ETU). However, these are only examples of thioureas used in the examples described below, and any compound that has the structural characteristics described above and that exhibits similar effects can be used.
For example, 3-mercaptopropyl sulfonate (MPS), hydroxyethyl cellulose (HEC), and peptides such as Nippi Peptide (PBF) (trade name, Nippi Corporation) can be used as organic additives other than thiourea compounds.

[0067] For example, the reason for using thiourea compounds as organic additives is that these compounds readily change to an [=S] structure in solution, and the [=S] structure preferentially adsorbs on copper to form an adsorption layer of organic molecules, and then the tungsten oxide adsorbs onto the adsorption layer, so that the tungsten is incorporated together with the thiourea compound into the foil.
Tungsten exists as an oxide in a solution of pH 4 or lower (for example, sulfuric acid acidic solution), but during copper electrodeposition using an electrolyte containing chlorine, the chlorine ions coat the copper deposition surface, so the tungsten oxide is not adsorbed by the copper, and incorporation of tungsten into the foil is unlikely to occur. When an organic additive such as a thiourea compound is added to the electrolyte, the [=S] structure adsorbs preferentially on the copper over chlorine ions, forming an adsorption layer of organic molecules on the copper. It is deduced that tungsten oxide is adsorbed on the adsorption layer, and tungsten is incorporated into the foil together with thiourea compounds.

[0068] The present inventors also repeated various tests to produce Cu-W alloy foils. As a result, it was found that in electrolytic solutions containing chlorine ions, tungsten is not incorporated sufficiently into the electrolytic copper foil even if a large amount of tungsten is added to the solution. In addition, the addition of tungsten and glue to the electrolyte containing chlorine ions, as disclosed in Patent Documents 4 and 5, did not result in the incorporation of tungsten into the electrolytic copper foil.

Electrolytic copper foil made with this electrolyte demonstrated a significant decrease in mechanical strength when measured at room temperature after heating to a high temperature of about 300°C.

However, it was discovered that tungsten can be incorporated into the foil under some foil-making conditions even if chlorine ions are present if thiourea compounds or the like are added to the electrolyte.

[0069] Thiourea compounds and the like, when added to sulfuric acid and copper sulfate electrolytes, are thought to form complexes with the metal elements and the chlorine in the electrolyte.

If tungsten is not added, the metallic element added to the electrolyte for electrolytic copper foil making is copper. Thus, copper-thiourea compounds and other compounds are formed in the electrolyte containing copper sulfate and sulfuric acid. When electrolytic copper foil is formed by copper electrodeposition using this electrolyte, the copper thiourea compounds and the like are adsorbed on the grain boundaries, inhibiting the growth of crystal nuclei, and refining the crystal grains, and thus an electrolytic copper foil with high mechanical strength under normal conditions can be formed.

[0070] However, with this copper foil, since the substance present at the grain boundary is a copper-thiourea compound or the like, the copper is bound to or absorbed by the bulk copper crystal, and the substance present at the grain boundary is only a thiourea compound, and the like, which decomposes when exposed to a high temperature of about 300°C, and as a result, the mechanical strength is thought to decrease.

[0071] The reason for the significant decrease in tensile strength when measured at room temperature after heating to a high temperature of about 300°C is thought to be that the compound present at the grain boundary is an organic compound, as described above, and the organic compound is easily decomposed by heating to about 300°C, thus lowering the mechanical strength.

[0072] The methods disclosed in the Patent Documents 1 to 3 use different organic compounds to electrodeposit and produce electrolytic copper foils, but all of the foils are produced from sulfuric acid and copper sulfate electrolyte containing organic additives and chlorine, and it is the organic compound component that is adsorbed on the grain boundary of the electrolytic copper foil. Therefore when these electrolytic copper foils are exposed to a high temperature of 300°C or higher, the mechanical strength of the foils decreases significantly when measured at room temperature after this heating, and this is thought to be because the compounds adsorbed on the crystal grain boundaries are all organic compounds that easily decompose under high-temperature heating to 300°C or higher.

[0073] In contrast, in the embodiment of the present invention, copper electrodeposition is performed with an electrolyte containing copper sulfate and sulfuric acid, tungsten, organic additives such as thiourea compounds, and a low concentration of chlorine (chloride ions) to form a copper alloy foil, so the tungsten oxide is adsorbed onto the copper together with the thiourea compound. The growth of crystal nuclei is inhibited by the adsorbed tungsten oxide, thiourea compounds, and the like, and the crystal grains are refined to form an electrolytic copper alloy foil with high mechanical strength under normal conditions.

[0074] Therefore, in the electrolytic copper alloy foil of the present invention, the tungsten oxide and thiourea compounds are present at the grain boundary, and unlike copper-thiourea compounds, the tungsten oxide is not bound to or absorbed by the bulk copper crystal, and the tungsten oxide and thiourea

compounds are thought to remain at the grain boundary. Thus, even when exposed to temperatures as high as 300°C, the tungsten oxide remains as ultrafine particles at the grain boundaries and prevents the copper microcrystals from recrystallizing due to heat, which causes crystal coarsening.

[0075] The reason why the amount of organic additives such as thiourea compounds added to the electrolyte is set at 1 ppm to 20 ppm in this embodiment of the present invention is because if the amount is too low, the tungsten cannot be incorporated into the copper foil in the specified amount and the tensile strength measured at room temperature after heating at 300°C for 1 hour will be too low, while if the amount is too high, excessive tungsten in the copper foil will result in excessively high tensile strength or elongation, both of which are undesirable properties. The amount of organic additives such as thiourea compounds is in the preferred range of 1 ppm to 20 ppm. More preferably, the amount of organic additives such as thiourea compounds is 1 ppm to 7 ppm.

EXAMPLES

[0076] Hereinafter, the present invention will be further described in detail based on examples, but the present invention is not limited thereto.

[0077] (Examples 1 to 11, Comparative Examples 1 to 9, and Reference Example)

In Examples 1 to 11 and Comparative Examples 1 to 6, the following baths were used as the basic bath composition for a sulfuric acid and copper sulfate electrolyte.

Cu:50 to 90 g/L

H_2SO_4:40 to 70 g/L

Various metal salt compounds (various metal sources) and sodium chloride (chloride ion source) listed in Table 1 were added as additives to the above basic bath in order to adjust the metal salt and chloride ion concentrations as listed in Table 1 to obtain the electrolyte.

Electrodeposition was performed in each case using these various electrolytes (the same applies to comparative examples 1 to 6) under the following conditions to produce electrolytic copper alloy foils with a thickness of 12 μm.

Current density: 40 to 70 A/dm^2

Liquid temperature: 40 to 60°C

[0078] In Comparative Example 7, the following amounts of sodium tungstate as additive A1, hydrochloric acid as additive B, and glue as additive C were added to a bath of sulfuric acid and copper sulfate electrolyte using the basic bath composition described above.

Sodium tungstate = 10mg/L to 100mg/L (as tungsten)

Chloride ions (Cl^-) = 20 mg/L to 100 mg/L

Glue = 2 to 10 mg/L

Electrodeposition was performed using this electrolyte under the same conditions (current density and liquid temperature) as described above to produce a 12 μm-thick electrolytic copper foil.

[0079] Comparative Example 8 was prepared as follows based on Patent Document 7 (Patent Publication No. 2000-17476). An electrolyte containing $CuSO_4$-$5H_2O$, H_2SO_4, and $SnSO_4$ was treated by bubbling with air to obtain an electrolyte containing $CuSO_4 \cdot 5H_2O$ = 250g/dm^3 (g/L), H_2SO_4 = 50 g/L, SnO_2 ultrafine particles = 3 g/L, $SnSO_4$ = 10 g/L, and polyethylene glycol as polyether = 0.001-0.1 g/L. Electrodeposition was performed using this electrolyte at a current density of 10 A/dm^2 and a bath temperature of 50°C to produce 12 μm-thick electrolytic copper alloy foils.

[0080] Comparative Example 9 was prepared as follows based on Patent Document 8 (Patent No. 3943214). The electrolyte was a sulfuric acid copper sulfate solution with a copper ion concentration of 70 to 120 g/L and a sulfate ion concentration of 50 to 120 g/L to which 50 ppm silver ions were added. Electrodeposition was performed using this electrolyte at a current density of 120 A/dm^2 and electrolyte temperature of 57°C to produce 12 μm-thick electrolytic copper foils.

[0081] A commercially available Cu-0.015 and 0.03 Zr rolled copper alloy foil (product name: HCL (registered trademark)-02Z, manufactured by Hitachi Cable, Ltd.) with a thickness of 12 μm was used as a reference example.

[0082] The obtained electrolytic copper (alloy) foils of each example and comparison example and the rolled copper alloy foils of the reference example were measured for tensile strength (tensile strength, TS) under normal conditions, tensile strength measured at normal temperature after exposure to 300°C x 1H heating, the ratio thereof, electrical conductivity (EC), chlorine content and metal content, as follows.
Tensile strength was measured according to JISZ2241-1880. The tensile strength of the copper foil under normal conditions was judged to be favorable if 500 MPa or higher and poor if less than 500 MPa. Furthermore, under more favorable conditions, the ratio of the value of tensile strength under normal conditions after heat treatment of the copper foil at 300°C for 1 hour (300°C x 1H) in an inert gas atmosphere to the value of tensile strength measured at room temperature was determined to be favorable at 80% or higher, and unfavorable at less than 80%.
Conductivity was measured by the 4-terminal method (current-voltage method) based on JIS-K6271. The conductivity of the copper foil was judged as good if the conductivity was 65% IACS or higher and poor if the conductivity was less than 65% IACS.
The content of Cl and metals such as W in the copper foil was determined by dissolving a fixed mass of electrolytic copper (alloy) foil in acid and then analyzing the amount of metals such as W in the resulting solution by ICP

atomic emission spectrometry. The chlorine content in the resulting solution was determined by the silver chloride titration method (detection limit: 10 ppm). These results are presented in Table 1.

[0083] Table 1

	Metal type	Metal salt compound type	Metal salt concentration in electrolyte*1	Chloride ion concentration in electrolyte	Tensile Strength (MPa)		Ratio of tensile strength after heating to 300°C x 1H to tensile strength under normal conditions (%)	Conductivity	Chlorine content	Metal content*2
			(mg/L)	(mg/L)	Normal state	After heating at 300°C x 1H		(%IACS)	(ppm)	(ppm)
Example 1	W	Sodium tungstate (IV) dihydrate	100	1	680	650	95.6	80	11	630
Example 2	W	Sodium tungstate (IV) dihydrate	500	1	815	803	98.5	66	15	2180
Example 3	W	Sodium tungstate (IV) dihydrate	800	3	730	700	95.9	70	29	1510
Example 4	W	Sodium tungstate (IV) dihydrate	1000	15	550	515	93.6	88	48	97
Example 5	W	Sodium tungstate (IV) dihydrate	800	15	505	420	83.2	90	46	55
Example 6	W	Sodium tungstate (IV) dihydrate	500	10	580	480	82.8	87	12	123
Example 7	W	Sodium tungstate (IV) dihydrate	500	6	640	600	93.8	85	36	202
Example 8	Mo	Sodium molybdate (IV) dihydrate	40	2	505	420	83.2	80	11	108
Example 9	Ti	Titanium (IV) sulfate	3	1	615	500	81.3	72	14	51
Example 10	Te	Tellurium (IV) oxide	10	2	522	441	84.5	74	13	150
Example 11	Mo	Sodium molybdate (IV) dihydrate	400	12	525	460	87.6	65	33	112

Note: Detection limit of chloride ion content: 10 ppm (0.001 mass%)

*1 The concentration of metal salt in the electrolyte was calculated as the respective metal, based on the amount of each metal salt added.

*2 The metal content in the foil includes the amount of the metal oxide ultrafine particles and the metal ultrafine particles, if present.

[0084] Table 1 (continued)

	Metal type	Metal salt compound type	Metal salt concentration in electrolyte*1	Chloride ion concentration in electrolyte	Tensile Strength (MPa)		Ratio of tensile strength after heating to 300°C x 1H to tensile strength under normal conditions (%)	Conductivity	Chlorine content	Metal content*2
			(mg/L)	(mg/L)	Normal state	After heating at 300°C x 1H		(%IACS)	(ppm)	(ppm)
Comparative Example 1	W	Sodium tungstate (IV) dihydrate	100	16	330	210	63.6	98	55	0
Comparative Example 2	W	Sodium tungstate (IV) dihydrate	1000	16	315	208	66.0	95	70	5
Comparative Example 3	W	Sodium tungstate (IV) dihydrate	1000	20	318	208	65.4	96	72	3
Comparative Example 4	W	Sodium tungstate (IV) dihydrate	10	1	460	410	89.1	89	8	93
Comparative Example 5	Mo	Sodium molybdate (IV) dihydrate	400	20	293	202	68.9	97	65	5

Comparative Example 6	Mo	Sodium molybdate (IV) dihydrate	1000	20	303	200	66.0	96	71	6
Comparative Example 7	W	Sodium tungstate (IV) dihydrate	40	30	340	259	76.2	97	<10	Below detection limit
Comparative Example 8	An	SnO_2 ultrafine particles	3000	0	631	576	91.3	50	<10	2980
Comparative Example 9	Ag	Ag ions	50	0	501	298	59.5	96	<10	520
Reference example	Zr	—	—	—	554	494	89.2	90	—	200

Note: Detection limit of chloride ion content: 10 ppm (0.001 mass%)

*1 The concentration of metal salt in the electrolyte was calculated as the respective metal, based on the amount of each metal salt added.

*2 The metal content in the foil includes the amount of the metal oxide ultrafine particles and the metal ultrafine particles, if present.

[0085] Examples 1 to 7 incorporated tungsten (W) oxide ultrafine particles, Examples 8 and 11 incorporated molybdenum (Mo) oxide ultrafine particles, Example 9 incorporated titanium (Ti) oxide ultrafine particles, and Example 10 incorporated tellurium (Te) oxide ultrafine particles in the electrolytic copper alloy foil as the metal oxides. The amount of incorporation was in a range of 50 to 2200 ppm for each metal, and the amount of chlorine in the foil was in a range of more than 10 ppm and less than 50 ppm. Therefore, these examples have a high tensile strength of 500 MPa or higher under normal conditions, and a low rate of decrease in tensile strength measured at room temperature after heating at 300°C. Conductivity is also high, at 65% or higher.

From the foregoing, it can be seen that, with the present invention, it is possible to control the concentration of chlorine and the concentration of metal elements in the electrolytic solution to an appropriate range. Furthermore, by including chlorine in the electrolytic solution and in the copper foil, a predetermined amount of metal can be incorporated in the copper foil as an oxide, thereby providing the resulting electrolytic copper foil with high strength and high heat resistance.

[0086] In Comparative Examples 1 to 3, 5, and 6, the chloride ion concentration in the electrolyte was higher than 15 ppm, so the resulting copper foil contained much more chlorine than 50 ppm. Therefore, the amount of tungsten (W) and molybdenum (Mo) oxide ultrafine particles incorporated was low, and tensile strength was also significantly lower than in Examples 1 to 11.

Comparative Example 4 is an example with low chloride ion concentration in the electrolyte, but the chlorine concentration in the resulting copper foil was

low, and although tungsten (W) oxide ultrafine particles were incorporated, the tensile strength was low.

[0087] Comparative Example 7 was prepared based on Patent Document 4 (Patent No. 3238278), and was prepared as a composition with the addition of glue.

The mechanical strength at room temperature was also low, and the electrolytic copper foil showed a significant decrease in mechanical strength measured at room temperature after heating to 300°C x 1H. The amount of W in the copper foil was measured and found to be below the lower detection limit (1 ppm (= 0.0001 mass%)).

It was confirmed that when chloride ions are included in the electrolytic solution in large amounts exceeding 15 mg/L, the electrodeposition of metals such as tungsten, which do not readily alloy with copper, is inhibited, and electrolytic copper foils are formed based on the effect of the addition of organic additives such as glue, for example, but electrolytic copper alloy foils were not formed.

As mentioned above, in the course of investigations leading to the present invention, the present inventors confirmed that if tungsten oxide converted from tungsten salt is present in the sulfuric acid and copper sulfate electrolyte and chloride ions are contained at a high concentration exceeding 15 mg/L, the tungsten cannot be co-deposited in the electrolytic copper, and as a result, the desired electrolytic copper alloy foil cannot be obtained. The present invention is based on this observation.

[0088] Comparative Example 8 is a test example prepared based on Patent Document 7 (Japanese Unexamined Patent Application Publication No. 2000-17476). Cu-Sn is also well known in rolled alloys. The electrodeposited copper foils of Comparative Example 8 have various properties, values, and production costs. No superiority was observed when compared to Cu-Sn rolled alloys. In addition, tin sulfate ($SnSO_4$), which is not an oxide, was forcibly oxidized by oxygen bubbling in a sulfuric acid electrolyte to form SnO_2 ultrafine particles, so not only is the manufacturing cost high, but the particle size (>20 nm) of the oxide

formed in the electrolyte and incorporated into the copper foil was significantly larger than with the present invention so the conductivity was also extremely low.

[0089] Comparative Example 9 is a test example prepared based on Patent Document 8 (Patent Publication No. 3943214). In the electrodeposited copper foil of Comparative Example 9, Ag was solidly soluble with Cu and incorporated as metallic Ag. Therefore, the heat resistance, or in other words, the ratio (%) of tensile strength measured at room temperature after heating at 300°C x 1H to the tensile strength under normal conditions, was inferior compared to the examples of the present invention, in which the metal was incorporated as ultrafine particles of oxide and precipitation strengthened. This indicates that a smaller particle size of particles dispersed in the base material leads to a higher effect of inhibiting dislocation (or in other words, heat resistance). In Comparative Example 9, the effect of inhibiting dislocation was low and the effect of preventing tensile strength reduction due to heating was extremely low.

[0090] The reference example is a Cu-0.02Zr “rolled copper alloy foil”. It can be seen that the electrolytic copper alloy foil of the present invention has comparable or better mechanical properties and electrical conductivity as compared to a rolled copper alloy foil.

[0091] <Examples 12 to 20>

In Examples 12 to 20, various metal salt compounds (various metal sources) and sodium chloride (chloride ion source) listed in Table 2 were added as additives to the bath of the above basic bath composition of sulfuric acid and copper sulfate electrolyte in order to adjust the metal salt and chloride ion concentrations as listed in Table 2. The electrolyte was obtained by adding the organic additives listed in Table 2 to achieve the concentrations listed in Table 2.
Note that the abbreviations used in the table for organic additives are as follows.
ETU: Ethylene Thiourea
TU: Thiourea

TMTU: Tetramethylthiourea

DMTU: N,N-dimethylthiourea

DETU: N,N-diethylthiourea

MPS: 3-mercaptopropyl sulfonate

HEC: Hydroxyethylcellulose

PBF: Nippi Peptide (trade name, manufactured by Nippi Corporation)

Electrodeposition was performed using one of these various electrolytes under the same conditions (current density and liquid temperature) as described above in each case to produce electrolytic copper alloy foils with a thickness of 12 μm.

[0092] For each of the electrolytic copper alloy foils obtained, the tensile strength (tensile strength, TS) under normal conditions, the tensile strength measured at normal temperature after heating to 300°C x 1H, the ratio thereof, electrical conductivity (EC), chlorine content, and metal content were measured in the same manner as described above.

These results are presented in Table 2.

[0093] Table 2

	Metal type	Metal salt compound type	Metal salt concentration in electrolyte*1	Chloride ion concentration in electrolyte	Organic additive type	Organic additive concentration in electrolyte	Tensile Strength (MPa)		Ratio of tensile strength after heating to 300°C x 1H to tensile strength under normal conditions (%)	Conductivity	Chlorine content	Metal content
			(mg/L)	(mg/L)		(mg/L)	Normal state	300°C x 1H after heating		(%IACS)	(ppm)	(ppm)
Example 12	W	Sodium tungstate (IV) dihydrate	100	1	ETU	5	760	730	96.1	78	15	1200
Example 13	W	Sodium tungstate (IV) dihydrate	100	3	ETU	3	850	820	96.5	75	48	450
Example 14	W	Sodium tungstate (IV) dihydrate	100	3	MPS	1	626	581	92.8	73	47	330
Example 15	W	Sodium tungstate (IV) dihydrate	100	3	HEC	3	641	556	86.7	72	23	280
Example 16	W	Sodium tungstate (IV) dihydrate	100	3	PBF	20	750	723	96.4	81	46	70
Example 17	Mo	Sodium molybdate (IV) dihydrate	80	4	TU	12	540	500	92.6	66	48	100
Example 18	Mo	Sodium molybdate (IV) dihydrate	100	3	TMTU	6	510	440	86.3	69	28	75
Example 19	Ti	Titanium (IV) sulfate	3	1	DMTU	7	630	620	98.4	70	30	55

Example 20	Te	Tellurium (IV) oxide	10	2	DETU	5	544	455	83.6	71	28	170

Note: Detection limit of chloride ion content: 10 ppm (0.001 mass%)

*1 The concentration of metal salt in the raw electrolyte was calculated as the respective metal, based on the amount of each metal salt added.

*2 The metal content in the foil includes the amount of the metal oxide ultrafine particles and the metal ultrafine particles, if present.

[0094] The results in Table 2 above show that electrolytic copper alloy foils with high tensile strength and excellent heat resistance equivalent to those in the previous examples can be obtained even when a given organic additive is included in the electrolyte during the production of the electrolytic copper foils.

INDUSTRIAL APPLICABILITY

[0095] The electrolytic copper alloy foil of the present invention is suitable as a component material in the field of printed circuit board materials that require high mechanical strength even after heating, such as HDD suspension materials or TAB materials.

[0096] It is also suitable for use not only as a printed wiring board material, but also as a constituent material in fields that require high mechanical strength and electrical conductivity even after heating at high temperatures. Furthermore, the electrolytic copper alloy foil of the present invention can be suitably used for battery component applications such as negative electrode current collectors for lithium-ion secondary batteries.

[0097] Although the present invention was described together with embodiments, there is no intention for the embodiments to limit the invention in any detail in the specification unless otherwise specified. It is thought that this invention should be interpreted broadly without contradicting the spirit and scope of the invention as set forth in the appended claims.

[0098] This application claims priority based on Patent Application 2013-011517 filed in Japan on January 24, 2013, which is hereby incorporated by reference as part of this specification.

Claims

1. An electrolytic copper foil containing a metal oxide or metal existing as an oxide in a solution with a pH of 4 or less and containing chlorine in an amount exceeding 10 ppm but less than 50 ppm.

2. The electrolytic copper foil according to claim 1, wherein the metal existing as an oxide in a solution of pH 4 or less is at least one of W, Mo, Ti, or Te.

3. The electrolytic copper foil according to claim 1 or 2, containing a metal oxide or a metal existing as an oxide in a solution with a pH of 4 or less and containing chlorine in an amount exceeding 50 ppm but less than 2200 ppm.

4. The electrolytic copper foil according to any one of claim 1 to 3, wherein the copper of the base material exists as fine crystal grains, and the metal oxide of the metal is dispersed in the base material as ultrafine particles.

5. The electrolytic copper foil according to any one of claim 1 to 4, wherein the electrical conductivity is 65% IACS or higher.

6. The electrolytic copper foil according to any one of claim 1 to 5, wherein the value of tensile strength in a normal state is 500 MPa or higher, and the ratio of the value of tensile strength measured at room temperature after heat treatment at 300°C to the value of tensile strength in normal state is 80% or higher.

7. The electrolytic copper foil according to any one of claim 1 to 6, produced using an electrolytic solution containing an aqueous copper sulfate solution, an aqueous solution of a metal salt of the aforementioned metal, and chloride ions at 15 mg/L or less.

8. A method of producing the electrolytic copper foil according to any one of claims 1 to 7, wherein an electrolytic solution is prepared by adding

hydrochloric acid or a water-soluble chlorine-containing compound to a mixture of an aqueous copper sulfate solution and an aqueous solution of a metal salt of the aforementioned metal to obtain a chloride ion concentration of 15 mg/L or less, and electrolytic copper foil is produced by electrodeposition using the electrolytic solution.

9. The method of producing the electrolytic copper foil according to claim 8, wherein the electrolyte contains at least one organic additive selected from a group consisting of thiourea compounds, 3-mercaptopropyl sulfonate, hydroxyethyl cellulose and peptides in an amount of 1 ppm to 20 ppm.

10. An electrolytic copper foil containing tungsten and containing chlorine in an amount exceeding 10 ppm but less than 50 ppm, the remainder being copper and unavoidable impurities.

11. The electrolytic copper foil according to claim 10, containing 50 to 2200 ppm of tungsten.

12. The method of producing the electrolytic copper foil according to claim 10 or 11, wherein an aqueous solution of tungsten salt is blended with a sulfuric acid and copper sulfate electrolyte with a chloride ion concentration of 15 mg/L or less to obtain an electrolyte, and electrolyzed copper foil is produced from this electrolyte by electrodeposition.

13. The method of producing the electrolytic copper foil according to claim 12, wherein the electrolyte contains at least one organic additive selected from the group consisting of thiourea compounds, 3-mercaptopropyl sulfonate, hydroxyethyl cellulose and peptides in an amount of 1 ppm to 20 ppm.

Abstract

PROBLEM:

To provide an electrolytic copper alloy foil having high mechanical strength under normal conditions and low thermal degradation even when heated to about 300°C.

SOLUTION

An electrolytic copper foil containing a metal oxide or metal existing as an oxide in a solution with a pH of 4 or less and containing chlorine in an amount exceeding 10 ppm but less than 50 ppm, as well as a manufacturing method thereof.

Questel

TRANSLATOR'S CERTIFICATE OF TRANSLATION

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To whom it may concern:

I, Dwaine Palmer, a translator fluent in the Japanese and English languages, on behalf of Questel, do solemnly and sincerely declare that the following is, to the best of my knowledge and belief, a true and correct translation of the document(s) listed below in a form that best reflects the intention and meaning of the original text.

I hereby declare that all statements made herein of my own knowledge are true and that all statements made on information and belief are believed to be true. I further declare that these statements were made with the knowledge that willful false statements and the like so made are punishable by fine or imprisonment, or both, under Section 1001 of Title 18 of the United States Code.

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