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(71) Applicant: **Mitsui Mining & Smelting Co., Ltd.**

Shinagawa-ku
Tokyo 141-8584 (JP)

(72) Inventor: **FUJIMOTO, Taku**

Takehara-shi, Hiroshima 725-0025 (JP)

(74) Representative: **Novagraaf Technologies**
Bâtiment O2

2, rue Sarah Bernhardt
CS90017
92665 Asnières-sur-Seine Cedex (FR)

(54) **SILVER-COATED FLAKE-FORM COPPER POWDER, AND METHOD FOR MANUFACTURING SAME**

(57) Provided is a silver-coated copper flake powder, wherein a ratio of the brightness L^* of the silver-coated copper flake powder to the dispersity of the silver-coated copper flake powder is 13 or more, where the dispersity is defined as D_{90}/D_{10} and the D_{90} and the D_{10} are the 90th percentile particle diameter (μm) and the 10th percentile particle diameter (μm), respectively, of the silver-coated copper flake powder in volume-weighted particle size distribution thereof as measured by laser diffraction scattering method. This powder is manufactured

using a method including: the step of treating a dispersion containing a copper base powder and a first complexing agent in a stirred media mill, thereby deforming copper base particles constituting the copper base powder into flakes; and the step of treating the copper base powder containing the copper base particles deformed into flakes, with an aqueous solution containing silver ions and a second complexing agent, thereby precipitating silver on the surface of the copper base particles.

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Description

Technical Field

5 **[0001]** The present invention relates to a silver-coated copper flake powder and a method for manufacturing the same.

Background Art

10 **[0002]** Copper flake particles have a large specific surface area due to their shape, and thus are likely to come into contact with each other, and thus conductivity is easily imparted to a resin by adding them to the resin. However, copper is likely to be oxidized, and accordingly, the electrical resistance of the copper particles tends to increase. With the intention of compensating for this disadvantage, various techniques have been proposed to coat the surface of copper particles with silver, which is a metal with lower electrical resistance than copper, to thereby suppress an increase in electrical resistance of the particles.

15 **[0003]** For example, Patent Literatures 1 to 3 propose silver-coated copper flake powders including copper flake particles obtained by flattening treatment, the particles having silver on the surface thereof.

Citation List

20 Patent Literatures

[0004]

Patent Literature 1: JP 2010-275638A

25 Patent Literature 2: JP 2015-71818A

Patent Literature 3: JP 2016-35098A

Summary of Invention

30 **[0005]** In the techniques described in Patent Literatures 1 to 3, an electrolytic copper powder is flattened using a milling device such as an attritor, and then the surface of the resulting copper powder is coated with silver by displacement plating. However, the silver-coated copper flake powder obtained by such a method has the following problems: the silver coating is not uniform, and the surface of the copper powder is thus likely to be partially exposed. This problem is particularly noticeable when the thickness of the electrolytic copper powder after flattening is small. When the silver-coated copper flake powder in such a coated state is mixed with a resin, copper is likely to dissolve into the resin, and as a result, the resin is likely to deteriorate over time.

[0006] It is an object of the present invention to provide a silver-coated copper flake powder that can overcome various disadvantages of the aforementioned conventional techniques, and a method for manufacturing the same.

40 **[0007]** The present invention solves the above-described problem by providing a silver-coated copper flake powder including silver-coated copper flake particles having the silver at least on a surface thereof, wherein a ratio of a brightness L^* of the silver-coated copper flake powder to a dispersity of the silver-coated copper flake powder is 13 or more, where the dispersity is defined by D_{90}/D_{10} , and the D_{90} and the D_{10} are the 90th percentile particle diameter (μm) and the 10th percentile particle diameter (μm), respectively, of the silver-coated copper flake powder in volume-weighted particle size distribution thereof as measured by laser diffraction scattering method.

45 **[0008]** Also, the present invention provides a method for manufacturing a silver-coated copper flake powder, including:

the step of treating a dispersion containing a copper base powder and a first complexing agent in a stirred media mill, thereby deforming copper base particles constituting the copper base powder into flakes; and

50 the step of treating the copper base powder containing the copper base particles deformed into flakes, with an aqueous solution containing silver ions and a second complexing agent, thereby precipitating silver on a surface of the copper base particles.

Description of Embodiment

55 **[0009]** Hereinafter, the present invention will be described based on its preferred embodiments.

[0010] The present invention relates to a silver-coated copper powder that is an aggregate of silver-coated copper particles each composed of a copper particle as a base material and silver on at least the surface of the copper particle. One of the characteristics of the silver-coated copper particles is their external shape. Specifically, the silver-coated

copper particles are each in the form of a flake. Therefore, the silver-coated copper particles are hereinafter referred to as "silver-coated copper flake particles", and a silver-coated copper powder is referred to as a "silver-coated copper flake powder".

[0011] As used herein, "flake" is synonymous with "flat" or "in the shape of small and thin pieces", and means that a particle is in a thin plate-like shape. A flake particle is specified by the aspect ratio thereof. The aspect ratio is the ratio of the long diameter D on the flat surface of the flake particle in plan view to the thickness T of the flake particle, D/T. The long diameter D on the flat surface is the length of the longest line segment among the line segments crossing the flat surface. In the present invention, the aspect ratio of the silver-coated copper flake particles is preferably from 5 to 160, more preferably from 10 to 160, even more preferably from 10 to 140, even more preferably from 15 to 140, even more preferably from 20 to 140, even more preferably from 30 to 120, and even more preferably from 30 to 80, in view of imparting high conductivity when adding the silver-coated copper flake powder to a resin.

[0012] The aspect ratio is the arithmetic mean of the D/T values obtained by measuring the long diameter D and thickness T of a particle and calculating the value of D/T, and performing this process for 50 or more particles.

[0013] The methods for measuring the long diameter D and thickness T are as follows.

[0014] Long diameter D: A sample is photographed using an electron microscope at an appropriate magnification, and the long diameter is measured using image analysis software for particle size distribution measurement (Mac-View manufactured by Mountech Co., Ltd.).

[0015] Thickness T: A sample is embedded in resin and cross-sectioned by a cross-section polisher. Then, the sample is photographed using an electron microscope at an appropriate magnification, and the thickness is measured in the same manner as for the long diameter D.

[0016] There is no particular limitation on the shape in plan view, i.e., the shape of the flat surface of the silver-coated copper flake particles, and the shape may be, for example, a substantially circular shape, a substantially elongated circular shape, a substantially oval shape, or an irregular shape. Among these shapes, a substantially circular shape is preferable in view of imparting high conductivity when adding the silver-coated copper flake powder to a resin.

[0017] When the flat surface of the silver-coated copper flake particles has a substantially circular shape, the circularity of the flat surface is preferably from 0.60 to 0.95, more preferably from 0.65 to 0.90, and even more preferably from 0.65 to 0.85. The circularity is defined as $4\pi/L^2$, where S represents the area of the flat surface and L represents the perimeter of the flat surface. The circularity is the arithmetic mean of the found values on 50 or more particles.

[0018] A specific method for measuring the circularity is as follows.

[0019] The circularity is measured using image analysis software for particle size distribution measurement (Mac-View manufactured by Mountech Co., Ltd.). Using this software, contours of 50 or more samples are traced and the areas within the contours are determined. The diameters of equivalent circles are calculated from the areas, and the resulting values are averaged.

[0020] If the surface of the copper flake particles as a base material in silver-coated copper flake particles is partially exposed, or in other words, if the silver coating is not uniform, copper is likely to come into contact with a resin when the silver-coated copper flake powder is mixed with the resin, and as a result, the resin may denature. Accordingly, it is preferable for the silver-coated copper flake particles that the surface of the copper flake particles as a base material should be coated with silver as uniformly as possible. In particular, it is preferable from an economic point of view that the surface of the copper flake particles should be uniformly coated with as little silver as possible.

[0021] The state of silver coating of the silver-coated copper flake particles can be evaluated on the basis of the brightness L* of the silver-coated copper flake powder. The reason for this is that the brightness of silver is higher than that of copper. However, the inventor of the present invention has conducted research and found that increasing the brightness by coating the surface of the copper flake particles with silver to a large thickness is not only economically disadvantageous, but also reduces the dispersibility of the resulting silver-coated copper flake powder in a resin. Therefore, a silver-coated copper flake powder cannot be said to be favorable only on the ground that the silver-coated copper flake powder has a high brightness L*.

[0022] The inventor of the present invention has conducted in-depth research in view of preventing denaturation of resin and improving dispersibility in resin when mixed with resin, and has found that the ratio between the value of D_{90}/D_{10} and the value of the brightness L* of the silver-coated copper flake powder can be advantageously used as a measure. The D_{90} and the D_{10} are the 90th percentile particle diameter (μm) and the 10th percentile particle diameter (μm), respectively, in the volume-weighted particle size distribution as measured by laser diffraction scattering method. The value of D_{90}/D_{10} is a measure of the particle size distribution of a powder and is generally referred to as the dispersity. As the dispersity is smaller, the degree of particle aggregation in the powder is lower, and also, the powder has a sharper particle size distribution. Therefore, as the value of the ratio L*/dispersion is larger, the silver coating is more uniform and the degree of aggregation in the silver-coated copper flake powder is lower.

[0023] The silver-coated copper flake powder of the present invention preferably has a value of the ratio L*/dispersion of 13 or more, more preferably 14 or more, and even more preferably 15 or more. The larger the value of the ratio L*/dispersion, the more desirable. However, the desired effects of the present invention can be sufficiently exhibited

when the value is as large as 25.

[0024] While the preferable value of $L^*/\text{dispersion}$ is as described above, the value of L^* is preferably 70 or more, more preferably 73 or more, and even more preferably 76 or more, in view of uniform silver coating. A silver-coated copper flake powder having such a value of L^* can be manufactured by the method described later. There is no particular limitation on the upper limit of L^* . The closer to 100, the more desirable. However, the desired effects of the present invention can be sufficiently exhibited when the value of L^* is as large as 86. The value of L^* is measured under the conditions of diffuse illumination/ 0° viewing angle specified in JIS Z 8722 (Geometric Condition c / specular component included), for example, using Chroma Meter (CR-400) manufactured by Konica Minolta Japan, Inc.

[0025] The value of the dispersity is preferably 5.3 or less, more preferably 5.0 or less, and even more preferably 4.5 or less, in view of improving the dispersibility of the silver-coated copper flake powder in resin. A silver-coated copper flake powder having such a dispersity can be manufactured by the method described later. There is no particular limitation on the lower limit of the dispersity. The closer to 1, the more desirable. However, the desired effects of the present invention can be sufficiently exhibited when the value of the dispersity is as small as 3.0.

[0026] The dispersity can be calculated, for example, by the following method. A small amount of silver-coated copper flake powder is placed in a beaker. Two or three droplets of 3 mass% Triton X solution (manufactured by Kanto Chemical Co., Inc.) are added thereto and allowed to permeate the powder, and then 50 mL of 0.1 mass% SN dispersant 41 solution (manufactured by San Nopco) is added thereto. Subsequently, dispersing treatment is performed on the resulting mixture for two minutes using an ultrasonic disperser TIP $\phi 20$ (manufactured by Nihonseiki Kaisha Ltd.; OUTPUT:8, TUNING:5) to prepare a measurement sample. The particle size distribution of the measurement sample is measured using a laser diffraction/scattering particle size distribution analyzer MT3300 (manufactured by MicrotracBEL Corp.) to determine the values of D_{90} and D_{10} . The dispersity is calculated from these values.

[0027] The inventor of the present invention has conducted research and found that the ratio of the thickness T (μm) of the silver-coated copper flake particles to the D_{50} (μm) can also be advantageously used as a measure, in view of preventing denaturation of resin and improving dispersibility in resin when mixed with the resin. The D_{50} is the 50th percentile particle diameter (μm) in volume-weighted particle size distribution as measured by the laser diffraction scattering method. In the present invention, the value of T/D_{50} is preferably 0.04 or less, and more preferably 0.03 or less. The value of T/D_{50} is preferably 0.005 or more, more preferably 0.01 or more, and even more preferably from 0.01 to 0.02. When the particle diameter D_{50} is considered to be fixed, the value of T/D_{50} means that the thickness T of the silver-coated copper flake particles is small relative to the particle diameter D_{50} . If the thickness is too small, the surface area of the particles will be too large and the particles will be highly reactive with a resin. It is meant that the silver-coated copper flake powder is effective in preventing denaturation of resin and improving dispersibility in resin when it is mixed with resin. Generally, in order to reduce the thickness T , external force may be applied to a copper base powder as a raw material for a long time to deform the particles into a sufficiently flat shape. However, when external force is applied for a long time, the copper base powder tends to aggregate and the D_{50} thus tends to become large. In other words, there is a tradeoff relationship between reducing thickness T and reducing the D_{50} . However, in the present invention, deforming the copper base powder into flakes by the later-described method enables reducing the thickness T while suppressing an increase in the D_{50} .

[0028] The thinner the thickness T , the more desirable. Specifically, the thickness is preferably 0.5 μm or less, more preferably 0.3 μm or less, even more preferably 0.25 μm or less, and even more preferably 0.20 μm or less. There is no particular limitation on the lower limit of the thickness T ; however, the desired effects of the present invention can be sufficiently exhibited when the thickness T is as small as 0.10 μm .

[0029] In view of improving the dispersibility of the silver-coated copper flake powder in a resin, the D_{50} is preferably from 7 to 17 μm , more preferably from 8 to 16 μm , and even more preferably from 9 to 15 μm . The D_{50} can be measured by the same method as described above for measuring the dispersity.

[0030] As described above, the degree of aggregation of the silver-coated copper flake powder of the present invention is low, or in other words, the above-described dispersity, D_{90}/D_{10} , is small. Therefore, in the silver-coated copper flake powder of the present invention, the values of D_{90} and D_{10} are preferably not far from the value of D_{50} . From this point of view, the D_{90} is preferably from 15 to 35 μm , more preferably from 16 to 31 μm , and even more preferably from 17 to 30.5 μm . The D_{10} is preferably from 3.0 to 8.0 μm , more preferably from 3.9 to 7.0 μm , and even more preferably from 5.0 to 6.2 μm .

[0031] As described above, the silver-coated copper flake particles constituting the silver-coated copper flake powder of the present invention are thin, and the degree of aggregation of the particles is low. As a result, the silver-coated copper flake powder of the present invention has a low tap density. Specifically, the tap density of the silver-coated copper flake powder of the present invention is preferably from 0.5 to 2.5 g/cm^3 , more preferably from 0.5 to 2.0 g/cm^3 , even more preferably from 0.7 to 2.0 g/cm^3 , even more preferably from 0.7 to 1.8 g/cm^3 , even more preferably from 0.7 to 1.5 g/cm^3 , and even more preferably from 0.8 to 1.3 g/cm^3 . The tap density is measured in accordance with JIS Z 2512.

[0032] In the silver-coated copper flake powder of the present invention, the surface of the copper flake particles as a base material is preferably coated with silver as thinly and uniformly as possible. Therefore, it is not desirable to

increase the silver content of the silver-coated copper flake powder of the present invention. Specifically, the silver content of the silver-coated copper flake powder of the present invention is preferably from 5 to 20 mass%, more preferably from 7 to 16 mass%, and even more preferably from 9 to 14 mass%. The silver content of the silver-coated copper flake powder can be measured by ICP optical emission spectrometry.

[0033] Next, a preferred method for manufacturing the silver-coated copper flake powder of the present invention will be described. The manufacturing method of the present invention generally includes the step of deforming copper particles as a base material into flakes (flake particles) and the step of coating the copper flake particles with silver.

[0034] The deforming step is a step of treating a dispersion containing a copper base powder and a first complexing agent in a stirred media mill, thereby deforming copper base particles constituting the copper base powder into flakes.

[0035] The coating step is a step of treating the copper base powder containing the copper base particles deformed into flakes, with an aqueous solution containing silver ions and a second complexing agent, thereby precipitating silver on the surface of the copper base particles.

[0036] Hereinafter, these steps will be described.

[0037] In the step of deforming a copper base powder into flakes, external force is applied to the copper base powder that is not in the form of flakes, thereby deforming the copper base powder into particles in a flat shape (i.e., flakes). Examples of the copper base powder include spherical copper base powders produced by a wet reduction method, electrolytic copper base powders obtained by electrolyzing an electrolyte containing copper ions, and spherical copper base powders produced by an atomization method. Among these copper base powders, a dendrite-like copper base powder produced by the electrolytic method is preferable in view of successfully obtaining a copper flake powder with a small thickness.

[0038] In a case where the dendrite-like copper particles produced by the electrolytic method are used as the base powder, it is preferable to mill the dendrite-like copper particles before deforming the particles into flakes, in view of more successfully obtaining a copper flake powder with a small thickness. There is no particular limitation on the milling method, and examples thereof include disc milling, roller milling, cylinder milling, impact milling, jet milling, and high-speed rotary milling. The milling may be either dry milling or wet milling. Dry milling is preferable in view of reliably separating branches from cores of dendrite-like copper particles. For dry milling, it is preferable to use, for example, a collision plate jet mill or a jet mill in which particles collide with each other.

[0039] The particle diameter D_{50} of the copper particles after milling is preferably from 2 to 8 μm , more preferably from 3 to 7 μm , and even more preferably from 4 to 6 μm , in view of obtaining copper flake particles with a desired particle diameter and thickness.

[0040] Next, the copper particles as a base material is deformed into flakes. For this purpose, a stirred media mill such as a bead mill, a ball mill, or an attritor may be used.

[0041] Before the copper particles are deformed into flakes using a stirred media mill, the copper particles are dispersed in a liquid medium to prepare a dispersion. Examples of the liquid medium for preparing a dispersion include water and an organic solvent. Mixtures of water and organic solvents can also be used. Examples of the organic solvent include: lower monoalcohols having 1 to 4 carbon atoms such as methanol and ethanol; lower polyhydric alcohols having 1 to 4 carbon atoms such as ethylene glycol; lower carboxylic acids having 1 to 4 carbon atoms; and lower amines having 1 to 4 carbon atoms, and these solvents may be used singly or in a combination of two or more thereof. Among these liquid media, an organic solvent is preferable in view of increasing the dispersibility of copper particles in the dispersion and improving the stability of quality during treatment in a stirred media mill. In particular, lower alcohols such as methanol are preferable in view of easily volatilizing the medium and less remaining on the target copper flake particles.

[0042] The concentration of copper particles in the dispersion is preferably from 10 to 60 mass%, and more preferably from 20 to 50 mass%, in view of ensuring productivity and preventing generation of coarse particles.

[0043] The dispersion can be prepared by simply mixing copper particles and a liquid medium. Optionally, a stirring disperser may be used to prepare the dispersion. Examples of the disperser include a fluid mill and a T.K.Filmix (registered trademark) manufactured by Primix Corporation.

[0044] In this manufacturing method, the dispersion preferably contains a first complexing agent. The first complexing agent effectively suppresses aggregation of copper particles during the deforming operation for obtaining flakes. Furthermore, oxides on the surface of the copper particles are removed by the first complexing agent, so that the surface of the copper flake particles can be thinly and uniformly coated with silver. From this point of view, the concentration of the first complexing agent in the dispersion is preferably from 0.1 to 40 mass%, more preferably from 0.5 to 20 mass%, and even more preferably from 1 to 10 mass%, provided that the concentration of the copper particles in the dispersion is within the range described above.

[0045] Conventionally, when a copper base powder is deformed into flakes using a stirred media mill, a dispersion containing the copper base powder often contains fatty acids to suppress aggregation of copper particles constituting the copper base powder. However, when fatty acids are used, they adhere to the surface of the copper particles and remain thereon after completion of deformation into flakes, and thus it is necessary to remove the fatty acids prior to coating the copper flake particles with silver. For removing the fatty acids, degreasing treatment is required, which

disadvantageously increases the number of processes, and in addition, the surface of the copper particles is disadvantageously oxidized by the degreasing treatment. In contrast, the present manufacturing method, in which the dispersion does not contain fatty acids but contains the first complexing agent, does not cause such issues.

[0046] The first complexing agent may be monodentate, or multidentate such as bidentate, tridentate or tetradentate. In view of ensuring high coordination to copper, examples of the first complexing agent include citric acid, ascorbic acid, and ethylenediaminetetraacetate. These complexing agents may be used singly or in a combination of two or more thereof. Among these complexing agents, ethylenediaminetetraacetate is preferable in view of effectively suppressing aggregation of copper particles in the deforming step.

[0047] In the step of deforming a copper base powder into flakes, the dispersion and milling media are placed in a stirred media mill, and mixed and stirred.

[0048] The diameter of the milling media is preferably from 0.1 to 1 mm. The material of the milling media is generally zirconia or alumina.

[0049] The operation time, rotation speed, number of passes, and other conditions of the stirred media mill may be tailored so as to obtain a desired copper flake powder.

[0050] After the copper base particles constituting the copper base powder are deformed into flakes in this manner, the coating step is performed. As described above, the copper base powder containing the copper base particles that have been deformed into flakes is treated with an aqueous solution containing silver ions and a second complexing agent in the coating step. This treatment preferably includes treatment 1 and treatment 2 below.

Treatment 1

[0051] Silver ions and the copper flake particles are brought into contact with each other in water to perform displacement plating, thereby precipitating silver on the surface of the copper flake particles. Precursor particles are obtained through this precipitation.

Treatment 2

[0052] The precursor particles obtained in the treatment 1, silver ions, and a reductant for silver ions are brought into contact with each other in water to further precipitate silver on the surface of the precursor particles.

[0053] Silver ions used in the treatment 1 and the treatment 2 are produced from a silver compound as a silver source. Examples of the silver compound include water-soluble silver compounds such as silver nitrate. The concentration of silver ions in water is preferably from 0.01 to 10 mol/L, and more preferably from 0.04 to 2.0 mol/L, in view of precipitating a desired amount of silver on the surface of the copper flake particles.

[0054] In the treatment 1, the amount of copper flake particles in the water is preferably from 1 to 1000 g/L, and more preferably from 50 to 500 g/L, in view of precipitating a desired amount of silver on the surface of the copper flake particles.

[0055] There is no particular limitation on the order of addition of the copper flake particles and silver ions in the treatment 1. For example, the copper flake particles and silver ions can be added to water at the same time. In view of ease of control of precipitation of silver by displacement plating, it is preferable to disperse copper flake particles in water to prepare a dispersion, and then add a silver compound as a silver source to the dispersion. In this case, the dispersion may be at room temperature or in the temperature range of 0 to 80°C.

[0056] To control the reduction of silver, a second complexing agent is preferably added to the dispersion before the addition of the silver compound. Examples of the second complexing agent include ethylenediaminetetraacetate, triethylenediamine, iminodiacetic acid and its salt, citric acid and its salt, and tartaric acid and its salt.

[0057] The first complexing agent described hereinbefore and the second complexing agent may be of the same type or different types; however, in view of matching the stability constants of the complexes, the first complexing agent and the second complexing agent are preferably of the same type. In particular, the first complexing agent and the second complexing agent are preferably both ethylenediaminetetraacetate, in view of effectively suppressing aggregation of copper particles in the deforming step and in view of forming a thin and uniform silver coating in the coating step.

[0058] In the treatment 1, the silver compound is preferably in the form of an aqueous solution when added. The aqueous solution may be added to the dispersion in a batch, or continuously or intermittently added to the dispersion over a predetermined time period. The aqueous solution of the silver compound is preferably added to the dispersion over a predetermined time period, in view of ease of control of the reaction of displacement plating.

[0059] In the treatment 1, the dispersion is preferably ultrasonicated, the ultrasonication being started before or concurrently with the addition of the silver compound to the dispersion. Through the ultrasonication, the copper flake particles are more likely to be dispersed in the dispersion, and thus the copper flake particles are more likely to be uniformly coated with silver. Although any ultrasonication brings about a certain effect, the frequency is preferably 200 kHz or less, and more preferably 45 kHz or less. A frequency of 10 kHz is sufficient as the lower limit.

[0060] In the treatment 1, silver is precipitated on the surface of the copper flake particles through the above-described

displacement plating, thereby obtaining precursor particles. In view of forming a thin and uniform silver coating, the amount of silver precipitated on the precursor particles is preferably from 0.1 to 50 mass%, and more preferably from 1 to 10 mass%, based on the amount of silver in the final silver-coated copper flake powder.

[0061] Next, the treatment 2 will be described. In the treatment 2, silver ions and a reductant for silver ions are added to the dispersion containing the precursor particles obtained in the treatment 1. In this case, the precursor particles obtained in the treatment 1 may be once solid-liquid separated and then dispersed in water to form a dispersion, or the dispersion of the precursor particles obtained in the treatment 1 may be used as is in the treatment 2. In the latter case, the silver ions added in the treatment 1 may or may not remain in the dispersion.

[0062] Silver ions added in the treatment 2 are produced from a water-soluble silver compound as in the treatment 1. Preferably, the silver compound in the form of an aqueous solution is added to the dispersion. The concentration of silver ions in the aqueous solution is preferably from 0.01 to 10 mol/L, and more preferably from 0.1 to 2.0 mol/L. In view of forming a thin and uniform silver coating, the aqueous solution containing silver ions at a concentration in the above-described range is preferably added in an amount of 0.1 to 55 parts by mass, and more preferably 1 to 25 parts by mass, per 100 parts by mass of precursor particles in the dispersion containing 1 to 1000 g/L, in particular 50 to 500 g/L of the precursor particles.

[0063] The reductant added in the treatment 2 is a reductant having enough reducing power to allow silver displacement plating and silver reduction plating to proceed simultaneously. The use of such a reductant enables successful formation of a thin and uniform silver coating. If a strong reductant is used, the reduction plating proceeds unilaterally and it is not easy to form a silver coating with a desired structure. On the other hand, if a weak reductant is used, the reduction plating of silver ions is unlikely to proceed, and thus it is not easy to form a silver coating with a desired structure. In view of these, the reductant is preferably an organic reductant that is acidic when dissolved in water. Specific examples thereof include formic acid, oxalic acid, L-ascorbic acid, erythorbic acid, and formaldehyde. These organic reductants may be used singly or in a combination of two or more thereof. Among these organic reductants, L-ascorbic acid is preferable. The term "acidic" used herein means that an aqueous solution obtained by dissolving 0.1 mol of the organic reductant in 1000 g of water has a pH of 1 to 6 at 25°C.

[0064] The amount of the reductant added is preferably from 0.5 to 5.0 equivalents, and more preferably from 1.0 to 2.0 equivalents, to silver ions in the aqueous solution to which the reductant is to be added, in view of easily allowing silver displacement plating and silver reduction plating to proceed simultaneously.

[0065] There is no particular limitation on the order of addition of the reductant and silver ions to the dispersion containing the precursor particles. In view of forming a thin and uniform silver coating by controlling reduction of silver ions, it is preferable to add the silver ions after the reductant is added to the dispersion. The silver compound as a silver source may be added to the dispersion in a batch, or continuously or intermittently added to the dispersion over a predetermined time period. Preferably, the silver compound in the form of an aqueous solution is added to the dispersion over a predetermined time period, in view of ease of control of the reduction of silver ions.

[0066] When silver displacement plating and silver reduction plating are allowed to proceed simultaneously in the treatment 2, the dispersion may be at room temperature or may be in the temperature range of 0 to 80°C by optionally heating.

[0067] In the treatment 2, the dispersion is preferably ultrasonicated, the ultrasonication being started before or concurrently with the addition of the reductant to the dispersion, as in the treatment 1. Through the ultrasonication, the precursor particles are more likely to be dispersed in the dispersion, and thus the precursor particles are more likely to be uniformly coated with silver. Although any ultrasonic irradiation brings about a certain effect, the frequency is preferably 200 kHz or less, and more preferably 45 kHz or less. A frequency of 10 kHz is sufficient as the lower limit.

[0068] The thus obtained silver-coated copper flake powder is preferably used in the form of a conductive composition containing the copper powder and resin. For example, the silver-coated copper flake powder may be mixed with a resin, an organic solvent, and glass frit to form a conductive paste. Alternatively, the silver-coated copper flake powder may be mixed with an organic solvent and others to form a conductive ink. The conductive paste or conductive ink can be applied to the surface of an application target to obtain a conductive film with a desired pattern.

[0069] In the silver-coated copper flake powder of the present invention, the silver coating is thin and uniform, and accordingly, the dissolution of copper of the silver-coated copper flake powder into the conductive composition is effectively suppressed. As a result, the denaturation of the resin contained in the conductive composition is suppressed.

[0070] Furthermore, the degree of aggregation of the silver-coated copper flake powder of the present invention is low, and accordingly, the powder has a good dispersibility in the conductive composition. Therefore, the conductive film obtained from the conductive composition has high conductivity.

Examples

[0071] Hereinafter, the present invention will be described in more detail by way of examples. However, the scope of the invention is not limited to these examples. Unless otherwise specified, "%" and "part(s)" mean "mass%" and "part(s)"

by mass", respectively.

Example 1

(1) Manufacture of Electrolytic Copper Powder

[0072] Nine cathode plates and nine insoluble anode plates each having a size of $1.0\text{ m} \times 1.0\text{ m}$ (DSE (manufactured by De Nora Permelec Ltd)) were suspended in an electrolyzer having a size of $2.5\text{ m} \times 1.1\text{ m} \times 1.5\text{ m}$ (about 4 m^3) such that the distance between electrodes was 5 cm. A copper sulfate solution as an electrolyte was circulated at 20 L/min in the electrolyzer. The anodes and cathodes were immersed in the electrolyte, and direct current was applied to them to perform electrolysis, thereby precipitating powder-like copper on the cathode surface.

[0073] Electrolysis was performed for 40 minutes under the conditions that the concentration of copper ions and that of sulfuric acid (H_2SO_4) in the electrolyte circulated were 5 g/L and 100 g/L, respectively, and that the current density was 100 A/m^2 .

[0074] Copper precipitated on the cathode surface was mechanically scraped off, collected, and then washed to obtain a hydrous copper powder cake. The cake was dispersed in 3 L of water, and the resultant was stirred for 10 minutes, and filtered through a Buchner funnel. The residue on the filter was washed, and then dried under reduced pressure ($1 \times 10^{-3}\text{ Pa}$) at 80°C for 6 hours to obtain an electrolytic copper powder.

(2) Milling of Electrolytic Copper Powder

[0075] The electrolytic copper powder was milled using a collision plate jet mill (IDS jet mill, IDS-5, manufactured by Nippon Pneumatic Mfg. Co., Ltd.) at a milling pressure of 6 kgf/cm^2 and a feed rate of 6.7 kg/hr . The particle diameter D_{50} of the milled copper powder was $4.5\text{ }\mu\text{m}$.

(3) Deformation into Flakes

[0076] Then, 3 kg of the milled electrolytic copper powder, 9 kg of methanol, and 1 kg of disodium ethylenediamine-tetraacetate (alternatively referred to as "EDTA2Na" hereinafter) were mixed to prepare a dispersion of copper powder in methanol. Then, 12 kg of the dispersion was placed in a bead mill (Starmill (registered trademark) LMZ, manufactured by Ashizawa Finetech Ltd.), and 4.85 kg of zirconia beads with a diameter of 0.2 mm was further placed therein. The bead mill was run for 180 minutes to deform the copper powder into flakes. Subsequently, the dispersion and the beads were separated by filtration, and the dispersion was allowed to stand to settle the copper flake particles. The supernatant was removed, and the copper flake particles were collected by filtration. The copper flake particles were then washed with water, followed by washing with methanol two times.

(4) Coating with Silver

[0077] Then, 100 g of copper flake particles were added to 500 mL of pure water heated to 40°C to form a dispersion. While stirring the dispersion, 4.3 g of EDTA2Na was added and dissolved therein. To the resulting dispersion, 48 mL of 0.44 mol/L silver nitrate aqueous solution was added continuously over 6 minutes to perform displacement plating, thereby precipitating silver on the surface of the copper flake particles to obtain precursor particles. At this time, the dispersion was ultrasonicated (100 W, 28 kHz).

[0078] Next, L-ascorbic acid as a reductant was added to the dispersion and dissolved therein. Further, 192 mL of 0.44 mol/L silver nitrate aqueous solution was continuously added to the dispersion over 24 minutes. This process allowed reduction plating and displacement plating to proceed simultaneously to further precipitate silver on the surface of the precursor particles to obtain a target silver-coated copper flake powder. Ultrasonic irradiation was continued during this process.

Examples 2 to 8

[0079] A silver-coated copper flake powders was manufactured in the same manner as in Example 1, except that the conditions shown in Table 1 below were employed.

Comparative Example 1

[0080] A silver-coated copper flake powder was manufactured in the same manner as in Example 1, except that the deforming step was performed for 20 minutes without using EDTA2Na, and that ultrasonication was not performed in

the coating step.

Table 1

	Milling	Deformation into Flakes	Silver content
Ex. 1	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 1 kg added Run for 180 min.	10.8%
Ex. 2	Milling pressure 8 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 1 kg added Run for 200 min.	10.0%
Ex. 3	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 2 kg added Run for 240 min.	11.2%
Ex. 4	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 2 kg added Run for 200 min.	14.0%
Ex. 5	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 2 kg added Run for 280 min.	10.4%
Ex. 6	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 2 kg added Run for 140 min.	9.8%
Ex. 7	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 2 kg added Run for 160 min.	10.0%
Ex. 8	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na 2 kg added Run for 180 min.	9.9%
Com.Ex. 1	Milling pressure 6 kgf/cm ² Feed rate 6.7 kg/hr	EDTA2Na not added Run for 20 min.	9.8%

Evaluation 1

[0081] On the silver-coated copper flake powders obtained in the examples and the comparative example, the particle size distribution, the brightness, the circularity of the flat surface of the particle, the thickness of the particle, the tap density, and the silver content were measured according to the methods described above. Table 2 below shows the results.

Evaluation 2

[0082] Conductive compositions were prepared by using the silver-coated copper flake powders obtained in the examples and the comparative example.

[0083] Epoxy resin (EPICLON850, manufactured by DIC) and butyl carbitol were mixed in a mass ratio of 35:65, and a silver-coated copper flake powder was added thereto to a concentration of 70% to prepare a conductive composition in the form of a paste.

[0084] The conductive composition was applied to one side of a polyethylene terephthalate (PET) film using a bar coater. The width of the coating was 200 mm. The gap of the bar coater was 30 μ m.

[0085] The coating film was dried in a vacuum dryer at 90°C for 60 minutes. Subsequently, the PET film with the coating film formed thereon was sandwiched between sheets and vacuum pressed at 160°C and 20 kN. On the resulting sample, the thickness of the conductive film was measured using a micrometer (Digimicro MF-501, manufactured by Nikon). Also, the resistance of the conductive film was measured using a resistivity measuring instrument (MCP-T600, manufactured by Mitsubishi Chemical Corporation) by the four point probe method. Table 2 below shows the results.

Evaluation 3

[0086] For the silver-coated copper flake powders obtained in the examples and the comparative example, the amount of copper ions dissolved therefrom was measured.

[0087] First, 0.2 g of silver-coated copper flake powder, 10 mL of hydrochloric acid (concentration 15%), and 2 mL of methanol were mixed to prepare a dispersion. The dispersion was allowed to stand at 25°C for 10 minutes. Subsequently, the dispersion was filtered, and the concentration of copper ions in the filtrate was measured by ICP optical emission spectrometry. Table 2 below shows the results.

Table 2

	Ex. 1	Ex. 2	Ex. 3	Ex. 4	Ex. 5	Ex. 6	Ex. 7	Ex. 8	Com.Ex. 1
Thickness T (μm)	0.23	0.18	0.18	0.22	0.16	0.40	0.30	0.24	1.80
Long diameter D (μm)	7.9	6.9	8.6	7.6	10.0	6.9	7.2	8.5	4.1
Aspect ratio	34.3	38.3	47.8	34.5	62.5	17.3	24.0	35.4	2.3
Circularity	0.79	0.68	0.65	0.74	0.65	0.68	0.72	0.74	0.82
Particle diameter D_{10} (μm)	4.7	3.9	5.2	4.3	6.2	5.6	5.8	6.0	2.3
Particle diameter D_{50} (μm)	10.5	9.2	11.5	9.6	14.6	12.0	12.1	12.8	4.2
Particle diameter D_{90} (μm)	18.8	18.8	20.5	19.2	30.5	22.3	23.5	23.5	12.6
Tap density (g/cm^3)	1.3	0.9	1.0	0.8	0.9	1.6	1.4	1.2	4.0
Dispersity (D_{90}/D_{10})	4.0	4.8	4.0	4.5	4.9	4.0	4.1	3.9	5.4
Brightness L^*	74	73	76	82	83	81	81	81	69
Silver content (%)	10.8	10.0	11.2	14.0	10.4	9.8	10.0	9.9	9.8
$L^*/(D_{90}/D_{10})$	18.5	15.1	19.2	18.4	16.9	20.4	20.1	20.8	12.7
T/D_{50}	0.02	0.02	0.02	0.02	0.01	0.03	0.02	0.02	0.43
Resistance of conductive film ($\Omega \cdot \text{cm}$)	2.80×10^{-5}	3.40×10^{-5}	3.44×10^{-5}	2.00×10^{-5}	3.80×10^{-5}	8.2×10^{-5}	5.2×10^{-5}	3.3×10^{-5}	4.32×10^{-3}
Amount of copper dissolved (%)	0.39	0.35	0.44	0.27	0.42	0.45	0.41	0.33	0.53

[0088] As is clear from the results shown in Table 2, the conductive films formed by using the silver-coated copper flake powders obtained in the examples are more conductive than the conductive film formed by using the silver-coated copper flake powder obtained in the comparative example.

[0089] It can also be seen that the dissolution of copper ions was suppressed from the silver-coated copper flake powders obtained in the examples, compared to that from the silver-coated copper flake powder obtained in the comparative example.

Industrial Applicability

[0090] The present invention provides a silver-coated copper flake powder, and when mixed with resin, the silver-coated copper flake powder has a good dispersibility in resin, causes less degradation of the resin, and can impart a reduced electrical resistance to a film formed from the resin. The present invention also provides a method for manufacturing the same.

Claims

1. A silver-coated copper flake powder comprising silver-coated copper flake particles having the silver at least on a surface thereof,
wherein a ratio of a brightness L^* of the silver-coated copper flake powder to a dispersity of the silver-coated copper flake powder is 13 or more, where the dispersity is defined as D_{90}/D_{10} , and the D_{90} and the D_{10} are the 90th percentile particle diameter (μm) and the 10th percentile particle diameter (μm), respectively, of the silver-coated copper flake powder in volume-weighted particle size distribution thereof as measured by laser diffraction scattering method.
2. A silver-coated copper flake powder comprising silver-coated copper flake particles having the silver at least on a surface thereof,
wherein a ratio of a thickness T (μm) of the silver-coated copper flake particles to a particle diameter D_{50} of the silver-coated copper flake powder is 0.04 or less, where the D_{50} is the 50th percentile particle diameter (μm) in volume-weighted particle size distribution of the silver-coated copper flake powder as measured by a laser diffraction scattering method.
3. The silver-coated copper flake powder according to claim 1 or 2, wherein a thickness T of the silver-coated copper flake particles is from 0.1 μm to 0.5 μm .
4. The silver-coated copper flake powder according to claim 3, wherein the thickness T of the silver-coated copper flake particles is from 0.1 μm to 0.3 μm .
5. The silver-coated copper flake powder according to any one of claims 1 to 4, having a tap density of from 0.5 g/cm^3 to 2.5 g/cm^3 .
6. The silver-coated copper flake powder according to any one of claims 1 to 5, having a silver content of from 5 mass% to 20 mass%.
7. The silver-coated copper flake powder according to any one of claims 1 to 6, wherein the silver-coated copper flake particles has a circularity of from 0.60 to 0.95.
8. The silver-coated copper flake powder according to any one of claims 1 to 7, having a brightness L^* of from 70 to 86.
9. The silver-coated copper flake powder according to any one of claims 1 to 8, having the 90th percentile particle diameter D_{90} of from 15 μm to 35 μm in the volume-weighted particle size distribution thereof as measured by the laser diffraction scattering method.
10. The silver-coated copper flake powder according to any one of claims 1 to 9, having the 10th percentile particle diameter D_{10} of from 3 μm to 8 μm in the volume-weighted particle size distribution thereof as measured by the laser diffraction scattering method.
11. The silver-coated copper flake powder according to claim 10, having a dispersity, D_{90}/D_{10} , of from 3.0 to 5.3.

12. The silver-coated copper flake powder according to any one of claims 1 to 11, having the 50th percentile particle diameter D_{50} of from 7 μm to 17 μm in the volume-weighted particle size distribution thereof as measured by the laser diffraction scattering method.

13. A method for manufacturing a silver-coated copper flake powder, comprising:

the step of treating a dispersion containing a copper base powder and a first complexing agent in a stirred media mill, thereby deforming copper base particles constituting the copper base powder into flakes; and
the step of treating the copper base powder containing the copper base particles deformed into flakes, with an aqueous solution containing silver ions and a second complexing agent, thereby precipitating silver on a surface of the copper base particles.

14. The method according to claim 13, wherein the first complexing agent and the second complexing agent are of a same type or different types.

15. The method according to claim 14, wherein the first complexing agent and the second complexing agent are both ethylenediaminetetraacetate.

16. The method according to any one of claims 13 to 15, wherein the copper base powder is an electrolytic copper powder obtained by electrolyzing an electrolyte containing copper ions.

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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2021/027964

A. CLASSIFICATION OF SUBJECT MATTER

Int. Cl. B22F1/02 (2006.01)i, B22F9/04 (2006.01)i, C25C5/02 (2006.01)i, H01B5/00 (2006.01)i, C23C18/31 (2006.01)i, C23C18/42 (2006.01)i, B22F1/00 (2006.01)i
 FI: B22F1/00 L, B22F1/02 A, C25C5/02, H01B5/00 C, B22F9/04 C, C23C18/42, C23C18/31 A

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

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

Int. Cl. B22F1/00, B22F1/02, B22F9/04, C25C5/02, H01B5/00, C23C18/31, C23C18/42

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

Published examined utility model applications of Japan 1922-1996
 Published unexamined utility model applications of Japan 1971-2021
 Registered utility model specifications of Japan 1996-2021
 Published registered utility model applications of Japan 1994-2021

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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Y	JP 2008-533307 A (NANO-DYNAMICS INC.) 21 August 2008 (2008-08-21), claims, paragraphs [0002], [0020]-[0022]	1-16
Y	JP 2014-116315 A (APPLIED NANOTECH HOLDINGS INC.) 26 June 2014 (2014-06-26), claim 16, paragraph [0126]	1-12, 15-16
X	JP 2010-275638 A (DOWA HOLDINGS CO., LTD.) 09 December 2010 (2010-12-09), claims, paragraphs [0039]-[0053], fig. 1	1, 3, 5-6, 8, 10-11

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

☒ See patent family annex.

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"P" document published prior to the international filing date but later than the priority date claimed

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INTERNATIONAL SEARCH REPORT

International application No. PCT/JP2021/027964
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C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	WO 2007/040195 A1 (MITSUI MINING & SMELTING CO., LTD.) 12 April 2007 (2007-04-12), claims, paragraphs [0053]-[0101]	2, 5-6, 9, 12

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INTERNATIONAL SEARCH REPORT
Information on patent family members

International application No.
PCT/JP2021/027964

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JP 2008-533307 A	21.08.2008	US 2006-0207385 A1 claims, paragraphs [0002], [0026]-[0028]	
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JP 2010-275638 A	09.12.2010	(Family: none)	
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REFERENCES CITED IN THE DESCRIPTION

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- JP 2016035098 A [0004]