

Description

ELECTRICALLY CONDUCTIVE COMPOSITION, ELECTRICALLY CONDUCTIVE SINTERED PART, AND MEMBER HAVING ELECTRICALLY CONDUCTIVE SINTERED PART

Technical Field

[0001] The present invention relates to an electrically conductive composition, an electrically conductive sintered part, a member having a sintered part or a bonding part in which the electrically conductive composition is used, a method for bonding a member, and a method for producing an electrically conductive sintered part, and particularly relates to an electrically conductive composition to be applied to an electronic component, for example, an electronic component for vehicle mounting or for a communication device, and to an electronic component having a sintered part obtained by sintering the electrically conductive composition.

Background Art

[0002] In the field of electronics, as an adhesive for forming a bonding part in an electronic component, for example, a semiconductor element, and as an electrically conductive paste for forming a circuit of a circuit board, for example, an electrically conductive composition containing an organic resin and an electrically conductive filler such as a metal fine particle is used. Such an electrically conductive composition is applied to a member and then sintered or heat-cured to form a sintered part or a bonding part.

[0003] Regarding the metal fine particle used as the electrically conductive filler, it is known from Patent Literature 1 that the electrically conductive

property and the thermally conductive property in the electrically conductive composition after sintering are improved by using a combination of a micrometer-sized particle and a nanometer-sized particle.

[0004] It is disclosed in Patent Literatures 2 and 3 that a composition having an excellent thermal conductivity, low stress property, adhesive property, and reflow peeling resistance can be obtained by using a plate-like silver fine particle having a median particle diameter of 0.3 to 15 μm and a thickness of 10 to 200 nm in an electrically conductive thermosetting resin composition.

[0005] In Patent Literature 4, an electrically conductive composition for sintering comprising (A) a silver fine particle having a number average particle diameter of a primary particle of 40 nm to 400 nm, (B) a solvent, and (C) a thermoplastic resin particle having a maximum value of an endothermic peak in the range of 80°C to 170°C in a DSC chart obtained by measurement using a differential scanning calorimeter, wherein a number average particle diameter of primary particles of the (C) thermoplastic resin particle of 1 to 50 μm is disclosed. It is disclosed that in this electrically conductive composition, the thermoplastic resin particles in the electrically conductive composition are melted and deformed when the electrically conductive composition is sintered, and thereby it is possible to suppress the occurrence of voids that can be generated by shrinkage of the electrically conductive composition when the composition is cured, and suppress cracks in a member to be adhered, cracks in a bonding part, peeling at the bonding interface, or the like.

[0006] In Patent Literature 5, an electrically conductive adhesive composition containing an electrically conductive filler (B) having an average particle diameter of 0.5 to 10 μm and particles of a thermoplastic resin (A) that is in the form of a solid at 25°C is disclosed. In addition, in Patent Literature 6, an electrically conductive adhesive composition containing an electrically

conductive filler (A) containing metal particles (a1) having an average particle diameter of 0.5 to 10 μm and silver particles (a2) having an average particle diameter of 10 to 200 nm, and particles of a thermoplastic resin (B) that are in the form of a solid at 25°C is disclosed. It is disclosed that in the electrically conductive adhesive composition disclosed in Patent Literature 6, the thermal conductivity is improved by using a combination of micrometer-sized metal particles and nanometer-sized silver particles. It is disclosed in these Patent Literatures that the electrically conductive adhesive composition contains thermoplastic resin particles that are in the form of a solid at 25°C, thereby the thermoplastic resin particles are melted when the electrically conductive adhesive composition is sintered or heat-cured to fill voids present at the adhesive interface between a cured electrically conductive adhesive and a material to be adhered, and thereby the adhesive strength and the stress relaxation performance are improved, making it possible to suppress the occurrence of peeling caused by the temperature change. Similarly, in Patent Literature 7 as well, an electrically conductive adhesive composition containing micrometer-sized metal particles and nanometer-sized silver particles as electrically conductive fillers, and containing particles of a thermoplastic resin having an average particle diameter of 2 to 14 μm and a melting point of 130 to 250°C is disclosed. It is also disclosed in this literature that the particles of the thermoplastic resin are melted by heating to fill voids in the cured electrically conductive adhesive, and thereby peeling of the adhered material can be prevented.

Document List

Patent Literatures

[0007]

Patent Literature 1: Japanese Patent Application Laid-Open No. 2015-162392

Patent Literature 2: Japanese Patent Application Laid-Open No. 2016-65146

Patent Literature 3: Japanese Patent Application Laid-Open No. 2014-194013

Patent Literature 4: International Publication No. WO 2016/063931

Patent Literature 5: International Publication No. WO 2019/013230

Patent Literature 6: International Publication No. WO 2019/013231

Patent Literature 7: International Publication No. WO 2020/145170

Summary of Invention

Technical Problem

[0008] In the electrically conductive composition according to the prior art, a sintered part or a bonding part obtained after sintering the electrically conductive composition exhibits an excellent bonding strength and a good electrically conductive property by using an electrically conductive filler containing silver particles that can be sintered at a low temperature. However, on the other hand, in the sintered part or the bonding part in which the nanometer-sized silver particles are used, the shrinkage due to the sintering of the nanometer-sized silver particles becomes large, and thus voids are likely to occur inside the bonding part. In addition, the strain between the sintered part or the bonding part and the member adhered becomes large, and thus use of the nanometer-sized silver particles is disadvantageous from the viewpoint of the long-term reliability of the bonding part where a silicon chip and a material which is different such as a lead frame or a substrate are bonded. On the other hand, it is known that by using thermoplastic resin particles having a specific maximum value of an endothermic peak, the thermoplastic resin is melted and deformed when the electrically conductive composition is sintered, to fill voids in the sintered part, and thereby the void formation in the bonding part is suppressed,

making it possible to suppress the peeling of the bonding part and improve the bonding strength (see Fig. 1 and Fig. 2). However, even when such an electrically conductive composition is used, the following problem is still present in an electronic component having a relatively large size, for example, a chip having a size of about 5×5 mm to 8×8 mm: when a cooling and heating cycle is repeated, peeling is likely to occur.

[0009] Particularly for an electronic component for vehicle mounting, the operating temperature thereof fluctuates sharply in the range of about -50°C to 150°C , and thus an electrically conductive composition that allows a highly reliable bonding part to be obtained in an electronic component having a large surface area even under such a harsh condition is desired.

[0010] Therefore, an object of the present invention is to provide an electrically conductive composition that has a high electrically conductive property and thermally conductive property after sintering of the electrically conductive composition and, even in the case of a member having a large surface area, allows a sintered part or a bonding part where peeling of the member from a bonding target due to repeated cooling and heating cycles is unlikely to occur to be obtained, and a method for bonding a member or a method for producing an electrically conductive sintered part or bonding part, by using the electrically conductive composition.

Solution to Problem

[0011] The present inventors have found surprisingly that by micrometer-sized particles formed of a resin or the like that are uniformly dispersed in a sintered part in the state of maintaining the shape thereof before sintering without being remarkably deformed by melting due to heating in a sintered body matrix of an electrically conductive composition containing nanometer-sized

silver fine particles and micrometer-sized metal particles as electrically conductive fillers, such resin particles can not only relax stress but also disperse the stress, and eventually can achieve both a high electrically conductive property and long-term bonding reliability in a bonding part of a dissimilar material bonded using the electrically conductive composition, particularly in a bonding part for bonding a chip having a relatively large surface area, and have completed the present invention.

[0012] The configurations of the present invention are as follows:

[1] An electrically conductive composition comprising an electrically conductive filler and resin particles, wherein a rate of change in a maximum Feret's diameter of the resin particles between before and after sintering the electrically conductive composition is less than 1.20.

[2] The electrically conductive composition according to [1], wherein the rate of change in a maximum Feret's diameter is in the range of 0.9 to 1.1.

[3] The electrically conductive composition according to [1] or [2], wherein a temperature at which the electrically conductive composition is sintered is in the range of 80°C to 300°C.

[4] The electrically conductive composition according to any one of [1] to [3], comprising (A) silver fine particles having an average particle diameter of 10 to 300 nm as the electrically conductive filler.

[5] The electrically conductive composition according to [4], comprising (B) metal particles having an average particle diameter of 0.5 to 10 μm as the electrically conductive filler.

[6] The electrically conductive composition according to [5], comprising (C) resin particles having an average particle diameter of 2 to 15 μm as the resin particle.

[7] The electrically conductive composition according to [6], wherein a resin forming the resin particles (C) is selected from a group of a thermoplastic resin, a thermosetting resin, and a silicone resin.

[8] The electrically conductive composition according to [7], wherein the thermoplastic resin is selected from a group of a polyolefin and a polyamide.

[9] The electrically conductive composition according to any one of [6] to [8], wherein the average particle diameter of the resin particles (C) corresponds to 1 to 85% of the thickness of a sintered part or a bonding part obtained after sintering the electrically conductive composition.

[10] The electrically conductive composition according to any one of [6] to [9], wherein the electrically conductive composition comprises 5 to 50% by mass of the silver fine particles (A), 35 to 85% by mass of the metal particles (B), and 0.1 to 10% by mass of the resin particles (C), based on the mass of the electrically conductive composition.

[11] The electrically conductive composition according to any one of [1] to [10], wherein the electrically conductive composition further comprises (D) 0.5 to 10% by mass of a binder resin based on a mass of the electrically conductive composition.

[12] The electrically conductive composition according to any one of [5] to [11], wherein a ratio of the silver fine particles (A) : the metal particles (B) in the electrically conductive composition is in the range of 5:95 to 60:40 in terms of mass ratio.

[13] The electrically conductive composition according to any one of [1] to [12], further comprising at least one component selected from a group consisting of a curing agent, a curing accelerator, a solvent, an antioxidant, an ultraviolet absorber, a tackifier, a viscosity modifier, a dispersant, a coupling agent, a toughness-imparting agent, and an elastomer.

[14] A method for bonding a member using the electrically conductive composition according to any one of [1] to [13], comprising a step of sintering the electrically conductive composition such that the rate of change of the maximum Feret's diameter of the resin particles after sintering to the maximum Feret's diameter of the resin particle before sintering is less than 1.20.

[15] A method for producing an electrically conductive sintered part or bonding part using the electrically conductive composition according to any one of [1] to [13], comprising a step of sintering the electrically conductive composition such that the rate of change of the maximum Feret's diameter of the resin particle after sintering to the maximum Feret's diameter of the resin particle before sintering is less than 1.20.

[16] The method according to [14] or [15], wherein a temperature at which the electrically conductive composition is sintered is in the range of 80°C to 300°C.

[17] The method according to any one of [14] to [16], wherein a temperature increase rate when sintering the electrically conductive composition is 1 to 10°C/min.

[18] Use of the electrically conductive composition according to any one of [1] to [13] for forming a bonding part of a member, an electrically conductive layer, or a circuit.

[19] A sintered part or a bonding part comprising an electrically conductive filler and a resin particle, wherein the sintered part or the bonding part is obtained by sintering the electrically conductive composition according to any one of [1] to [13], the proportion at which the electrically conductive filler accounts for a cross-sectional area of the sintered part or the bonding part is 60 to 95% by area, and the proportion at which the resin particle accounts therefor is 1 to 35% by area, the proportion at which a component or components other than the resin

particles and the electrically conductive filler and voids account therefor is 4 to 25% by area, and the average particle diameter of the resin particles is 2 to 15 μm .
[20] A member comprising the sintered part or the bonding part according to [19].

Effects of Invention

[0013] According to the present invention, by applying the electrically conductive composition to a member, preferably an electronic component, more preferably an electronic component for vehicle mounting or an electronic component for a communication device and sintering the electrically conductive composition such that the maximum Feret's diameter of the resin particles contained in the electrically conductive composition before sintering is equal to or less than a certain rate of change, a sintered part or a bonding part which has a high electrically conductive property and thermally conductive property after sintering or heat-curing of the electrically conductive composition and in which, even in the case of a member having a large surface area, for example, a silicon chip, peeling from a bonding target is unlikely to occur can be obtained.

Brief Description of Drawings

[0014]

[Fig. 1] A diagram showing a member having a bonding part in which the electrically conductive composition according to the prior art is used.

[Fig. 2] A diagram showing a member having a bonding part in which the electrically conductive composition according to the prior art is used.

[Fig. 3] A diagram showing a member having a bonding part in which the electrically conductive composition according to the present invention is used.

[Fig. 4] A diagram showing the measurement of the Feret's diameters in particles having various shapes.

[Fig. 5] A diagram showing a DSC measurement result of a resin particles.

[Fig. 6] A diagram showing a DSC measurement result of a resin particles.

[Fig. 7] A diagram showing a DSC measurement result of a resin particles.

[Fig. 8] A diagram showing a DSC measurement result of a resin particles.

[Fig. 9] A diagram showing electron micrographs before heating and after heating of a resin particles according to the prior art.

[Fig. 10] A diagram showing electron micrographs before heating and after heating of a resin particles according to the present invention.

[Fig. 11] A diagram showing electron micrographs of cross sections of the electrically conductive compositions according to the present invention and a Comparative Example after sintering.

[Fig. 12] A diagram showing a pore distribution and cracks of the electrically conductive composition according to the present invention after sintering.

Description of Embodiments

[0015] The electrically conductive composition according to the present invention contains an electrically conductive filler and micrometer-sized particles formed of a resin and the like, and in the particle, the rate of change in the maximum Feret's diameter between before and after heating or sintering the electrically conductive composition is less than 1.20. According to the present invention, it is preferable for the rate of change in the maximum Feret's diameter of the resin particle between before and after sintering to be less than 1.10 and it is particularly preferable for the rate of change to be in the range of 0.9 to 1.0, from the viewpoint of peeling resistance. That is, the particle formed of a resin and the like to be used in the electrically conductive composition according to the present invention can substantially maintain the initial shape thereof without

being melted or deformed at a temperature at which the electrically conductive composition is sintered or heat-cured.

[0016] In general, there are various notations for specifying the size of the particles. When the particle shape is spherical, the particle diameter refers to the diameter thereof, and in the case of a polygonal particle or a particle having a distorted shape, it is not necessarily possible to define the particle diameter in the same way as in the case of the spherical particle. There is a unidirectional diameter as one criterion for defining the particle diameter of a polygonal particle. The unidirectional diameter is a particle diameter that can be analyzed by observing a projected image of a particle using a microscope, and there is Feret's diameter as one thereof. The Feret's diameter is represented by a straight line connecting any two points on the contour of a selected particle, in other words, by the length of a perpendicular line sandwiched between two parallel lines in a certain direction, and the longest one of the straight line or the perpendicular line is referred to as the maximum Feret's diameter, and the shortest one is referred to as the minimum Feret's diameter. The maximum Feret's diameter is also referred to as the maximum caliper length. The measurement of the Feret's diameter of the resin particle according to the present invention can be carried out by observing a cross section of a member to which the electrically conductive composition is applied, using, for example, a scanning electron microscope (SEM) or a high-magnification optical microscope (digital microscope), specifying the contours of particles from the acquired image using the image analysis software Image-J, and selecting 100 to 200 particles whose shape can be clearly confirmed.

[0017] According to the present invention, the rate of change in the maximum Feret's diameter of the particles can be calculated according to the following expression after determining the average value of the maximum Feret's diameter

of the particles before sintering the electrically conductive composition and the average value of the maximum Feret's diameter of the particles after sintering the electrically conductive composition:

Rate of change in maximum Feret's diameter = average value of maximum Feret's diameter after heating or sintering/average value of maximum Feret's diameter before heating or sintering

In Fig. 4, the particle enclosed by the solid line is a polygonal particle, and the particle enclosed by the dotted line is a circular or elliptical particle. The equivalent circle diameters of the particle enclosed by the solid line and the particle enclosed by the dotted line are the same. Examples of a major diameter 15, a minor diameter 11, a maximum Feret's diameter 14, and a minimum Feret's diameter 10 are shown in Fig. 4. As is clear from the illustration of Fig. 4, the maximum Feret's diameter of a particle, when compared with another particle having the same equivalent circle diameter, does not necessarily coincide with the major diameter (major axis) of such a particle, and the minimum Feret's diameter of a particle does not necessarily coincide with the minor diameter (minor axis) of the particle.

[0018] In the micrometer-sized particles formed of a resin and the like to be used in the present invention, the rate of change in the maximum Feret's diameter of the particles is less than 1.20, preferably 0.9 to 1.1, and further preferably 1.0, between before and after sintering the electrically conductive composition, that is, the particles may be formed of a resin such as a thermoplastic resin, a thermosetting resin, or a silicone resin or may be formed of another material that can absorb stress, for example, an inorganic material such as tin, gold, or an alloy of tin and gold, as long as the particle can satisfy the requirement that the maximum Feret's diameter of the particle is substantially unchanged. Those skilled in the art can appropriately select a suitable material in consideration of

the use of the electrically conductive composition, the application method, or a desirable physical property such as a thermally conductive property or an electrically conductive property.

[0019] It is preferable for the particles to be resin particles from the viewpoint of peeling resistance. When resin particles are used, a resin where the rate of change in the maximum Feret's diameter of the particles is no more than 1.20, preferably 0.9 to 1.1, and further preferably no more than 1.0 under a condition where the electrically conductive composition is sintered in consideration of the sintering temperature of the electrically conductive composition and the melting point of the resin should be selected.

[0020] The temperature at which the electrically conductive composition is sintered depends on the type of the electrically conductive filler or the resin particles to be used, the particle diameter, and the like, and is usually in the range of 80°C to 300°C. When the sintering temperature is lower than about 80°C, the electrically conductive composition is not cured, and when the sintering temperature exceeds about 300°C, the resin particle is melted and deformed or the melted resin flows into voids or pores, and thus the effects of the present invention cannot be obtained. The sintering of the electrically conductive composition can also be carried out in two stages at different temperatures. When resin particles are used, for example, it is possible to heat and hold the electrically conductive composition at about 80 to 200°C, advantageously about 130 to 200°C, and further advantageously about 140 to 180°C for a period of time in a first stage (preliminary firing), and then carry out sintering at a temperature higher than the above temperature, for example, 150°C or more, advantageously 180°C or more, and further advantageously 200°C or more in a second step (sintering). The temperature increase rate in preliminary firing and sintering is usually 1 to 10°C/min, preferably 3 to 7°C/min, and further preferably 5°C/min.

In addition, the temperature increase rate until the first stage (preliminary firing) and the temperature increase rate from the first stage (preliminary firing) to the second stage (sintering) may not be the same rate. Sintering can be carried out under the air atmosphere or under an inert gas atmosphere, for example, under the nitrogen atmosphere. When the surface of a member to be bonded is a material that is likely to form an oxide film, for example, copper, it is preferable to carry out sintering under an inert gas atmosphere, for example, under a nitrogen purge, in order to avoid the formation of an oxide film or discoloration. In this case, the oxygen concentration in the nitrogen atmosphere is 500 ppm or less, preferably 80 ppm or less, and further preferably 50 ppm or less from the viewpoint of preventing the oxidation or discoloration of the surface of the member to be bonded. At the above oxygen concentration, almost no oxidation or discoloration of copper occurs, and when oxygen is present at a concentration of about 0.1% (1000 ppm), discoloration of copper is observed. In addition, when about 0.1% of oxygen is present in the sintering atmosphere, the oxygen also affects the combustion of an organic substance such as an additive contained in the electrically conductive composition. When the oxygen concentration in the sintering atmosphere exceeds 0.1%, the sintering result thereof is equivalent to that of sintering under the air atmosphere. In this case, copper is completely discolored. The time for sintering the electrically conductive composition is usually 15 minutes to 180 minutes. The time for sintering the electrically conductive composition is not particularly limited as long as the electrically conductive composition is thermally cured to obtain a bonding part or a sintered part. For example, when sintering is carried out after preliminary firing, the sintering time of each may be 15 to 120 minutes, preferably 30 to 90 minutes, and further preferably 60 minutes from the viewpoint of process control. In addition, it is also possible to control heating to a constant temperature increase

rate, for example, 1 to 10°C/min, preferably 3 to 7°C/min, in addition to preliminary firing or instead of preliminary firing, and, after the sintering temperature is reached, maintain the sintering temperature for a certain period of time to carry out sintering. In this case, the sintering time is, for example, about 30 minutes to 180 minutes, and preferably about 60 minutes to 120 minutes. The temperature at the time of sintering, the heating or temperature increase rate, and the sintering atmosphere can be appropriately selected by those skilled in the art based on the above descriptions, depending on the type of the electrically conductive filler or the resin particle to be used in the electrically conductive composition, the particle diameter, an additive such as a solvent or another resin, the material of the member to be bonded, or the like.

[0021] [Electrically conductive filler (A) silver fine particles]

The electrically conductive composition according to the present invention contains (A) nanometer-sized silver fine particles, advantageously silver fine particles having an average particle diameter of 10 to 300 nm, as the electrically conductive filler.

The average particle diameter of the silver fine particles (A) according to the present invention is preferably 20 to 180 nm, more preferably 30 to 170 nm, and further preferably 40 to 160 nm from the viewpoint of sintering property. If the average particle diameter of the silver fine particles (A) is less than 10 nm, when the silver fine particles (A) have a coating on the surface, it may be difficult to remove the coating, causing sintering to be disturbed. When the average particle diameter of the silver fine particles (A) exceeds 300 nm, the specific surface area may be correspondingly reduced, causing sintering to be disturbed.

[0022] The tap density of the silver fine particles (A) is not particularly limited, and it is preferable for the tap density to be 4 g/cm³ or more, it is more preferable for the tap density to be 5 g/cm³ or more, and it is further preferable for the tap

density to be 5.5 g/cm³ or more, from the viewpoint of sintering property of the electrically conductive composition. In addition, it is preferable for the tap density to be 8 g/cm³ or less, it is more preferable for the tap density to be 7.5 g/cm³ or less, and it is further preferable for the tap density to be 7 g/cm³ or less, from the viewpoint of avoiding precipitation of the silver fine particles (A) when the electrically conductive composition is stored for a long period of time. The tap density of the silver fine particles (A) can be measured and calculated by, for example, the metal powder - tap density measuring method of JIS standard Z2512:2012.

[0023] The shape of the silver fine particles (A) is not particularly limited, and can be, for example, a flake shape, a plate shape, a spherical shape, a cubic shape, or a rod shape. When a flake shape or a plate shape is adopted as the shape of the silver fine particles (A), a sintered part having an excellent electrically conductive property and/or thermally conductive property can be obtained after sintering the electrically conductive composition. In addition, flake-shaped or plate-shaped silver fine particles are sintered mainly in the minor diameter direction, and thus the internal stress is smaller than when spherical silver fine particles are used, and the silver fine particles are highly oriented and thereby a sintered part or a bonding part having an excellent reflectance can be obtained. Further, the flake-shaped or plate-shaped silver fine particles are unlikely to be affected by the presence or absence of oxygen, and thus sintering can be carried out either under the air atmosphere or under an atmosphere of an inert gas such as nitrogen. When controlling the oxygen concentration in the sintering atmosphere, the material of the bonding part and the sintering property of the electrically conductive composition are taken into consideration, and sintering is carried out at an oxygen concentration of about, for example, 1000 ppm, preferably 500 ppm, further preferably 80 ppm, and most preferably 50 ppm.

Even when preliminary firing is carried out prior to sintering, it can also be carried out under the air atmosphere or under an inert gas atmosphere, or under an inert gas atmosphere having the same oxygen concentration as described above.

[0024] The surface of the silver fine particles (A) may be coated. A coating agent for such coating is known to those skilled in the art, and examples thereof include an amine or a carboxylic acid. The carboxylic acid coating agent is likely to be removed at the time of sintering and thus is preferable from the viewpoint of facilitating the curing of the electrically conductive composition after sintering and improving the heat dissipation of the sintered part. Examples of the carboxylic acid include monocarboxylic acid, polycarboxylic acid, and oxycarboxylic acid. In addition, as the carboxylic acid, a saturated fatty acid and/or an unsaturated fatty acid having 12 to 24 carbon atoms are/is preferable from the viewpoint of dispersibility in a resin or a solvent.

[0025] The coating agent may be one, or two or more coating agents may be used in combination. A method for coating the silver fine particles (A) with a coating agent is known to those skilled in the art, and examples thereof include a method involving stirring and mixing the silver fine particles (A) and a coating agent in a mixer and a method involving impregnating the silver fine particles (A) with a solution of a coating agent.

[0026] The content of the silver fine particles (A) in the electrically conductive composition according to the present invention is not particularly limited, and it is preferable for the content to be 5 to 50% by mass based on a total mass of the electrically conductive composition of 100% from the viewpoint of suppressing shrinkage due to sintering, and the content is more preferably 10 to 40% by mass and particularly preferably 15 to 35% by mass from the viewpoint of improving the electrically conductive property and/or the thermally conductive property.

[0027] [Electrically conductive filler (B) metal particles]

The electrically conductive composition according to the present invention further contains (B) micrometer-sized metal particles, advantageously metal particles having an average particle diameter of 0.5 to 10 μm , as the electrically conductive filler.

The average particle diameter of the metal particles (B) according to the present invention is preferably 0.6 to 8 μm , more preferably 0.7 to 7 μm , and further preferably 0.8 to 6 μm from the viewpoint of rheology of the electrically conductive composition. When the average particle diameter of the metal particles (B) is less than 0.5 μm , the shrinkage suppressing effect when sintering the electrically conductive composition is lowered, and the tight contact between the member to be adhered and the sintered part is lowered. When the average particle diameter of the metal particles (B) exceeds 10 μm , the sintering property of the electrically conductive composition is impaired, and thereby the tight contact between the member to be adhered and the sintered part is lowered.

[0028] The distribution of the average particle diameter of the metal particles (B) may have a single peak or may have a plurality of peaks.

[0029] The BET specific surface area of the metal particles (B) is not particularly limited, and it is preferable for the BET specific surface area to be 0.1 to 3 m^2/g , it is more preferable for the BET specific surface area to be 0.2 to 2 m^2/g , and it is further preferable for the BET specific surface area to be 0.3 to 1 m^2/g . It is preferable for the BET specific surface area of the metal particles (B) to be 0.1 m^2/g or more from the viewpoint of ensuring the surface area in contact with the member to be adhered. In addition, it is preferable for the BET specific surface area of the metal particles (B) to be 3 m^2/g or less from the viewpoint of reducing the amount of the (D) binder resin and/or the solvent used, which will be described later. The BET specific surface area of the metal particles (B) can be

measured using a BET specific surface area measuring apparatus according to a BET one-point method.

[0030] The tap density of the metal particles (B) is not particularly limited, and it is preferable for the tap density to be 4 g/cm³ or more, it is more preferable for the tap density to be 5 g/cm³ or more, and it is further preferable for the tap density to be 5.5 g/cm³ or more, from the viewpoint of the adhesive strength of the electrically conductive composition to the member to be adhered. In addition, it is preferable for the tap density to be 8 g/cm³ or less, it is more preferable for the tap density to be 7.5 g/cm³ or less, and it is further preferable for the tap density to be 7 g/cm³ or less, from the viewpoint of avoiding precipitation of the metal particles (B) when the electrically conductive composition is stored for a long period of time. The tap density of the metal particles (B) can be measured and calculated by, for example, the metal powder - tap density measuring method of JIS standard Z2512:2012.

[0031] The shape of the metal particles (B) is not particularly limited. The shape thereof can be, for example, a shape known to those skilled in the art such as a flake shape, a plate shape, a spherical shape, a cubic shape, or a rod shape. When a flake shape or a plate shape is adopted as the shape of the metal particles (B), a sintered part having an excellent electrically conductive property and/or thermally conductive property can be obtained after sintering the electrically conductive composition. In addition, a flake-shaped or plate-shaped metal particle is sintered mainly in the minor diameter direction, and thus the internal stress is smaller than when spherical metal particles are used, and the metal particles are highly oriented and thereby a sintered part or a bonding part having an excellent reflectance can be obtained. Further, the flake-shaped or plate-shaped metal particles are unlikely to be affected by the presence or absence of

oxygen, and thus sintering can be carried out under an atmosphere of an inert gas such as nitrogen.

[0032] The metal forming the metal particles (B) according to the present invention is not particularly limited as long as the metal can contribute to the electrically conductive property of the sintered part. As the metal that can contribute to the electrically conductive property, a metal known to those skilled in the art, for example, a metal such as silver, copper, nickel, aluminum, chromium, gold, platinum, palladium, tungsten, or molybdenum, can be used as a simple substance, as a mixture, as an alloy, and/or as an oxide. The alloy of the metal may be a binary alloy or a ternary alloy, and an element other than the metal may be included in the alloy. In addition, it is also possible to use a carbon nanotube as a material forming the metal particles (B). In addition, the metal particles (B) may be a mixture of two or more.

[0033] The ratio of the silver fine particles (A) and the metal particles (B) in the electrically conductive composition according to the present invention is not particularly limited, and it is preferable for the ratio to be in the range of 5:95 to 60:40, the ratio is more preferably in the range of 10:90 to 50:50 and particularly preferably in the range of 15:85 to 40:60, in terms of mass ratio, from the viewpoint of the balance between the thermal conductivity and the bonding property.

[0034] [(C) Resin particles]

According to the present invention, as the particles having the above rate of change in the maximum Feret's diameter, (C) resin particles having an average particle diameter of 2 to 15 μm are used.

It is preferable for the average particle diameter of the resin particles (C) to be 3 μm or more, and it is further preferable for the average particle diameter to be 4 μm or more, from the viewpoint of stress relaxation and crack

growth suppressing effect in the sintered part after sintering the electrically conductive composition. It is preferable for the average particle diameter of the resin particles (C) to be 13 μm or less, and it is further preferable for the average particle diameter to be 12 μm or less, from the viewpoint of stress dispersion in the sintered part after sintering the electrically conductive composition and the thickness of the sintered part. When the average particle diameter of the resin particles (C) is too large, the number of the resin particles (C) per volume of the electrically conductive resin composition becomes small and it becomes difficult to uniformly disperse the resin particles (C), and thereby the stress relaxing effect is lowered. In addition, when the average particle diameter of the resin particles (C) is large, the thickness of the sintered part cannot be accordingly reduced, and thus the heat generated from the member to be adhered cannot be efficiently dissipated.

[0035] In addition, when a member is bonded, the thickness of the bonding part may be about 200 μm at the maximum depending on the use, but is usually 10 μm to 50 μm . Therefore, in consideration of also the shrinkage rate of about 15% occurring when the electrically conductive composition is heat-cured, it is preferable for the average particle diameter of the resin particles (C) to be in the range of about 85% or less of the thickness of the bonding part after heat-curing from the viewpoint of uniform dispersion of the resin particles (C) as well as uniform stress relaxation and dispersion in the bonding part and eventually peeling suppression.

[0036] It is preferable for the shape of the resin particles (C) to be spherical or substantially spherical, but the shape may be a shape such as a cubic shape, a cylindrical shape, a prismatic shape, a conical shape, a pyramidal shape, or a flake shape.

[0037] It is preferable for the melting point of the resin particles (C) to be higher than the sintering temperature of the electrically conductive composition or the electrically conductive filler, and the melting point is 140 to 250°C and preferably 170°C to 250°C, from the viewpoint of the rate of change in the maximum Feret's diameter. According to the present invention, surprisingly, it has been found that when an electrically conductive composition containing an electrically conductive filler and resin particles is used as an adhesive to bond a member to be adhered, for example, a substrate and a chip, a sintering condition is controlled such that the rate of change in the maximum Feret's diameter of the resin particle in the electrically conductive composition is less than 1.20, preferably 0.9 to 1.1, and more preferably 1.0, and thereby a more reliable sintered part or bonding part than the bonding part or by the bonding method according to the prior art can be obtained. Therefore, the present invention provides a method for bonding a member to be adhered, for example, a substrate and a chip for an electronic component by sintering an electrically conductive composition, a method for producing an electrically conductive sintered part or bonding part, and an electrically conductive sintered part or bonding part obtained by sintering or heat-curing the electrically conductive composition, and a member having the sintered part or bonding part, particularly an electronic component, for example an electronic component for vehicle mounting or for a communication device.

[0038] As the resin forming the resin particles (C), a resin selected from the group consisting of a thermoplastic resin, a thermosetting resin, and a silicone resin can be used. As the above resin, a resin known to those skilled in the art can be used. Examples of the thermoplastic resin include particles of a polyamide, for example a nylon resin such as nylon 11, nylon 12, or nylon 6, AS resin, ABS resin, AES resin, vinyl acetate resin, polystyrene, a polyolefin resin

such as polyethylene or polypropylene, polyvinyl chloride, acrylic resin, methacrylic resin, polyvinyl alcohol resin, polyvinyl ether, polyacetal, polycarbonate, polyethylene terephthalate, polybutylene terephthalate, polyvinyl butyral, polysulfone, polyetherimide, ethyl cellulose, cellulose acetate, various fluororesins, a polyolefin elastomer, or a saturated polyester resin.

[0039] Examples of the thermosetting resin include a urea resin such as polyurethane resin, polyimide resin, phenol resin, epoxy resin, melamine resin, an unsaturated polyester resin, and alkyd resin.

[0040] The silicone resin, also called a silicon resin, is a series of resins whose main chain is an organopolysiloxane.

[0041] The above resins forming the resin particles (C) may be used singly, or two or more of the above resins may be used in combination. In addition, the resin may be a homopolymer consisting of one monomer forming the resin, or a copolymer consisting of two or more monomers.

[0042] Resin particles having a melting point or a DSC peak in the range of 140 to 250°C, preferably 170°C to 250°C, are preferable from the viewpoint of effectively preventing peeling of the sintered part or the bonding part from the member to be adhered. Examples of the resin having a melting point in the range of 140 to 250°C include nylon 12, nylon 11, nylon 6, polyethylene, polypropylene, vinyl acetate resin, and a saturated polyester resin. Among these, nylon 12, nylon 11, nylon 6, and polyethylene are preferably used, nylon 12, nylon 11, and nylon 6 are more preferably used, and nylon 12 and nylon 11 are further preferably used.

[0043] According to the present invention, by controlling a condition for sintering the electrically conductive composition, the resin particles (C) can substantially maintain the shape of the particle before sintering even at a temperature of 80°C or more and 300°C or less, which is the temperature at which

the electrically conductive composition is sintered, preferably 140°C or more and 250°C or less, and further preferably 165°C or more. Therefore, the rate of change of the maximum Feret's diameter of the resin particles after sintering the electrically conductive composition to the maximum Feret's diameter of the resin particles before sintering the same is less than 1.20, preferably 0.9 to 1.1, and further preferably 1.0. Examples of the condition for sintering the electrically conductive composition include the sintering temperature, the sintering time, and the sintering atmosphere. If sintering is carried out by separating the same into preliminary firing and sintering, a member to which the electrically conductive composition according to the present invention is applied is heated to a predetermined preliminary firing temperature at a constant temperature increase rate, and when the preliminary firing temperature is reached, the member is heated at a predetermined preliminary firing temperature for a certain period of time, for example, 15 minutes to 90 minutes, preferably 30 minutes to 60 minutes. After the preliminary firing, the member to which the electrically conductive composition is applied continues to be heated to the sintering temperature at a constant temperature increase rate, and when the sintering temperature is reached, the member is heated at the predetermined sintering temperature for a certain period of time, for example, 15 minutes to 90 minutes, preferably 30 minutes to 60 minutes. Alternatively, the electrically conductive composition may be sintered by heating the same to the predetermined sintering temperature at a constant temperature increase rate without carrying out preliminary firing. Here, the preliminary firing means to heat at and hold a constant temperature, and does not necessarily carry out up to sintering. Preliminary firing and sintering can be carried out under an inert gas atmosphere, for example, under the nitrogen atmosphere, having an oxygen concentration of 1000 ppm or less, preferably 500 ppm or less, further preferably 80 ppm or less,

and most preferably 50 ppm or less. By sintering the electrically conductive composition under the above conditions, the resin particles contained in the electrically conductive composition substantially maintains the initial shape thereof before sintering without being melted at the time of sintering to fill a void in the sintered part as in the case of the method according to the prior art, and is uniformly dispersed in the electrically conductive resin composition before and after heating or sintering, and thus the stress at the sintered part or the bonding part obtained after sintering is relaxed and dispersed. In addition, for the method according to the prior art, in the sintered part or the bonding part after sintering the electrically conductive composition, the resin particle is melted at the time of sintering and enters a void in the sintered part, and thus no longer has the particle diameter of the resin particles before sintering, whereas according to the method according to the present invention, the average particle diameter of the resin particles (C) after sintering substantially maintains the initial diameter of 2 to 15 μm . Because of this, even if the member has a larger area than the bonding part obtained by the electrically conductive composition according to the prior art, the progress of cracks in the bonding part is suppressed, and eventually peeling between the member adhered and the bonding part, for example, a silicon chip and the bonding part, or the bonding part and a lead frame or a substrate, is greatly suppressed. Thereby, a member having high bonding reliability, preferably an electronic component having excellent bonding reliability with a bonding partner, and more specifically, an electronic component for vehicle mounting or for a communication device having excellent bonding reliability with a bonding partner can be obtained.

[0044] It is preferable for the content of the resin particles (C) in the electrically conductive composition to be 0.1% by mass or more, it is more preferable for the content to be 0.5% by mass or more, it is further preferable for the content to be

1% by mass or more, and it is particularly preferable for the content to be 2% by mass or more, based on the mass of the electrically conductive composition, from the viewpoint of effectively preventing peeling of the sintered part or the bonding part from the member adhered after a cooling and heating cycle. It is preferable for the content of the resin particles (C) to be 10% by mass or less, it is more preferable for the content to be 7% by mass or less, and it is further preferable for the content to be 5% by mass or less, based on the mass of the electrically conductive composition, from the viewpoint of preventing a decrease in thermal conductivity of the sintered part or the bonding part after the electrically conductive composition is cured.

[0045] As used herein, the average particle diameter of each of the metal particles (B) and the resin particles (C) is the particle diameter corresponding to a cumulative volume percentage of 50% by volume as measured using a laser diffraction/scattering type particle size analyzer (50% average particle diameter in a particle diameter distribution) (D50). For such a measurement, for example, a laser diffraction/scattering type particle size analyzer MT-3000 manufactured by Nikkiso Co., Ltd. can be used. The average particle diameter of the silver fine particles (A) is the 50% average particle diameter (D50) in a particle diameter distribution measured using a dynamic light scattering method. Such a particle diameter can be measured using, for example, a Nanotrak particle diameter distribution measuring apparatus manufactured by Nikkiso Co., Ltd.

[0046] The melting point of the resin particles (C) is determined according to the type of the resin and is well known to those skilled in the art. In order to measure the melting point of the resin, for example, a differential scanning calorimeter (DSC) can be used. DSC peaks of the resin particles (c1), (c3), (c4), and (c11) shown in Table 1 below are shown as examples in Fig. 5 to Fig. 8, respectively.

[0047] In addition to the silver fine particles (A), the metal particles (B), and the resin particles (C), each component described below may be further blended in the electrically conductive composition according to the present invention.

[(D) Binder resin]

The electrically conductive composition of the present invention may further contain a binder resin (D), if necessary. By containing a binder resin (D), fluidity and adhesiveness can be further imparted to the electrically conductive composition. The binder resin (D) is not particularly limited as long as it is in the form of a liquid alone or after dissolved in a solvent from the viewpoint of workability, and for example, a thermoplastic resin such as a polyolefin, polyvinyl butyral, polyvinyl alcohol, ethyl cellulose, a saturated polyester resin, or acrylic resin, a thermosetting resin such as epoxy resin, phenol resin, urethane resin, or polyimide resin, or a silicone resin can be used. These resins may be used singly or in combinations of two or more. In addition, it is preferable for the binder resin (D) to be a thermosetting resin, and it is particularly preferable for the binder resin (D) to be epoxy resin, from the viewpoint of heat resistance because the temperature becomes high during sintering.

[0048] It is preferable for the content of the binder resin (D) to be 10% by mass or less, it is more preferable for the content to be 8% by mass or less, and it is further preferable for the content to be 6% by mass or less, based on the mass of the electrically conductive composition. When the content of the binder resin (D) is 10% by mass or less based on the mass of the electrically conductive composition, a network due to necking of the silver fine particles (A) and/or the metal particles (B) is likely to be formed, and a stable electrically conductive property and thermally conductive property can be obtained. In addition, it is preferable to use the binder resin in an amount of 0.5% by mass or more based

on the mass of the electrically conductive composition from the viewpoint of fluidity and adhesiveness.

[0049] <Curing agent>

The electrically conductive composition according to the present invention may contain a curing agent in addition to the above components. Examples of the curing agent include an amine-based curing agent such as a tertiary amine, an alkyl urea, or an imidazole, and a phenol-based curing agent.

It is preferable for the content of the curing agent to be 2% by mass or less based on the mass of the electrically conductive composition. By doing so, the uncured curing agent is less likely to remain, and the tight contact to the member to be adhered is improved.

<Curing accelerator>

The electrically conductive composition of the present invention may further contain a curing accelerator. Examples of the curing accelerator include an imidazole such as 2-phenyl-4,5-dihydroxymethylimidazole, 2-phenyl-4-methyl-5-hydroxymethylimidazole, 2-methyl-4-methylimidazole, or 1-cyano-2-ethyl-4-methylimidazole, a tertiary amine, a triphenylphosphine, a urea compound, a phenol, an alcohol, and a carboxylic acid. Two or more curing accelerators may be used in combination.

When a curing accelerator is used, the content thereof is usually 0.5% by mass or less based on the mass of the electrically conductive composition.

[0050] <Solvent/Diluent>

The electrically conductive composition according to the present invention may further contain a solvent or a diluent for forming the electrically conductive composition into a paste to facilitate the application thereof. When a solvent or a diluent is used, a solvent or a diluent that does not dissolve the resin particles is used so that the shape of the resin particles in the paste can be

maintained. In other respects, the solvent or the diluent to be used is not particularly limited, and a solvent or a diluent having a boiling point of 350°C or less is preferable, and a solvent or a diluent having a boiling point of 300°C or less is more preferable, from the viewpoint of volatility at the time of sintering. As the solvent or the diluent, one known to those skilled in the art, for example, an acetate, ether, or a hydrocarbon, and more specifically, dibutyl carbitol, butyl carbitol acetate, or the like can be used.

The content of the solvent or the diluent is usually 15% by mass or less based on the mass of the electrically conductive composition, and is preferably 10% by mass or less from the viewpoint of workability.

[0051] <Additive>

In addition to the above components, the electrically conductive composition according to the present invention further contains an additive known to those skilled in the art, such as an antioxidant, an ultraviolet absorber, a tackifier, a viscosity modifier, a dispersant, a coupling agent, a toughness-imparting agent, or an elastomer in a range that does not impair the effects of the present invention.

[0052] The electrically conductive composition according to the present invention can be produced by mixing, in any order, and stirring the silver fine particles (A), the metal particles (B), the resin particles (C), and if necessary, the binder resin (D) described above, and, if necessary, the other components described above. As the method therefor, a method known to those skilled in the art such as a two-roll mill, a three-roll mill, a sand mill, a roll mill, a ball mill, a colloid mill, a jet mill, a bead mill, a kneader, a homogenizer, and a propellerless mixer can be adopted.

[0053] According to the present invention, by applying the electrically conductive composition according to the present invention to a member and

sintering or heat-treating the same, a sintered part or a bonding part which has a high electrically conductive property and thermally conductive property and in which peeling of the member to be adhered is unlikely to occur can be obtained. The electrically conductive composition according to the present invention contains at least an electrically conductive filler and resin particles, and surprisingly, it has been found that when the electrically conductive composition is applied to a member and sintered, the electrically conductive composition is sintered under a condition where the rate of change of the maximum Feret's diameter of the resin particle after sintering to the maximum Feret's diameter of the resin particle before sintering is less than 1.20, preferably in the range of 0.9 to 1.1, and more preferably 1.0, and thereby peeling of a chip having a particularly large surface area, for example, a chip having a large size such as 7×7 mm or 8×8 mm can be effectively prevented. In the sintered part or the bonding part obtained by the present invention, the proportion at which the electrically conductive filler accounts for the cross-sectional area thereof (metal area) is 60 to 95% by area, and the proportion at which the resin particles account therefor (resin particle area) is 1 to 35% by area. The balance (other area), 4 to 25% by area, is voids and residues of the binder resin and the like. The "residues of the binder resin and the like" depend on the composition of the electrically conductive composition, for example, residues of the resin particles (C) partially melted by heating or sintering, an additive such as a curing agent, a curing accelerator, an antioxidant, an ultraviolet absorber, a tackifier, a viscosity modifier, a dispersant, a coupling agent, a toughness-imparting agent, or an elastomer, and a solvent can be included. As described above, according to the present invention, the resin particles in the electrically conductive composition after sintering have a rate of change in the maximum Feret's diameter of less than 1.20 and are not substantially deformed at the time of sintering, and thus the

average particle diameter before sintering is maintained. The metal area, the resin particle area, and the other area are obtained by observing a cross section of the sintered part by SEM.

[0054] Therefore, the target of the present invention is also a sintered part or a bonding part obtained by sintering an electrically conductive composition by the method according to the present invention, and a member having the sintered part or the bonding part, preferably an electronic component having the sintered part or the bonding part, more preferably an electronic component for vehicle mounting or for a communication device having the sintered part or the bonding part.

[0055] Next, an example of a method for using the electrically conductive composition of the present invention will be described.

[0056] A member having a sintered part or a bonding part in which peeling due to repetition of a cooling and heating cycle is unlikely to occur can be obtained with a high electrically conductive property and thermal conductivity even if the member has a large surface area, from the electrically conductive composition of the present invention by applying the electrically conductive composition according to the present invention to a member such as a silicon chip or an electronic component for vehicle mounting by a method known to those skilled in the art such as a dispenser, a metal mask, screen printing, or spin coating to form an electrically conductive composition layer; then if the electrically conductive composition is used for bonding the member, mounting the member such that the electrically conductive composition layer is in contact with a bonding partner (for example, a lead frame) of the member; and then heat-treating (sintering) the electrically conductive composition under a condition where the rate of change of the maximum Feret's diameter of the resin particle

after sintering to the maximum Feret's diameter of the resin particle before sintering is less than 1.20.

[0057] The temperature at which the electrically conductive composition according to the present invention is sintered is not particularly limited as long as the electrically conductive composition is heat-cured, that is, sintered, and a temperature in the range of 80°C to 300°C is advantageous. The temperature increase rate is usually 1 to 10°C/min, preferably 3 to 7°C/min, and further preferably 5°C/min. Sintering of the electrically conductive composition can also be carried out in two stages. For example, in a first stage (preliminary firing), sintering is carried out at a relatively low temperature, for example, a temperature of 80 to 200°C, advantageously 130 to 200°C, and further advantageously 140 to 180°C, and then in a second stage (sintering), in order to stabilize the shape of the sintered part or the bonding part, sintering can also be carried out at a temperature higher than that in the first stage, for example, a temperature of 150°C or more, advantageously 180°C or more, and further advantageously 200°C or more.

[0058] In addition, in order to prevent the sintered part or the bonding part from being shrunk and being brought into a state of being too hard by excessive progress of binding of the silver fine particles (A) and/or the metal particles (B), it is preferable for the sintering temperature to be 300°C or less, it is more preferable for the sintering temperature to be 275°C or less, and it is further preferable for the sintering temperature to be 250°C or less.

[0059] The time for heating the electrically conductive composition is not particularly limited as long as the electrically conductive composition is sintered and a sintered part or a bonding part is obtained, and is usually 15 minutes to 180 minutes.

[0060] The above heating may be carried out in air or may be carried out in an atmosphere of an inert gas such as argon or nitrogen. In the case of heating in air, removal of the coating agent on the surface of the silver fine particles (A) is likely to progress, and thus sintering is easy to carry out, but on the other hand, the silver fine particles (A) and/or the metal particles (B) are/is likely to be oxidized, and when an oxide film is formed, the electrically conductive property and the thermal conductivity of the resulting cured electrically conductive adhesive may be impaired. For example, in the case of heating in air, when a member to be adhered that is likely to be oxidized (for example, a Cu substrate) is used, the member to be adhered may be oxidized to inhibit the bonding or cause discoloration, and in addition thereto, surrounding members that are likely to be oxidized may also be oxidized and degraded.

[0061] Therefore, in order to avoid the above problems, it is preferable to carry out heating in an inert gas atmosphere, for example, in the nitrogen atmosphere. When sintering is carried out in the nitrogen atmosphere, the oxygen concentration in the nitrogen atmosphere is 1000 ppm or less, preferably 500 ppm or less, further preferably 80 ppm or less, and most preferably 50 ppm or less. The oxygen concentration in the nitrogen atmosphere at the time of sintering may be 0 ppm.

[0062] In order to efficiently dissipate the heat generated from a member adhered such as a semiconductor element, it is preferable for the electrically conductive composition layer to be thin. For example, it is preferable for the thickness of the electrically conductive composition after sintering to be 50 μm or less, it is further preferable for the thickness to be 40 μm or less, and it is further preferable for the thickness to be 30 μm or less.

[0063] On the other hand, in order to relax the internal stress caused by the difference in the coefficient of thermal expansion between a member adhered

such as a substrate and the sintered part in the thickness direction of the sintered part, a larger thickness of the electrically conductive composition layer is more desirable. Specifically, it is preferable for the thickness of the electrically conductive composition after sintering to be 5 μm or more, it is more preferable for the thickness to be 10 μm or more, and it is further preferable for the thickness to be 20 μm or more.

[0064] According to the present invention, the shape or the particle diameter of the resin particles (C) is maintained at a constant rate of change even after sintering, and thus the average particle diameter of the resin particles (C) should be selected depending on the thickness of the electrically conductive composition layer to be applied to the member. When the thickness of the electrically conductive composition layer is large, the resin particles (C) having a relatively large average particle diameter can be used, whereas when an electrically conductive composition layer having a small thickness is desirable, it is preferable for the average particle diameter of the resin particles (C) to also be correspondingly small. The suitable average particle diameter of the resin particles (C) can be appropriately selected by those skilled in the art based on the use, composition, layer thickness, and the like of the electrically conductive composition.

[0065] In order to ensure the heat dissipation of the member adhered, it is preferable for the thermal conductivity of the sintered part or the bonding part obtained by sintering the electrically conductive composition according to the present invention to be 20 $\text{W/m}\cdot\text{K}$ or more, it is more preferable for the thermal conductivity to be 35 $\text{W/m}\cdot\text{K}$ or more, and it is further preferable for the thermal conductivity to be 50 $\text{W/m}\cdot\text{K}$ or more. As a method for calculating the thermal conductivity, the method described in the following Examples can be used.

[0066] As a method for evaluating whether, when a member such as an electronic component is adhered using the electrically conductive composition according to the present invention, peeling is less likely to occur even when cooling and heating cycles are repeated, that is, repeated temperature changes of high and low temperatures are undergone, there are various methods. For example, a method for carrying out a cooling and heating cycle test by the method described in the following Examples and measuring the proportion of the peeled area after the test can be used. From the viewpoint of thermal resistance, it is preferable for the proportion of the peeled area measured by the above method to be 20% or less, it is further preferable for the proportion to be 15% or less, it is more preferable for the proportion to be 10% or less, and it is extremely preferable for the proportion to be 5% or less.

Examples

[0067] The present invention will be described in detail with reference to the following Examples, and the present invention is not limited whatsoever by these Examples.

A. Preparation of electrically conductive composition

The materials listed below were used in their respective amounts (% by mass) shown in Table 2 and kneaded using a three-roll mill to thereby produce electrically conductive compositions (sample Nos. 1 to 28).

[(A) Silver fine particles]

- a1. Spherical particles, average particle diameter $d_{50} = 90$ nm, manufactured by Tanaka Kikinzoku Kogyo K.K.
- a2. Spherical particles, average particle diameter $d_{50} = 150$ nm, manufactured by Tanaka Kikinzoku Kogyo K.K.

a3. Spherical particles, average particle diameter $d_{50} = 250$ nm, manufactured by Tanaka Kikinzoku Kogyo K.K.

[(B) Metal particles]

b1. Flake-shaped silver particles, average particle diameter $d_{50} = 5.5$ μm , tap density of 7.0 g/cm^3 , manufactured by Tanaka Kikinzoku Kogyo K.K.

b2. Flake-shaped silver particles, average particle diameter $d_{50} = 4$ μm , tap density of 6.7 g/cm^3 , manufactured by Tanaka Kikinzoku Kogyo K.K.

b3. Spherical silver particles, average particle diameter $d_{50} = 0.8$ μm , tap density of 5.5 g/cm^3 , manufactured by Tanaka Kikinzoku Kogyo K.K.

b4. Spherical silver particles, average particle diameter $d_{50} = 5$ μm , tap density of 5.0 g/cm^3 , manufactured by Mitsui Mining & Smelting Co., Ltd.

[(C) Resin particles]

c1. Silicone resin particles "KMP-600," manufactured by Shin-Etsu Chemical Co., Ltd., rate of change in maximum Feret's diameter at 165°C : 0.9

c2. Thermoplastic resin particles "TR-1" (polyamide), manufactured by Toray Industries, Inc., rate of change in maximum Feret's diameter at 140°C : 1.01

c3. Thermoplastic resin particles "PPW-5" (polypropylene), manufactured by Seishin Enterprise Co., Ltd., rate of change in maximum Feret's diameter at 140°C : 1.02, rate of change in maximum Feret's diameter at 165°C : 1.22

c4. Thermoplastic resin particles "SP-500" (polyamide), manufactured by Toray Industries, Inc., rate of change in maximum Feret's diameter at 150°C : 1.02, rate of change in maximum Feret's diameter at 165°C : 0.96

c5. Thermoplastic resin particles "SP-10" (polyamide), manufactured by Toray Industries, Inc.

c6. Thermoplastic resin particles "SP500" (polyamide), classified product, manufactured by Toray Industries, Inc.

c7. Thermoplastic resin particles "SP-10" (polyamide), classified product, manufactured by Toray Industries, Inc.

c9. Thermoplastic resin particles (Comparative Example) "PM-200" (polyethylene), manufactured by Mitsui Chemicals, Inc.

c10. Thermoplastic resin particles (Comparative Example) "Oragasol 3501EXD" (polyamide), manufactured by ARKEMA

c11. Thermoplastic resin particles (Comparative Example) "PW Powder" (polyester), manufactured by Tanaka Kikinzoku Kogyo K.K.

Various properties of the above resin particles are as shown in Table 1 below:

[Table 1]

	Examples						Comparative Examples			
	Resin particle (c1)	Resin particle (c2)	Resin particle (c3)	Resin particle (c4)	Resin particle (c5)	Resin particle (c6)	Resin particle (c7)	Resin particle (c8) (resin of WO2016/063931, Example 15)	Resin particle (c10) (resin of WO2016/063931, Example 12)	Resin particle (c11)
Resin particle (C)	Resin particle (c1)	Resin particle (c2)	Resin particle (c3)	Resin particle (c4)	Resin particle (c5)	Resin particle (c6)	Resin particle (c7)	Resin particle (c8) (resin of WO2016/063931, Example 15)	Resin particle (c10) (resin of WO2016/063931, Example 12)	Resin particle (c11)
Resin name	KMP-600	TR-1	PPW-5	SP500(common product)	SP10(common product)	SP500 (classified product)	SP10 (classified product)	PM-200	Oragaso3501EXD	PW Powder (P01CW35)
Resin type	Silicone resin	Polyamide	Polypropylene	Nylon 12	Nylon 12	Nylon 12	Nylon 12	Polyethylene	Nylon copolymer	Polyester
Particle diameter (d50)	5 μm	13 μm	5 μm	5 μm	10 μm	3 μm	15 μm	10 μm	10 μm	15 μm
DSC peak	None	210 to 220°C	142 to 152°C	165 to 175°C	165 to 175°C	165 to 175°C	165 to 175°C	130 to 140°C	137 to 147°C	70 to 80°C
Particle shape	Spherical	Spherical	Indefinite	Spherical	Spherical	Spherical	Spherical	Spherical	Spherical	Indefinite
Rate of change in maximum Ferrel's diameter at sintering temperature	Good	Good	Good	Good	Good	Good	Good	Poor	Poor	Poor

[0068] In the "Rate of change in maximum Feret's diameter at sintering temperature" in Table 1, "Good" indicates that the rate of change in the maximum Feret's diameter after heating the electrically conductive composition under predetermined conditions as compared with the maximum Feret's diameter of the particle before sintering was less than 1.20, and "Poor" indicates that the rate of change was 1.20 or more.

[0069] In addition, electron micrographs of the resin particles (c3) according to the prior art before heating and after heating were shown in Fig. 9, and electron micrographs of the resin particles (c1) according to the present invention before heating and after heating were shown in Fig. 10. In each figure, the upper part shows the electron micrograph before heating (room temperature), and the lower part shows the electron micrograph after heating at 165°C for 30 minutes. From Fig. 9, it is clear that the shape of the resin particles PPW-5 of c3 greatly changed after heating, and in this case, the rate of change in the maximum Feret's diameter of the resin particles of c3 is 1.20. On the other hand, from Fig. 10, it is clear that the resin particles KMP-600 of c1 used by the present invention substantially maintained the initial shape thereof even after heating, and in this case, the rate of change in the maximum Feret's diameter of the resin particles of c1 is 0.99.

[(D) Binder resin]

d1. "EPICLON 830-S" (epoxy resin in the form of liquid at room temperature), manufactured by Dainippon Ink and Chemicals, Incorporated, epoxy equivalent of 169 g/eq

d2. "ERISYS GE-21" (epoxy resin in the form of liquid at room temperature), manufactured by CVC Thermoset Specialties, Inc., epoxy equivalent of 125 g/eq

In addition to the above (A) to (D), a phenol-based curing agent (MEH8000H, manufactured by Meiwa Plastic Industries, Ltd.), 2-phenyl-4,5-dihydroxymethylimidazole (2PHZ, curing accelerator manufactured by Shikoku

Chemicals Corporation), and dibutyl carbitol (manufactured by Tokyo Chemical Industry Co., Ltd., solvent 1) or butyl carbitol acetate (manufactured by Tokyo Chemical Industry Co., Ltd., solvent 2) as a solvent were used.

B. Physical property evaluation

The electrically conductive compositions (sample Nos. 1 to 28) obtained in A were applied to silver-plated 10 × 10 mm copper lead frames, respectively, and a 5 × 5 mm or 7 × 7 mm silicon chip subjected to silver sputtering was mounted on the application surface of each. The temperature was raised from room temperature to 250°C at a temperature increase rate of 3 to 7°C/min under the nitrogen atmosphere and heating was carried out at this temperature for 60 minutes to obtain metal bonded bodies in which the copper lead frame and the silicon chip were bonded by the sintered and cured electrically conductive compositions, respectively (Examples 1 to 21 and Comparative Examples 1 to 8). The thermal conductivity λ of each of the obtained metal bonded bodies is shown in Table 2.

[0070] The heat conductivity λ (W/m•K) was calculated by measuring the heat diffusion according to ASTM-E1461 using a laser flash method heat constant measurement system, TC-7000 (manufactured by ULVAC-RIKO, Inc.), calculating the specific density d at room temperature by a pycnometer method, and measuring the specific heat C_p at room temperature according to JIS-K7123 2012 using a differential scanning calorimeter, DSC-7020 (manufactured by Seiko Instruments & Electronics Ltd.), and using the relational expression $\lambda = a \times d \times C_p$.

[0071] In addition, a cooling and heating cycle test was carried out using the obtained metal bonded bodies, and the peeled area was measured. In the cooling and heating cycle test, the operation of holding the metal bonded body at -50°C for 30 minutes and then holding the same at 150°C for 30 minutes was

defined as one cycle, and this cycle was repeated 2000 times. Then, the proportion of the peeled area of the silicon chip generated after this cooling and heating cycle test was measured. The proportion of the peeled area was determined by acquiring images of the state of peeling in the metal bonded body after the cooling and heating cycle test using Scanning Acoustic Tomograph Fine SAT (manufactured by Hitachi Power Solutions Co., Ltd.), and image-converting the shades in these images into 2 shades of white and black using the binarization software Image-J, and using the following relational expression:

Proportion of peeled area (%) = $\frac{\text{peeled area (number of black pixels)}}{\text{silicon chip area (number of black pixels + number of white pixels)}} \times 100$

Results obtained are shown in Table 2.

[Table 2]

Sample No.		Example 1	Example 2	Example 3	Example 4	Example 5	Example 6	Example 7	Example 8	Example 9	Example 10	Example 11	Example 12	Example 13	Example 14	Example 15	Example 16	Example 17	Example 18	Example 19	Example 20	Example 21	Comparison Example 1	Comparison Example 2	Comparison Example 3	Comparison Example 4	Comparison Example 5	Comparison Example 6	Comparison Example 7	Comparison Example 8
Elasticity conductive filler	Metal particle (B)	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21								
		Metal particle (D1)	-	20.55	-	-	-	-	-	-	20.55	20.13	21.51	20.70	20.70	27.03	-	20.55	20.55	20.55	-	20.55	-	20.55	20.55	-	42.80	-	-	-
		Metal particle (D2)	61.05	-	65.04	63.64	62.78	61.05	60.34	44.25	-	-	-	-	-	-	-	-	-	-	61.05	-	-	-	63.04	-	-	55.52		
		Metal particle (D3)	-	35.40	-	-	-	-	-	-	25.40	30.83	53.76	35.71	36.04	35.40	35.40	35.40	35.40	35.40	-	35.40	-	-	-	57.14	-	-	-	
		Metal particle (D4)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20.55	-	-	-	-	-	-	-	-	-	-	-	-	-
	Silver fine particle (A)	Silver particle (a1)	20.55	20.55	27.27	27.27	20.91	20.55	25.00	44.25	20.55	10.42	10.75	20.70	20.70	27.03	20.55	-	20.55	20.55	20.55	20.55	20.55	-	27.27	-	27.27	87.38	23.70	
		Silver particle (a2)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20.55	-	-	-	-	-	-	-	-	-	-	-	-
		Silver particle (a3)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	20.55	-	-	-	-	20.55	-	-	-	-	-	-
		Epoxy resin (d1)	0.08	0.08	0.01	0.01	0.00	0.00	0.00	0.00	0.00	0.07	1.00	0.45	-	1.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.01	0.00	0.01	0.00	0.00	
		Epoxy resin (d2)	0.44	0.44	0.45	0.45	0.45	0.44	0.43	0.44	0.44	0.40	0.54	7.37	-	0.00	0.44	0.44	0.44	0.44	0.44	0.44	0.44	0.45	0.44	0.45	0.44	0.45	0.45	0.43
Binder resin Curing agent (MC18000H) Curing accelerator Solvent	Curing agent (MC18000H)	0.35	0.35	0.30	0.30	0.30	0.35	0.34	0.35	0.35	0.30	0.43	0.18	-	0.72	0.35	0.35	0.35	0.35	0.35	0.35	0.35	0.30	0.35	0.30	0.35	0.30	0.34		
	Curing accelerator	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.10	0.11	0.04	-	0.10	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00	0.00		
	Solvent 1	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	7.00	-	-	-	-	-	-	-	
	Solvent 2	7.00	7.00	7.27	6.30	6.73	7.00	7.70	7.00	7.00	7.77	6.00	-	6.04	5.60	7.00	7.00	7.00	7.00	7.00	7.00	7.00	7.27	7.00	7.27	7.00	7.27	8.62		
	Resin particle (c1)	2.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.00	-	-	-	-	-	-	-	-	-	-	-
Resin particle (C)	Resin particle (c2)	2.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Resin particle (c3)	-	-	2.05	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Resin particle (c4)	-	-	-	0.01	1.70	2.05	4.31	2.05	2.01	3.23	2.00	0.45	2.05	2.05	2.05	2.05	2.05	2.05	-	-	-	-	2.05	-	2.05	-	10.34	2.01	
	Resin particle (c5)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.05	-	-	-	-	-	-	-	-	-	-
	Resin particle (c6)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.05	-	-	-	-	-	-	-	-	-
	Resin particle (c7)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.05	-	-	-	-	-	-	-	-
	Resin particle (c8)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-
	Resin particle (c9)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.00	-	-	-	-	-	-	-	-
	Resin particle (c10)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.05	-	-	-	-	-	-
	Resin particle (c11)	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	-	2.00	-	-
Thermal conductivity A (W/mK)		130	130	90	150	140	125	60	155	140	125	110	190	200	130	100	80	100	125	130	140	100	90	120	180	100	80	170	35	
	Peeling test 1 (peel area %)	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Poor	Poor	Good
	Peeling test 2 (peel area %)	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Good	Poor	Poor	Poor	Poor	Poor	Poor	Poor	Poor

[0072] In Table 2, those having a peeled area proportion of less than 20% after the cooling and heating cycle test were rated as "Good", and those having a peeled area proportion exceeding 20% were rated as "Poor" from the viewpoint of thermal resistance. In peeling test 1, a 5×5 mm Si chip was used, and in peeling test 2, a 7×7 mm Si chip was used. Both chips are provided with a silver coating by sputtering on the back surface.

[0073] From the results in Table 2, when the 5×5 mm silicon chip was used, even in the case of the Comparative Examples, the peeled area was small and good results were obtained, whereas it is clear that when the 7×7 mm silicon chip, which was larger, was used, the peel resistance was insufficient in all of Comparative Examples 1 to 3, 5, and 8, which showed good results when the 5×5 mm silicon chip was used. In contrast, for the sintered parts (Examples 1 to 21) obtained by the present invention, even when the 7×7 mm silicon chip was used, the peeled area after the cooling and heating cycle test for 2000 cycles was small, and it is clear that a highly reliable bonding part was obtained.

[0074] Next, the electrically conductive composition was applied to a copper substrate whose surface was coated with a noble metal such as Au, Pd, or Ag, and a copper substrate whose surface was not coated, and a chip (2×2 mm or 7×7 mm) whose surface to be bonded was coated with a noble metal was mounted on the resulting application surface followed by sintering. The coating of the substrate and the chip with a noble metal was carried out by means well known to those skilled in the art, such as plating, sputtering, or metalizing. The size of the chips mounted in Examples 22 to 26 is 2×2 mm, and the size of the chips mounted in Examples 27 to 40 (Table 3) and Comparative Examples 9 to 12 (Table 4) is 7×7 mm. In Reference Examples 1 to 5, sintering was carried out without mounting a chip. The temperature increase rate at the time of sintering is 3 to

7°C/min. In each of Examples 22 and 27, the temperature was raised to 250°C at the above temperature increase rate without carrying out preliminary firing to prepare a sintered part. A cross section of the obtained sintered part was observed by SEM, and the proportion at which the electrically conductive filler accounted for the entire cross section of the sintered part (Metal area in Table 3 and Table 4) and the proportion at which the resin particles accounted therefor (Resin particle area in Table 3 and Table 4) were calculated. The electrically conductive compositions used, the chip size, the sintering conditions, the proportion of the metal and the proportion of the resin particles to the cross-sectional area of the sintered part, the bonding strength, and the results of the reliability test (cooling and heating cycle test) are summarized in Table 3 and Table 4 shown below.

[Table 3]

	Example 22	Example 23	Example 24	Example 25	Example 26	Example 27	Example 28	Example 29	Example 30	Example 31	Example 32	Example 33	Example 34	Example 35	Example 36	Example 37	Example 38	Example 39	Example 40
Sample No.	8	8	8	8	8	8	8	8	8	8	8	8	4	7	15	6	8	8	8
Chip size	2x2mm	2x2mm	2x2mm	2x2mm	2x2mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm	7x7mm
Noble metal species of chip bonding surface	Au	Au	Au	Au	Au	Au	Au	Au	Au	Au	AuPd	Ag	Ag	Ag	Ag	Au	Au	Au	Au
Noble metal species of copper substrate surface	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu	AuPd	Ag	Ag	Ag	Ag	Cu	Cu	Cu	Cu
(Amount of resin particle in electrically conductive composition after curing)	3%	3%	3%	3%	3%	3%	3%	3%	3%	3%	3%	3%	1%	5%	3%	3%	3%	3%	3%
Average particle diameter of resin particle in sintered part	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm	5µm
Electrically conductive filler	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	57 parts by mass of silver + 43 parts by mass of copper	Silver	Silver	Silver	Silver
Temperature increase rate	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min	1°C/min	3°C/min	7°C/min	10°C/min
Preliminary sintering temperature (60 min)	None	50°C	100°C	150°C	200°C	None	50°C	100°C	150°C	200°C	200°C	200°C	200°C	200°C	200°C	200°C	200°C	200°C	200°C
Regular sintering temperature (60 min)	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C
Oxygen concentration	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	500ppm	21%	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm
Metal area																			
Left edge	75.4	76.6	72.7	76.2	79.8	80.2	75.9	80.7	77.8	80.4	78.8	80.8	80.2	63.9	83.8	81.1	80.4	81.2	81.2
Center	76.7	74.3	78.5	78	80.3	70.7	74.4	73.1	69.7	69.9	87.1	88.6	87.6	73.7	80.3	78.9	85	88.3	88.7
Resin particle area																			
Left edge	12.4	10	12.2	13.8	11	7	9.8	8.4	12.5	12.8	12.5	11.9	1.9	28.3	9.3	11.5	12.4	10.5	9.8
Center	8.7	12.8	8.5	9.9	9.1	8.8	8.4	7.5	9.2	3	4.2	3.2	3.8	18.3	2.5	9.8	6.2	2.8	2.5
Other area																			
Left edge	12.2	13.4	15.1	10.2	9.2	12.8	14.3	10.9	0.7	6.8	7.7	7.3	7.9	7.8	6.9	7.4	7.2	8.3	8
Center	12.6	12.9	13	12.1	10.6	22.5	17.2	18.4	21.1	7.1	8.7	8.2	8.6	8	7.2	10.5	8.8	8.8	8.8
Peeling area after reliability test (-50°C ↔ 150°C)	<1	<1	<1	<1	<1	4	2	3	3	2	2	1	9	6	10	3	2	3	5

*Other area: voids + residues of binder, resin and the like

[Table 4]

Sample No.		Comparative Example 9	Comparative Example 10	Comparative Example 11	Comparative Example 12	Reference Example 1	Reference Example 2	Reference Example 3	Reference Example 4	Reference Example 5
Chip size		24	28	8	8	8	8	8	8	8
Noble metal species of chip bonding surface		7x7mm	7x7mm	7x7mm	7x7mm	None	None	None	None	None
Noble metal species of copper substrate surface		Ag	Au	Au	Au	-	-	-	-	-
(Amount of resin particle in electrically conductive composition after curing)		Ag	Cu	Cu	Cu	Cu	Cu	Cu	Cu	Cu
Average particle diameter of resin particle in sintered part		0%	12%	3%	3%	3%	3%	3%	3%	3%
Electrically conductive filler		5μm	5μm	5μm	5μm	5μm	5μm	5μm	5μm	5μm
Temperature increase rate		Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver	Silver
Preliminary sintering temperature (60 min)		5°C/min	5°C/min	20°C/min	Not controlled	5°C/min	5°C/min	5°C/min	5°C/min	5°C/min
Regular sintering temperature (60 min)		200°C	200°C	200°C	200°C	None	50°C	100°C	150°C	200°C
Oxygen concentration		250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C	250°C
		50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm	50ppm
Metal area	Left edge	96	49.8	80.4	82.7	80	78.7	79.5	80.6	77.5
	Center	87.8	54.8	89.9	88.8	74.5	75.5	76	74.8	77.4
Resin particle area	Left edge	0	43.7	7.4	3.4	11.4	13.5	11.7	12.1	13.2
	Center	0	38.3	0.7	0	14.5	12.1	13.8	13	12.5
Other area	Left edge	4	6.5	12.2	13.9	8.6	7.8	8.8	7.3	9.3
	Center	12.2	6.9	9.4	11.2	11	12.4	10.2	12.2	10.1
Peeling area after reliability test (-50°C ↔ 150°C)		95	45	23	54	-	-	-	-	-

*Other area: voids + residues of binder resin and the like

[0075] In Table 3, Examples in which a substrate and a chip were bonded according to the present invention using the electrically conductive compositions of sample Nos. 4, 7, 8, and 15, respectively, shown in Table 2 are shown. In addition, in the table, the distribution proportions of the metal area (electrically conductive filler), the resin particle area (resin particle (C)), and the other area (void and residues of binder resin and the like) in the left edge part and the central part of a cross section of the sintered part obtained by the method according to the present invention are shown. A smaller difference between the left edge part and the central part shows that the electrically conductive filler and the resin particles are more uniformly dispersed in the sintered part. When the chip size was 2×2 mm (Examples 22 to 26), the difference between the left edge part and the central part was small, and the peeled area in the reliability test was also very small, whereas when a 7×7 mm chip was mounted followed by sintering (Examples 27 to 40), the difference between the left edge part and the central part was slightly large, but the peeled area in the reliability test was small, and it can be seen that a highly reliable bonding part was still obtained. On the other hand, in Table 4, the sintered parts obtained by using the same electrically conductive compositions (sample Nos. 24 and 28) as in the cases of Comparative Examples 3 and 8 shown in Table 2, the sintered parts obtained by using the electrically conductive composition (sample No. 8) having the composition according to the present invention and sintering under sintering conditions not according to the present invention, and Reference Examples 1 to 5 in which sintering was carried out without mounting a chip are shown. In Comparative Example 9 obtained by using the electrically conductive composition (sample No. 24) containing no resin particles (C), the peeled area after the cooling and heating cycle is 95%, and in Comparative Example 10 obtained by using sample No. 28 having a content of the resin particles (C) of more than 10%, the peeled area is

45%, whereas the peeled areas of the sintered parts obtained by the present invention are all 10% or less. In addition, even in Comparative Examples 11 and 12 in which the electrically conductive composition according to the present invention was used but the temperature increase rate was above a certain range or sintering was carried out without controlling the temperature increase rate, the peeled areas after the cooling and heating cycle, are very large. From these results as well, it is clear that according to the present invention, a highly reliable bonding part can be obtained even when the area of a chip is large. In Reference Examples 1 to 5, the electrically conductive composition according to the present invention was applied to a substrate and sintered without mounting a chip. In each of these Reference Examples, the deviation of the distribution of the resin particles (C) between the left edge part and the central part of a cross section of the sintered part (the difference between the area % at the left edge and the area % at the center) is small, and thus it can be seen that the resin particles (C) is uniformly dispersed over the entire sintered part. It is preferable for the resin particles (C) to be uniformly dispersed from the viewpoint of stress relaxation and dispersion in the sintered part or the bonding part. In Examples 22 to 40 according to the present invention as well, the deviation of the distribution of the resin particles (C) is smaller as in the Reference Examples than in the Comparative Examples, and it is clear that a highly reliable bonding part was obtained.

[0076] Fig. 11 is electron micrographs each showing a cross section of the electrically conductive composition after applied to a 7×7 mm member (Si chip) and sintered. From the cross-sectional views of Examples 3 and 8, in each of the electrically conductive compositions according to the present invention, as shown in Fig. 3, it is clear that the resin particles are uniformly dispersed in the electrically conductive composition after sintering while substantially

maintaining the initial shape thereof. As described above, the resin particles are uniformly dispersed in the electrically conductive composition after sintering, and thereby according to the present invention, the stress is relaxed and dispersed, and a highly reliable bonding part can be obtained. On the other hand, in Comparative Example 6, as shown in Fig. 2, it is clear that the resin particles are melted and deformed and distributed in a non-uniform shape.

[0077] Fig. 12 shows an example of the progress of cracks in the bonding part obtained by the electrically conductive composition according to the present invention. By using the electrically conductive composition according to the present invention and carrying out sintering under a condition where the rate of change in the maximum Feret's diameter of the resin particles between before and after sintering is less than 1.20, the resin particles can substantially maintain the initial shape thereof even after sintering. Because of this, the cracks occurring in the cooling and heating cycle do not occur at the interface of the bonding part, but fine cracks are occurring by following the resin particles present in the bonding part. Thereby, the stress is dispersed, cracks due to the cooling and heating cycle are minimized, and as a result, large peeling at the interface between the member and the bonding part is prevented.

[0078] As described above, the present invention has been described in detail based on specific aspects, but it is clear to those skilled in the art that various changes and modifications can be made without departing from the technical idea and scope of the present invention.

Industrial Applicability

[0079] According to the present invention, provided are an electrically conductive material containing an electrically conductive filler, which can be applied to a member, particularly a member used in the field of electronics, for

example, an electronic component, and more specifically, an electronic component for vehicle mounting or for a communication device, wherein the electrically conductive material exhibits a good thermal conductivity after sintering thereof and is less likely to cause peeling, cracks, or the like of a relatively large member or a bonding part even after repeated remarkable temperature changes and can form a highly reliable bonding part, a method for bonding a member using the electrically conductive composition, and a method for producing an electrically conductive sintered part or bonding part.

List of Reference Signs

[0080]

- 1 member
- 2 electrically conductive composition
- 3 resin particle
- 4 void
- 10 Minimum Feret's diameter
- 11 minor diameter
- 14 Maximum Feret's diameter
- 15 major diameter

Claims

1. An electrically conductive composition comprising:
an electrically conductive filler; and
a resin particle, wherein
a rate of change in a maximum Feret's diameter of the resin particle between
before and after sintering the electrically conductive composition is less than 1.20.
2. The electrically conductive composition according to claim 1,
wherein the rate of change in a maximum Feret's diameter is in the range of 0.9
to 1.1.
3. The electrically conductive composition according to claim 1 or 2,
wherein a temperature at which the electrically conductive composition is
sintered is in the range of 80°C to 300°C.
4. The electrically conductive composition according to any one of
claims 1 to 3, comprising (A) a silver fine particle having an average particle
diameter of 10 to 300 nm as the electrically conductive filler.
5. The electrically conductive composition according to claim 4,
comprising (B) a metal particle having an average particle diameter of 0.5 to 10
μm as the electrically conductive filler.
6. The electrically conductive composition according to claim 5,
comprising (C) a resin particle having an average particle diameter of 2 to 15 μm
as the resin particle.

7. The electrically conductive composition according to claim 6, wherein the resin forming the resin particle (C) is selected from a group of a thermoplastic resin, a thermosetting resin and a silicone resin.

8. The electrically conductive composition according to claim 7, wherein the thermoplastic resin is selected from a group of a polyolefin and a polyamide.

9. The electrically conductive composition according to any one of claims 6 to 8, wherein the average particle diameter of the resin particle (C) corresponds to 1 to 85% of the thickness of a sintered part or a bonding part to be obtained after sintering the electrically conductive composition.

10. The electrically conductive composition according to any one of claims 6 to 9, wherein the electrically conductive composition comprises 5 to 50% by mass of the silver fine particle (A), 35 to 85% by mass of the metal particle (B), and 0.1 to 10% by mass of the resin particle (C), based on the mass of the electrically conductive composition.

11. The electrically conductive composition according to any one of claims 1 to 10, wherein the electrically conductive composition further comprises 0.5 to 10% by mass of (D) a binder resin based on the mass of the electrically conductive composition.

12. The electrically conductive composition according to any one of claims 5 to 11, wherein a ratio of the silver fine particle (A) : the metal particle (B)

in the electrically conductive composition is in the range of 5:95 to 60:40 in terms of mass ratio.

13. The electrically conductive composition according to any one of claims 1 to 12, further comprising at least one component selected from a group consisting of a curing agent, a curing accelerator, a solvent, an antioxidant, an ultraviolet absorber, a tackifier, a viscosity modifier, a dispersant, a coupling agent, a toughness-imparting agent, and an elastomer.

14. A method for bonding a member using the electrically conductive composition according to any one of claims 1 to 13, comprising a step of sintering the electrically conductive composition such that the rate of change of the maximum Feret's diameter of the resin particle after sintering to the maximum Feret's diameter of the resin particle before sintering is less than 1.20.

15. A method for producing an electrically conductive sintered part or bonding part using the electrically conductive composition according to any one of claims 1 to 13, comprising a step of sintering the electrically conductive composition such that the rate of change of the maximum Feret's diameter of the resin particle after sintering to the maximum Feret's diameter of the resin particle before sintering is less than 1.20.

16. The method according to claim 14 or 15, wherein the temperature at which the electrically conductive composition is sintered is in the range of 80°C to 300°C.

17. The method according to any one of claims 14 to 16, wherein the temperature increase rate when sintering the electrically conductive composition is 1 to 10°C/min.

18. Use of the electrically conductive composition according to any one of claims 1 to 13 for forming a bonding part of a member, an electrically conductive layer, or a circuit.

19. A sintered part or a bonding part comprising:
an electrically conductive filler; and
a resin particle, wherein
the sintered part or the bonding part is obtained by sintering the electrically conductive composition according to any one of claims 1 to 13, the proportion at which the electrically conductive filler accounts for a cross-sectional area of the sintered part or the bonding part is 60 to 95% by area, and the proportion at which the resin particle accounts therefor is 1 to 35% by area, the proportion at which a component or components other than the resin particle and the electrically conductive filler and voids account therefor is 4 to 25% by area, and the average particle diameter of the resin particle is 2 to 15 μm .

20. A member comprising the sintered part or the bonding part according to claim 19.