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(54) **HIGHLY CRYSTALLINE SILVER POWDER AND PROCESS FOR PRODUCTION OF THE SAME**

(57) Object of the present invention is to provide a production method of a highly crystalline silver powder containing powder particles in fine particle region and having a good particle size distribution as well as the highly crystalline silver powder obtained by the production method. In order to achieve the object, the present invention adopts a production method **characterized in that** the method comprises preparation of a first aqueous solution in which gelatin, silver nitrate and nitric acid are dissolved in water, preparation of a second aqueous so-

lution in which L-sorbic acid and/or ascorbic acid and a water-soluble organic acid are dissolved, adding of the second aqueous solution slowly to mix with the first aqueous solution, stirring of the mixture to grow the silver particles after finishing the mixing, keeping of the mixture still to settle the silver particles, discarding of the supernatant, filtration and rinsing to obtain the highly crystalline silver powder.

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Description

Technical Field

5 **[0001]** The present invention relates to highly crystalline silver powder among the silver powders and production method of the highly crystalline silver powder.

Background Art.

10 **[0002]** Conventionally, highly crystalline silver powder (which has a large crystal diameter) has been widely used for processing into silver ink and silver paste for the reason that it is excellent in thermal shrinkage resistance at the time of sintering. For example, it has been used in wiring circuit of printed wiring board, via hole filling, adhesive for mounting devices and the similar applications in which a silver powder is mixed and cured with various kinds of resin components as well as applications in which a silver powder is sintered at relatively high temperatures such as circuit formation by
15 co-sintering with a ceramic substrate. Silver powder excellent in thermal shrinkage resistance at the time of sintering has been demanded from the point of view for improving accuracy of shape as a conductor particularly in silver powder used for silver ink and silver paste used for wiring and electrodes in circuits.

[0003] The crystallinity of silver powder is greatly affected by the production method. For example, as a method for producing silver powder, atomize process as disclosed in Patent Document 1 (Japanese Patent Laid-Open No. 2003-286502) can be used. However, even though silver powder having high crystallinity may be obtained by the atomize process, it is difficult to obtain silver powder consisting of fine particles with a sharp particle size distribution. Although it can be surely supposed that silver powder as a product having a sharp particle size distribution may be obtained by performing classification repeatedly, it is not preferable at all from the point of view of production cost. Therefore, obtaining silver powder by a wet production process described below has been examined.

25 **[0004]** For example, Patent Document 2 (Japanese Patent Publication No. 57-21001) discloses a method to deposit fine silver powder by adding a fatty acid to an aqueous mixture solution of a silver nitrate and formalin in an amount of 0.1 wt% to 5.0 wt% against to amount of silver to be deposited while stirring followed by adding an alkaline solution into the mixture solution. Patent Document 2 also discloses the production method which gives fine silver powder having an average particle diameter of 0.8 μm to 0.9 μm .

30 **[0005]** In addition, Patent Document 3 (Japanese Patent Laid-Open No. 04-323310) discloses a method for forming fine spherical particles by dissolving a metal, an alloy or a metal salt in an aqueous solvent, followed by adjusting pH by adding a base chemical thereto and adding a reducing agent to this to deposit fine metal powder. In which, the temperature of the solution is adjusted to a range of 10°C to 30°C to obtain spherical fine powder. When the temperature is adjusted to a range of 50°C or more, fine polyhedron-like metal powder can be obtained. In addition, the particle size
35 distribution of the obtained metal powder is approximately from 0.3 μm to 2.0 μm by the production method.

[0006] Since the deposition of crystals in the silver powders obtained by the production methods disclosed in above-mentioned Patent Document 2 and Patent Document 3 are not controlled, thermal shrinkage when sintering process was performed was significant. Therefore, in order to solve such problem, Patent Document 4 (Japanese Patent Laid-Open No. 2000-1706) discloses a method for producing the highly crystalline silver powder wherein UV is irradiated at
40 the time of the reaction when an aqueous solution of silver nitrate and a solution prepared by dissolving acrylic acid monomer in an aqueous solution of L-ascorbic acid are mixed and react simultaneously. The highly crystalline silver powder obtained by the method consists of high crystals single crystals and quasi-crystals whose crystal diameter is 2 μm to 4 μm . In addition, the Patent Document 4 discloses that if the crystal diameter is not more than 2 μm , the shrinkage factor at the time of sintering is large and if the crystal diameter exceeds 4 μm , irregularity of the conductor surface is large to result problems such as increase in losses as an electric circuit. The highly crystalline silver particle as referred
45 to here indicates those having a crystal diameter of 400 Å or more calculated from half-value width of (1.1.1) peak by X-ray diffraction method.

[0007] Further, Patent Document 5 (Japanese Patent Laid-Open No. 2003-49202) discloses silver particles having a crystal diameter of 400 Å to 600 Å, tap density of 5 g/cm³ or more and specific surface area of 0.15 m²/g or less. And
50 it is clearly described that the silver particle is obtained by a production method characterized by reacting an alkaline aqueous solution (ammonium hydroxide aqueous solution + one or more kind selected from a group consisting of sodium hydroxide and potassium hydroxide) containing a silver ion and a hydrogen peroxide aqueous solution (added with one or more kind selected from a group consisting of fatty acids, fatty acid salts and derivatives thereof as required). And it is clearly described that the range of the crystal diameter of silver particles obtained is from 400 Å to 600 Å and, if it is
55 less than 400 Å, crystallinity is low for silver particles for high temperature sintering conductive paste, and if it exceeds 600 Å, shape of the silver particles may show deviation. Also, Patent Document 5 discloses that tap density of the silver particles should be 5 g/cm³ or more and specific surface area of the silver particles should be 0.15 m²/g or less. But these are not sufficient as properties to identify the powder because there is no description about particle diameter even

though the both conditions should be inherently based on relations with particle diameter.

[0008]

[Patent Document 1] Japanese Patent Laid-Open No. 2003-286502

[Patent Document 2] Japanese Patent Publication No. 57-21001

[Patent Document 3] Japanese Patent Laid-Open No. 04-323310

[Patent Document 4] Japanese Patent Laid-Open No. 2000-1706

[Patent Document 5] Japanese Patent Laid-Open No. 2003-49202

Disclosure of the Invention

[0009] L ascorbic acid, which is used as a reducing agent in the production method disclosed in above Patent Document 4 relating to high crystalline silver powder, is expensive and may result increasing of the product price. As for the highly crystalline silver particle obtained by substantially using ascorbic acid as a reducing agent and irradiating ultraviolet in the reductive reaction, particle diameter and crystal diameter has an approximately proportional relationship. And products having constantly stable quality can be obtained when large powder particles of 2 μm to 4 μm are aimed. However, when fine silver powder particles having a particle diameter less than 2 μm with a crystal diameter of more than 400 Å are aimed, lack of process stability of the production method may result wide variation in the crystal diameter. Further, it has been confirmed in many case that the fine particles cannot satisfy thermal shrinkage resistance because shrinkage factor after sintering of the fine silver powder particles less than 2 μm is too large.

[0010] In addition, the solution used in the production method disclosed in Patent Document 5 consists of ammonia aqueous solution and ammonium nitrate. They are strongly odorous substances, and therefore, it may pollute the working atmosphere as well as causing a problem of accelerated damage on the apparatuses made of copper applied in the facilities. Besides, the method uses a hydrogen peroxide aqueous solution whose ability tends to change largely and lacks in stability of the quality of the solution. Therefore, the average particle diameter of the obtained silver powder deviates significantly and controlling of the particle size and particle size distribution is difficult.

[0011] As described above, the highly crystalline silver powder consisting of fine particles has been demanded but there has not been the highly crystalline silver powder which sufficiently satisfies market needs.

[0012] Accordingly, the present inventors have conducted intensive studies to solve the problems, and consequently have found that the silver powder obtained with the production method described below has high crystallinity with the fine particle level of which conventional silver powder has never achieved.

[0013] Production method of the highly crystalline silver powder: The production method of the highly crystalline silver powder of the present invention is characterized by comprising followings. Preparation of a first aqueous solution in which gelatin, silver nitrate and nitric acid are dissolved in water. Preparation of a second aqueous solution in which L-sorbic acid and a water-soluble organic acid are dissolved. Adding of the second aqueous solution slowly to mix with the first aqueous solution with stirring of the mixture to make the particles to grow to form silver particles after the addition is completed. Keeping of the mixture still to settle the silver particles. Discarding of the supernatant. Filtration and rinsing. Then the highly crystalline silver powder is obtained.

[0014] In the production method of the highly crystalline silver powder of the present invention, it is preferable that gelatin concentration in the first aqueous solution is 2g/l to 10g/l.

[0015] In the production method of the highly crystalline silver powder of the present invention, it is preferable that the silver nitrate concentration in the first aqueous solution is 50 g/l to 150 g/l as silver.

[0016] In the production method of the highly crystalline silver powder of the present invention, it is preferable that nitric acid is added to arrange the free nitric acid concentration of 40 g/l to 120 g/l in the first aqueous solution by adjusting the nitric acid aqueous solution.

[0017] In the production method of the highly crystalline silver powder of the present invention, it is preferable that the L-sorbic acid concentration in the second aqueous solution is 45 g/l to 120 g/l.

[0018] In the production method of the highly crystalline silver powder of the present invention, it is preferable that the water-soluble organic acid concentration in the second aqueous solution is 1 g/l to 50 g/l.

[0019] In the production method of the highly crystalline silver powder of the present invention, it is preferable for the water-soluble organic acid which is one or combination of two or more kinds selected from DL-malic acid, citric acid, formic acid, valeric acid, isovaleric acid, succinic acid, propionic acid, lactic acid and adipic acid.

[0020] Highly crystalline silver powder: The highly crystalline silver powder of the present invention is the silver powder obtained through reductive deposition by adding L-sorbic acid and/or ascorbic acid as a reducing agent and a water-soluble organic acid to a silver ion containing solution.

[0021] The highly crystalline silver powder is characterized in that the powder has a primary particle diameter of 0.07 μm to 4.5 μm and a crystal diameter of 200 Å or more.

[0022] It is also preferable that the highly crystalline silver powder shows powder characteristics as followings. Volume

accumulated average particle diameter D_{50} of 0.1 μm to 5.0 μm when measured by laser diffraction scattering-type particle size distribution measurement method and particle size distribution index $(D_{90} - D_{10})/D_{50}$ of not more than 1.5.

[0023] Furthermore, the highly crystalline silver powder of the present invention has the volume accumulated maximum particle diameter D_{max} measured by laser diffraction scattering-type particle size distribution measurement method of 16.0 μm or less, even usually contains coarse particles in a certain ratio.

[0024] In addition, the specific surface area of the highly crystalline silver powder of the present invention is preferably 0.2 m^2/g or more.

[0025] The production method of the highly crystalline silver powder of the present invention is suitable for the production of the highly crystalline silver powder whose particles have fine diameter to large diameter by using a water-soluble organic acid together with a reducing agent. In particular, the process is hard to be affected by process changes such as temperature variation, concentration variation at the time of the reductive reaction and the process enables production of the highly crystalline silver powder at a high yield.

[0026] The highly crystalline silver powder shows powder characteristics as followings. Volume accumulated average particle diameter D_{50} of 0.1 μm to 5.0 μm when measured by laser diffraction scattering-type particle size distribution measurement method and particle size distribution index $(D_{90} - D_{10})/D_{50}$ of not more than 1.5. As is apparent from the powder characteristics, the powder has a sharp particle size distribution at a level which has not been conventionally achieved in the particle diameter range (2 μm to 5 μm) of the conventional particles. And the powder has a stably large crystal diameter and a sharp particle size distribution even if it is a product having a particle diameter less than 2 μm . Therefore, conductor layers formed by a silver paste produced by using the highly crystalline silver powder of the present invention are excellent in thermal shrinkage resistance and have a smoother surface roughness.

Best Mode for Carrying Out the Invention

[0027] Best modes for carrying out the inventions of the highly crystalline silver powder of the present invention and the production method thereof are described below.

[0028] Production method of the highly crystalline silver powder: The production method of the highly crystalline silver powder of the present invention is characterized by comprising followings. Preparation of a first aqueous solution in which gelatin, silver nitrate and nitric acid are dissolved in water, a second aqueous solution in which L-sorbic acid and a water-soluble organic acid are dissolved. Adding of the second aqueous solution slowly to mix with the first aqueous solution with stirring of the mixture to make the particles to grow to form silver particles after the addition is completed. Then keep the mixture still to settle the silver particles, discarding the supernatant, followed by filtration with rinsing. Then the highly crystalline silver powder is obtained.

[0029] The first aqueous solution is described first. The first aqueous solution is a silver salt containing solution in which gelatin, silver nitrate and nitric acid are dissolved in water. The term gelatin herein is used as a concept which includes glue inferior to gelatin in purification degree. The gelatin is used to control the reduction rate (reaction rate) in the reductive deposition of the highly crystalline silver powder. Gelatin also performs as a steric hindrance agent to restrain aggregation of the reductively deposited particles and restrains cohesion between the particles which have been reductively deposited. As a result, the particle size distribution of the obtained the highly crystalline silver powder is made sharp, which is preferable. And it is preferable that the gelatin concentration in the above first aqueous solution is 2 g/l to 10 g/l. When the gelatin concentration is less than 2 g/l, the rate of the reduction reaction when the first aqueous solution reacts with the second aqueous solution is too fast to make the crystal diameter of the deposited silver particles grow large and the cohesion between particles becomes remarkable. Accordingly, silver powder having a sharp particle size distribution cannot be obtained. On the other hand, when the gelatin concentration exceeds 10 g/l, the rate of the reduction reaction becomes too slow not to satisfy industrial productivity and the variation in the crystal diameter becomes large.

[0030] And it is preferable that the silver nitrate concentration in the above first aqueous solution is 50 g/l to 150 g/l as silver. When the silver nitrate concentration (as silver) is less than 50 g/l, the amount of the reductively deposited silver is small and the particle diameter of the deposited silver is too small resulting small crystal diameter. On the other hand, when the silver nitrate concentration (as silver) exceeds 150 g/l, judging from balance with a reducing agent, silver ions not reduced remain leading to waste of resources. Also, reductive reaction sites increase too much and the aggregation of the deposited particles is remarkable and the yield of the highly crystalline silver powder having a volume accumulated average particle diameter D_{50} of 0.1 μm or more, which is excellent in particle dispersibility, decreases.

[0031] Furthermore, it is preferable to adjust the free nitric acid concentration in the first aqueous solution to be within 40 g/l to 120 g/l by adding a nitric acid aqueous solution. The free nitric acid concentration is a condition to be managed to prevent the silver ions from formation of a sludge in the first aqueous solution, which is a silver salt containing solution, and to efficiently perform the reductive deposition of silver particles with a reducing agent.

[0032] And it is preferable that the solution temperature of the first aqueous solution is 45 to 55°C. when the solution temperature is less than 45°C, it is difficult to mix gelatin, silver nitrate and nitric acid in a short time, and the rate of the

reduction reaction by adding the second aqueous solution (described later in the present description) becomes too slow and thus making it difficult to produce the highly crystalline silver powder having an appropriate particle size distribution. On the other hand, when the solution temperature exceeds 55°C, decomposition of gelatin is promoted to make solution life shorter and silver powder having an appropriate crystal diameter cannot be obtained.

[0033] Next, the second aqueous solution is described. The second aqueous solution is an aqueous solution containing a reducing agent. The term [L-sorbic acid and/or ascorbic acid] which are reducing agents means that either one of L-sorbic acid or ascorbic acid may be used independently as a reducing agent, or L-sorbic acid and ascorbic acid may be used in combination. Therefore, the concentration of L-sorbic acid and/or ascorbic acid described below is a concept including the case where L-sorbic acid and ascorbic acid are used together. When they are used together, weight ratio [L-sorbic acid]:[ascorbic acid] can be 0.1:9.9 to 9.9:0.1, preferably [L-sorbic acid]:[ascorbic acid]=0.5:9.9 to 9.9:0.5 considering more stable process stability and further preferably [L-sorbic acid]:[ascorbic acid]=1:9 to 9:1 considering further stable process stability.

[0034] It is preferable that the concentration of L-sorbic acid and/or ascorbic acid in the above second aqueous solution is 45 g/l to 120 g/l. The reducing agent concentration is decided in relation with the silver content of the first aqueous solution. Both the concentration of silver in the first aqueous solution and the concentration of the reducing agent in the second aqueous solution in the appropriate range makes reductive deposition of silver powder consisting of fine particles which has a particle diameter of 2 μm or less possible. That is, when the concentration of L-sorbic acid and/or ascorbic acid in the second aqueous solution is less than 45 g/l, the reduction of silver ions in the first aqueous solution may be insufficient to result waste of resources, and the particle size distribution of the obtained silver powder may be broad and the highly crystalline silver powder having a good crystal diameter cannot be obtained. On the other hand, when the concentration of L-sorbic acid and/or ascorbic acid in the second aqueous solution exceeds 120 g/l, the amount of the reducing agent exceeds the amount necessary for the reduction of silver ions in the first aqueous solution to result waste of the reducing agent, and the reduction reaction proceeds so fast to make the crystal diameter small.

[0035] In addition, the second aqueous solution has a major characteristic in the point to use a water-soluble organic acid as well as the reducing agent. The water-soluble organic acid performs to increase the crystal diameter of the reductively deposited silver crystals and enables to increase the crystal diameter even if the fine particle silver powder has a particle diameter of less than 2 μm. Further, the water-soluble organic acid improves the particle size distribution of the reductively deposited silver powder to result sharp particle size distribution excellent in particle dispersibility. The water-soluble organic acid as referred to herein is one or combination of two or more kinds selected from DL-malic acid, citric acid, formic acid, valeric acid, isovaleric acid, succinic acid, propionic acid, lactic acid and adipic acid.

[0036] It is preferable that the concentration of the water-soluble organic acid is 1 g/l to 50 g/l. when the concentration of the water-soluble organic acid in the second aqueous solution is less than 1 g/l, the effect to increase the crystal diameter of the reductively deposited silver crystals cannot be obtained and purpose to use a water-soluble organic acid cannot be achieved. On the other hand, when the concentration of the water-soluble organic acid exceeds 50 g/l, the effect to increase the crystal diameter is saturated and rather a tendency to deteriorate the particle size distribution of the obtained silver powder may arise.

[0037] The second aqueous solution is slowly added to the first aqueous solution over 10 to 60 minutes. When the first aqueous solution and the second aqueous solution are mixed all at once, the particle size distribution of the obtained silver powder might be broad. Also, a product having a sharp particle size distribution cannot be obtained, and formation of coarse particles may be remarkable. Therefore, when the mixing time is less than 10 minutes, the situation is similar to that by the addition all at once, the particle size distribution of the obtained silver powder is broad, and formation of coarse particles increases. On the other hand, when the mixing time exceeds 60 minutes, it may only down productivity, and no improvement in the particle size distribution can be expected even if the addition is performed slowly more and more.

[0038] As for the amount of the second aqueous solution to be added to the first aqueous solution, the basic amount of a reducing agent to be added corresponds to the reaction equivalent to the reduction against to the amount of silver contained in the first aqueous solution and it is sufficient at the minimum. At this time, adding of an excess amount of a reducing agent corresponds to the reaction equivalent to the reduction against to the amount of silver contained in the first aqueous solution causes no problem at all. The temperature at the time of the reductive reaction is not limited in particular, but it is preferable to adopt a range from room temperature to 50°C because it hardly causes significant change in the temperature of the first aqueous solution. When a temperature more than 50°C is adopted, evaporation of water becomes remarkable and tends to cause change in the composition while mixing of the first aqueous solution and the second aqueous solution.

[0039] After finishing the addition of the second aqueous solution to the first aqueous solution, the mixture is kept being stirred for 3 to 5 minutes to grow particles to form silver particles. When the stirring time is less than 3 minutes, the reductive reaction may not be completely finished, so it is not preferable. On the other hand, when the stirring time is more than 5 minutes, the reductive reaction has already been completely finished and such a stirring is meaningless from a practical point of view.

[0040] When it is assumed that the addition of the second aqueous solution to the first aqueous solution is finished and reductive deposition of silver has not occurred, the composition balance of the first aqueous solution and the second aqueous solution in the reduction reaction at this stage is gelatin concentration of 2 g/l to 10 g/l, silver nitrate concentration (as silver) of 50 g/l to 150 g/l, free nitric acid concentration of 40 g/l to 120 g/l, concentration of reducing agent(s), L-sorbic acid and/or ascorbic acid, of 45 g/l to 120 g/l, water-soluble organic acid concentration of 1 g/l to 50 g/l.

[0041] After finishing the above reducing procedure, the mixture is kept still to settle the silver particles. Then the supernatant liquid is discarded, and filtration and rinsing are performed and thus the highly crystalline silver powder can be obtained.

[0042] Highly crystalline silver powder: The highly crystalline silver powder of the present invention is the silver powder obtained by adding L-sorbic acid and/or ascorbic acid as a reducing agent and a water-soluble organic acid to the silver ion containing solution to cause reductive deposition.

[0043] The powder is characterized in that the primary particle diameter is 0.07 μm to 4.5 μm and the crystal diameter is 200 Å or more. The highly crystalline silver powder of the present invention can be obtained from a silver ion containing solution by adding L-sorbic acid and/or ascorbic acid as a reducing agent with a water-soluble organic acid. Use of a water-soluble organic acid in combination in such a way enables to obtain the highly crystalline silver powder having a large crystal diameter. Also, a good crystal diameter and a sharp particle size distribution even when the primary particle diameter is in a fine particle region as low as less than 2.0 μm . Thus, high crystallinity with a crystal diameter of 200 Å or more in a wide particle diameter range of 0.07 μm to 4.5 μm can be achieved. Here, the primary particle diameter is the value determined as an average of the particle diameters observed with a scanning electron microscope on the high crystalline silver powder and directly measuring the particle diameters for 100 particles exist in the scope. In the range of primary particle diameter, particles which can be referred to as fine particles are in the range of 0.07 μm to less than 2.0 μm , preferably 0.07 μm to 1.5 μm , more preferably 0.07 μm to 1.0 μm . Generally, the particle diameter and the crystal diameter have a proportional relationship but crystal diameter more than 400 Å can be obtained when the primary particle diameter exceeds 0.3 μm . Further, in the case of the highly crystalline silver powder of the present invention, crystal diameter of 200 Å to 300 Å can be stably obtained even when the particle diameter is in the range of 0.07 μm to 0.3 μm . As described above, a fine silver powder in such a fine particle size range having a crystal diameter of 200 Å or more has not been present conventionally. By the way, RINT2000 X-ray diffraction device manufactured by Rigaku Corporation was used for the measurement of the crystal diameter mentioned in the present invention and the measurement was performed by Wilson method (measuring method of crystal diameter by X-ray diffraction).

[0044] Furthermore, when high crystalline silver powder having the above powder characteristics is measured by a laser diffraction scattering-type particle size distribution measurement method, it shows powder characteristics as followings. Volume accumulated average particle diameter D_{50} of 0.1 μm to 5.0 μm , and particle size distribution index $(D_{90} - D_{10})/D_{50}$ of not more than 1.5.

[0045] That is, the accumulated average particle diameter D_{50} measured by a laser diffraction scattering-type particle size distribution measurement method corresponding to the primary particle diameter range of from 0.07 μm to 4.5 μm is measured as a value in the range approximately from 0.1 μm to 5.0 μm . As for products having a primary particle diameter not less than 0.07 μm and less than 2.0 μm , which are classified as fine particles by the range of the primary particle diameter, the volume accumulated average particle diameter D_{50} mostly falls within the range of 0.1 μm to 1.6 μm . As for products having a primary particle diameter of 0.07 μm to 1.5 μm , the volume accumulated average particle diameter D_{50} mostly falls within the range of 0.1 μm to 1.2 μm . As for products having a primary particle diameter of 0.07 μm to 1.0 μm , the volume accumulated average particle diameter D_{50} mostly falls within the range of 0.1 μm to 0.7 μm .

[0046] Furthermore, the highly crystalline silver powder of the present invention has dispersibility $(D_{90} - D_{10})/D_{50}$ value of not more than 1.5 which is an index representing the particle dispersibility. Here, $(D_{90} - D_{10})/D_{50}$ is a value obtained by dividing the difference between D_{90} , volume accumulated particle diameter at 90% and D_{10} , volume accumulated particle diameter at 10%, by accumulated average particle diameter D_{50} . That is, it is a value showing how many times is the particle size distribution range against to the volume accumulated average particle diameter D_{50} as a basic property. So, the value approaches to 1 when the frequency curve of the particle size distribution becomes sharp. Therefore, a state with the value $(D_{90} - D_{10})/D_{50}$ of less than 1.5 means that the particle size distribution is considerably sharp, and it may be said that the particle diameter of most particles is equal to or less than 1.5 times of the volume accumulated average particle diameter D_{50} . On the other hand, the silver powder having a crystal diameter more than 400 Å can be also obtained in conventional cases where a reducing agent such as ascorbic acid alone is used when attention is paid only to crystal diameter. However, when the primary particle diameter is less than 1.6 μm (about 2.0 μm as volume accumulated average particle diameter D_{50}), the particle size distribution of the obtained silver powder may so broad to have a wide particle size distribution with a value of $(D_{90} - D_{10})/D_{50}$ exceeding 2.0. When a conductive film is formed with a paste of silver powder having such a broad particle size distribution, the surface of the conductive film may become irregular, so it is not preferable.

[0047] Furthermore, the highly crystalline silver powder obtained from silver ion containing solution by using L-sorbic acid and/or ascorbic acid as a reducing agent with a water-soluble organic acid usually contains coarse particles in a

certain ratio, wherein the volume accumulated maximum particle diameter $D_{\max}$ is 16.0 μm or less. The maximum particle diameter can be recognized as a coarse particle in a certain meaning, and may be eliminated from the product by classification as required.

[0048] The specific surface area of the highly crystalline silver powder of the present invention obtained by the above-mentioned production method is in the range of 0.2 m^2/g or more. Judging from the results of the studies by the present inventors, it is in the range of 0.2 m^2/g to 3.5 m^2/g . The value of the specific surface area decreases as the surface of the particles becomes smooth and the viscosity of a paste or ink made of the particles can be reduced.

[Example 1]

[0049] Preparation of the first aqueous solution: The solution was prepared by mixing 1.0 g of gelatin, 50 g of silver nitrate and 26.4 g of nitric acid to 250 g of pure water and elevating the temperature of the mixture to 50°C with stirring to finish dissolving.

[0050] Preparation of the second aqueous solution: The solution was prepared as a solution in which 26.4 g of L-sorbic acid as a reducing agent and 4.2 g of DL-malic acid as a water-soluble organic acid were dissolved in 250 g of pure water.

[0051] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the first aqueous solution at a solution temperature of 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0052] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 1 along with those of the other Examples and Comparative Examples.

[Example 2]

[0053] Preparation of the first aqueous solution: Same as in Example 1 and description is omitted to avoid redundancy.

[0054] Preparation of the second aqueous solution: The solution was prepared as a solution in which 26.4 g of L-sorbic acid as a reducing agent and 3.6 g of citric acid as a water-soluble organic acid were dissolved in 250 g of pure water.

[0055] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0056] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 1 along with those of the other Examples and Comparative Examples.

[Example 3]

[0057] Preparation of the first aqueous solution: The solution was prepared by mixing 3.3 g of gelatin, 55 g of silver nitrate and 27 g of nitric acid to 550 g of pure water and elevating the temperature of the mixture to 50°C with stirring to finish dissolving.

[0058] Preparation of the second aqueous solution: The solution was prepared as a solution in which 28.1 g of L-sorbic acid as a reducing agent and 4.47 g of DL-malic acid as a water-soluble organic acid were dissolved in 250 g of pure water.

[0059] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the above first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0060] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 2 along with those of the other Examples and Comparative Examples.

[Example 4]

[0061] Preparation of the first aqueous solution: Same as in Example 3 and description is omitted to avoid redundancy.

[0062] Preparation of the second aqueous solution: The solution was prepared as a solution in which 28.1 g of L-sorbic acid as a reducing agent and 3.83 g of citric acid as a water-soluble organic acid were dissolved in 550 g of pure

water.

[0063] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the above first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0064] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 2 along with those of the other Examples and Comparative Examples.

[Example 5]

[0065] Preparation of the first aqueous solution: The solution was prepared by adding 4.0 g of gelatin, 66 g of silver nitrate and 32.4 g of nitric acid to 700 g of pure water and elevating the temperature of the mixture to 50°C with stirring to finish dissolving.

[0066] Preparation of the second aqueous solution: The solution was prepared as a solution in which 33.8 g of ascorbic acid as a reducing agent and 4.6 g of citric acid as a water-soluble organic acid were dissolved in 700 g of pure water.

[0067] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the above first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0068] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 3 along with those of the other Examples and Comparative Examples.

[Example 6]

[0069] Preparation of the first aqueous solution: Same as in Example 5 and description is omitted to avoid redundancy.

[0070] Preparation of the second aqueous solution: The solution was prepared as a solution in which 33.8 g of ascorbic acid as a reducing agent and 6.0 g of DL-malic acid as a water-soluble organic acid were dissolved in 700 g of pure water.

[0071] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the above first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0072] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 3 along with those of the other Examples and Comparative Examples.

[Example 7]

[0073] Preparation of the first aqueous solution: Same as in Example 5 and description is omitted to avoid redundancy.

[0074] Preparation of the second aqueous solution: The solution was prepared as a solution in which 16.9 g of ascorbic acid and 16.9 g of L-sorbic acid as reducing agents and 6.0 g of DL-malic acid as a water-soluble organic acid were dissolved in 720 g of pure water.

[0075] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added to the above first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0076] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 4 along with those of the other Examples and Comparative Examples.

[Example 8]

[0077] Preparation of the first aqueous solution: Same as in Example 5 and description is omitted to avoid redundancy.

[0078] Preparation of the second aqueous solution: The solution was prepared as a solution in which 16.9 g of ascorbic acid and 16.9 g of L-sorbic acid as reducing agents and 4.6 g of citric acid as a water-soluble organic acid were dissolved in 720 g of pure water.

[0079] Reductive deposition of the highly crystalline silver powder: The second aqueous solution was slowly added

to the above first aqueous solution at 50°C for 30 minutes. After finishing addition of the second aqueous solution to mix with the first aqueous solution, stirring was kept for five minutes to grow deposited silver particles.

[0080] Collection by filtration of the highly crystalline silver powder: After finishing the five-minute stirring, the mixture was kept still to settle generated silver powder, supernatant liquid was discarded and filtration and rinsing were performed by popular methods, and the highly crystalline silver powder was obtained. The powder characteristics of the highly crystalline silver powder are shown in Table 4 along with those of the other Examples and Comparative Examples.

[Comparative Examples]

[Comparative Example 1]

[0081] In this Comparative Example, the silver powder was produced in the condition that the water-soluble organic acid (DL-malic acid) in the second aqueous solution of Example 1 was omitted and the other conditions were same as in Example 1. The powder characteristics of the silver powder are shown in Table 1 along with those of the other Examples and Comparative Examples.

[Comparative Example 2]

[0082] In this Comparative Example, the silver powder was produced in the condition that the water-soluble organic acid (DL-malic acid) in Example 3 of the second aqueous solution was omitted and the other conditions were same as in Example 1. The powder characteristics of the silver powder are shown in Table 2 along with those of the other Examples and Comparative Examples.

[Comparative Example 3]

[0083] In this Comparative Example, the silver powder was produced in the condition that the water-soluble organic acid (citric acid) in Example 5 of the second aqueous solution was omitted and the other conditions were same as in Example 1. The powder characteristics of the silver powder are shown in Table 3 along with those of the other Examples and Comparative Examples.

[Comparative Example 4]

[0084] In this Comparative Example, the silver powder was produced in the condition that the water-soluble organic acid (DL-malic acid) in Example 7 of the second aqueous solution was omitted and the other conditions were same as in Example 1. The powder characteristics of the silver powder are shown in Table 4 along with those of the other Examples and Comparative Examples.

<Comparison between Examples and Comparative Examples>

Comparison between Examples 1 and 2 and Comparative Example 1:

[0085] Example 1 and Example 2 are different in that the water-soluble organic acid used with a reducing agent is DL-malic acid or citric acid, and Comparative Example 1 does not use the water-soluble organic acid used in Example 1. Therefore, all of these are shown in Table 1 for comparison.

[0086]

[Table 1]

Sample	Primary particle diameter	D ₁₀	D ₅₀	D ₉₀	D _{max}	SSA	Crystallite diameter	(D ₉₀ -D ₁₀)/D ₅₀
	μm					m ² /g	Å	
Example 1	3.96	2.83	4.05	6.98	13.1	0.29	525	1.02
Example 2	3.86	2.54	4.12	7.02	15.6	0.28	522	1.08
Comparative Example 1	3.33	2.38	4.02	8.46	18.5	0.26	546	1.51

[0087] In the Table 1, primary particle diameter, D_{10} , D_{50} , D_{90} , D_{max} by the laser diffraction scattering-type particle size distribution measurement method, specific surface area (SSA), crystal diameter and a value of $(D_{90} - D_{10})/D_{50}$ are shown. Firstly, when attention is paid to the primary particle diameter, it is understood that silver powder having a slightly small primary particle diameter was obtained in Comparative Example 1, in which no water-soluble organic acid was used, as compared with Example 1 and Example 2. In the comparison between Examples 1 and 2 and Comparative Example 1 on each value of D_{10} , D_{50} , D_{90} , D_{max} , specific surface area (SSA) and crystal diameter, it cannot be said that there are significant differences between the values. In contrast, the value of $(D_{90} - D_{10})/D_{50}$ are definitely smaller in Examples 1 and 2 than in Comparative Example 1. That is, the particle size distributions in Examples 1 and 2 have sharper particle size distributions as compared with the particle size distribution in Comparative Example 1. It means that the particle diameters in the Examples 1 and 2 exist in a narrower range than the particle diameters in the Comparative Example 1.

[0088] From examination on the results, the silver powder obtained in Comparative Example 1 tends to be smaller in primary particle diameter as compared with those of Examples 1 and 2, but aggregation of the reductively deposited silver particles is so remarkable that practical use thereof is difficult. In contrast, since the highly crystalline silver powders obtained by the production method in Examples 1 and 2 are hard to aggregate, they may form only a small amount of coarse particles to be a product with good balance and excellent in particle dispersibility.

Comparison between Examples 3 and 4 and Comparative Example 2:

[0089] Example 3 and Example 4 are different in that the water-soluble organic acid used with a reducing agent is DL-malic acid or citric acid, and Comparative Example 2 does not use the water-soluble organic acid used in Example 3, and therefore all of these are shown in Table 2 for comparison.

[0090]

[Table 2]

Sample	Primary Particle Diameter	D_{10}	D_{50}	D_{90}	D_{max}	SSA	Crystallite diameter	$(D_{90} - D_{10}) / D_{50}$
	μm					m^2 / g	$\text{\AA}$	
Example 3	0.89	0.62	1.02	1.88	3.6	0.85	438	1.24
Example 4	0.94	0.69	1.08	1.98	3.9	0.83	432	1.19
Comparative Example 2	0.74	0.45	1.16	2.84	5.5	0.86	438	2.06

[0091] In the Table 2, primary particle diameter, D_{10} , D_{50} , D_{90} , D_{max} by the laser diffraction scattering-type particle size distribution measurement method, specific surface area (SSA), crystal diameter and a value of $(D_{90} - D_{10})/D_{50}$ are shown. Firstly, when attention is paid to the primary particle diameter, it is understood that silver powder having a small primary particle diameter was obtained in Comparative Example 2, in which no water-soluble organic acid was used, as compared with Example 3 and Example 4. Here, respective values of D_{10} , D_{50} , D_{90} , D_{max} , specific surface area (SSA) and crystal diameter of Examples 3 and 4 and Comparative Example 2 are compared. Firstly, when attention is paid to the primary particle diameter and to D_{10} , the values in Example 3 and Example 4 are larger than in Comparative Example 2. When attention is paid to D_{50} , there is no significant difference between Examples 3 and 4 and Comparative Example 2. When attention is paid to D_{90} and D_{max} , the value in Example 3 and Example 4 are smaller than in Comparative Example 2. At this stage, it can be expected that the particle size distributions in Example 3 and Example 4 are better and sharper than that in Comparative Example 2. Next, it cannot be said that there is no significant difference in specific surface area (SSA) and crystal diameter. Meanwhile, the value of $(D_{90} - D_{10})/D_{50}$ are definitely smaller in Examples 3 and 4 than in Comparative Example 2. That is, the particle size distributions in Examples 3 and 4 have sharper particle size distributions as compared with the particle size distribution in Comparative Example 2. It means that the particle diameters in the Examples 3 and 4 exist in a narrower range than the particle diameters in the Comparative Example 2.

[0092] From examination on the results, the silver powder obtained in Comparative Example 2 tends to be smaller in primary particle diameter as compared with those of Examples 3 and 4, but aggregation of the reductively deposited silver particles is so remarkable that practical use thereof is difficult. In contrast, since the highly crystalline silver powders obtained by the production method in Examples 3 and 4 are hard to aggregate, they may form only a small amount of coarse particles to be a product with good balance and excellent in particle dispersibility.

Comparison between Examples 5 and 6 and Comparative Example 3:

[0093] Example 5 and Example 6 are different in that the water-soluble organic acid used with a reducing agent is DL-malic acid or citric acid, and Comparative Example 3 does not use the water-soluble organic acid used in Example 5, and therefore all of these are shown in Table 3 for comparison.

[0094]

[Table 3]

Sample	Primary particle diameter	D ₁₀	D ₅₀	D ₉₀	D _{max}	SSA	Crystallite diameter	(D ₉₀ -D ₁₀)/D ₅₀
	μm					m ² /g	Å	
Example 5	0.85	0.65	0.98	1.82	3.5	0.90	408	1.19
Example 6	0.84	0.62	0.96	1.74	3.5	0.89	405	1.16
Comparative Example 3	0.68	0.50	1.10	2.94	3.5	0.95	407	2.22

[0095] In the Table 3, primary particle diameter, D₁₀, D₅₀, D₉₀, D_{max} by the laser diffraction scattering-type particle size distribution measurement method, specific surface area (SSA), crystal diameter and a value of (D₉₀ - D₁₀)/D₅₀ are shown. Firstly, when attention is paid to the primary particle diameter, it is understood that silver powder having a small primary particle diameter was obtained in Comparative Example 3, in which no water-soluble organic acid is used, as compared with Example 5 and Example 6. Here, respective values of D₁₀, D₅₀, D₉₀, D_{max}, specific surface area (SSA) and crystal diameter of Examples 5 and 6 and Comparative Example 3 are compared. When attention is paid to D₁₀, the values in Example 5 and Example 6 are larger than in Comparative Example 3. When attention is paid to D₅₀, there is no significant difference between Examples 5 and 6 and Comparative Example 3. When attention is paid to D₉₀ and D_{max}, the values in Example 5 and Example 6 are smaller than in Comparative Example 3. At this stage, it can be expected that the particle size distributions in Example 5 and Example 6 are better and sharper than that in Comparative Example 3. Next, it cannot be said that there is no significant difference in specific surface area (SSA) and crystal diameter. Meanwhile, the value of (D₉₀ - D₁₀)/D₅₀ are definitely smaller in Examples 5 and 6 than in Comparative Example 3. That is, the particle size distributions in Examples 5 and 6 have sharper particle size distributions as compared with the particle size distribution in Comparative Example 3. It means that the particle diameters in the Examples 5 and 6 exist in a narrower range than the particle diameters in the Comparative Example 3.

[0096] From examination on the results, the silver powder obtained in Comparative Example 3 tends to be smaller in primary particle diameter as compared with those of Examples 5 and 6, but aggregation of the reductively deposited silver particles is so remarkable that practical use thereof is difficult. In contrast, since the highly crystalline silver powders obtained by the production method in Examples 5 and 6 are hard to aggregate, they may form only a small amount of coarse particles to be a product with good balance and excellent in particle dispersibility.

Comparison between Examples 7 and 8 and Comparative Example 4:

[0097] Example 7 and Example 8 are different in that the water-soluble organic acid used with a reducing agent is DL-malic acid or citric acid, and Comparative Example 4 does not use the water-soluble organic acid used in Example 7, and therefore all of these are shown in Table 4 for comparison.

[0098]

[Table 4]

Sample	Primary particle diameter	D ₁₀	D ₅₀	D ₉₀	D _{max}	SSA	Crystallite diameter	(D ₉₀ -D ₁₀)/D ₅₀
	μm					m ² /g	Å	
Example 7	0.82	0.58	0.94	1.68	2.3	0.99	401	1.17
Example 8	0.86	0.59	0.92	1.58	2.1	1.01	400	1.08
Comparative Example 4	0.65	0.53	1.09	3.33	5.5	0.99	403	2.57

[0099] In the Table 4, primary particle diameter, D_{10} , D_{50} , D_{90} , D_{max} by the laser diffraction scattering-type particle size distribution measurement method, specific surface area (SSA), crystal diameter and a value of $(D_{90} - D_{10})/D_{50}$ are shown. Firstly, when attention is paid to the primary particle diameter, it is understood that silver powder having a small primary particle diameter was obtained in Comparative Example 4, in which no water-soluble organic acid is used, as compared with Example 7 and Example 8. Here, respective values of D_{10} , D_{50} , D_{90} , D_{max} , specific surface area (SSA) and crystal diameter of Examples 7 and 8 and Comparative Example 4 are compared. As for D_{90} and D_{max} , the values are definitely larger in Comparative Example 4 than in Example 7 and Example 8 and it is considered that coarse particles are formed in a higher ratio. It cannot be said that there is no significant difference in the other values. Meanwhile, the value of $(D_{90} - D_{10})/D_{50}$ are definitely smaller in Examples 7 and 8 than in Comparative Example 4. That is, the particle size distributions in Examples 7 and 8 have sharper particle size distributions as compared with the particle size distribution in Comparative Example 4. It means that the particle diameters in the Examples 7 and 8 exist in a narrower range than the particle diameters in the Comparative Examples 4.

[0100] From examination on the results, the silver powder obtained in Comparative Example 4 tends to be smaller in primary particle diameter as compared with those of Examples 7 and 8, but aggregation of the reductively deposited silver particles is so remarkable that practical use thereof is difficult. In contrast, since the highly crystalline silver powders obtained by the production method in Examples 7 and 8 are hard to aggregate, they may form only a small amount of coarse particles to be a product with good balance and excellent in particle dispersibility.

Industrial Applicability

[0101] The highly crystalline silver powder described above is a product which is the highly crystalline and has a sharp particle size distribution in the whole range from fine particles to particles with large diameter as compared with conventional highly crystalline silver powder. Therefore, conductor films formed by a silver paste produced by using the highly crystalline silver powder of the present invention are excellent in thermal shrinkage resistance and have a smoother surface roughness. Therefore, quality of a conductor formed with the conductive paste can be improved.

[0102] In addition, the production method of the highly crystalline silver powder of the present invention comprises adding a solution which contains a reducing agent and a water-soluble organic acid to a solution which contains a silver salt to cause reductive deposition. The presence of the water-soluble organic acid enables production of the highly crystalline silver powder having high crystallinity with a sharp particle size distribution and provides a process suitable for industrial production process.

Claims

1. A production method of highly crystalline silver powder from a silver ion containing solution by using L-sorbic acid and/or ascorbic acid as a reducing agent, **characterized in that** the method comprises preparation of a first aqueous solution in which gelatin, silver nitrate and nitric acid are dissolved in water, preparation of a second aqueous solution in which L-sorbic acid and/or ascorbic acid and a water-soluble organic acid are dissolved, adding of the second aqueous solution slowly to mix with the first aqueous solution, stirring of the mixture to grow the silver particles after finishing the mixing, keeping of the mixture still to settle the silver particles, discarding of the supernatant, filtration and rinsing to obtain highly crystalline silver powder.
2. The production method of the highly crystalline silver powder according to claim 1, wherein the gelatin concentration in the first aqueous solution is 2 g/l to 10 g/l.
3. The production method of the highly crystalline silver powder according to claim 1 or claim 2, wherein the silver nitrate concentration in the first aqueous solution is 50 g/l to 150 g/l as silver.
4. The production method of the highly crystalline silver powder according to any one of claims 1 to 3, wherein the free nitric acid concentration in the first aqueous solution is adjusted to 40 g/l to 120 g/l by adding the nitric acid aqueous solution.
5. The production method of the highly crystalline silver powder according to any one of claims 1 to 4, wherein the concentration of L sorbic acid and/or ascorbic acid in the second aqueous solution is 45 g/l to 120 g/l.
6. The production method of the highly crystalline silver powder according to any one of claims 1 to 5, wherein the concentration of the water-soluble organic acid in the second aqueous solution is 1 g/l to 50 g/l.

7. The production method of the highly crystalline silver powder according to claim 6, wherein the water-soluble organic acid is one or combination of two or more kinds selected from DL-malic acid, citric acid, formic acid, valeric acid, isovaleric acid, succinic acid, propionic acid, lactic acid and adipic acid.

5 8. The highly crystalline silver powder **characterized by** obtained by a production method according to any one of claims 1 to 7.

9. The highly crystalline silver powder according to claim 8 **characterized in that** the powder has a primary particle diameter of 0.07 μm to 4.5 μm and a crystal diameter of 200 Å or more.

10 10. The highly crystalline silver powder according to claim 8 **characterized in that** the powder has a volume accumulated average particle diameter D_{50} measured by laser diffraction scattering-type particle size distribution measurement method of 0.1 μm to 5.0 μm and a particle size distribution index $(D_{90} - D_{10})/D_{50}$ of not more than 1.5.

15 11. The highly crystalline silver powder according to claim 8 **characterized in that** the powder has a volume accumulated maximum particle diameter D_{max} measured by laser diffraction scattering-type particle size distribution measurement method of 16.0 μm or less.

20 12. The highly crystalline silver powder according to claim 8 **characterized in that** the powder has a specific surface area of 0.2 m^2/g or more.

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INTERNATIONAL SEARCH REPORT

International application No.

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A. CLASSIFICATION OF SUBJECT MATTER

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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)

B22F9/24, B22F1/00

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

Jitsuyo Shinan Koho 1922-1996 Jitsuyo Shinan Toroku Koho 1996-2006

Kokai Jitsuyo Shinan Koho 1971-2006 Toroku Jitsuyo Shinan Koho 1994-2006

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

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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Y	JP 2005-105376 A (Sumitomo Osaka Cement Co., Ltd.), 21 April, 2005 (21.04.05), Par. No. [0011] (Family: none)	1-12
Y	JP 2000-129318 A (Dowa Mining Co., Ltd.), 09 May, 2000 (09.05.00), Par. No. [0010] (Family: none)	1-12

☒ Further documents are listed in the continuation of Box C.☐ See patent family annex.

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Date of the actual completion of the international search
04 September, 2006 (04.09.06)Date of mailing of the international search report
12 September, 2006 (12.09.06)Name and mailing address of the ISA/
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INTERNATIONAL SEARCH REPORT

International application No.

PCT/JP2006/313320

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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REFERENCES CITED IN THE DESCRIPTION

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