

Title of the Invention

CONDUCTING THICK FILM COMPOSITION, THICK FILM ELECTRODE,
CERAMIC ELECTRONIC COMPONENT AND LAMINATED CERAMIC CAPACITOR

Background of the Invention

This invention relates to a conducting thick film composition and a ceramic electronic component such as a laminated ceramic capacitor wherein this conducting thick film composition is used for a thick film electrode.

Conventionally, a thick film electrode of a ceramic electronic component, for example an external electrode of a laminated ceramic capacitor, is made by coating onto an end surface of a stack of alternately laminated ceramic dielectric layers and internal electrodes and then baking a conducting thick film composition comprising Ag powder or Ag-Pd powder, which are conducting powders, glass powder, which is a filler, and an organic vehicle consisting of a base resin and an organic solvent.

After an external electrode is formed, plating is carried out to increase the solderability of the electrode, and for example a Ni/Sn solder layer is formed by electroplating.

A large quantity of glass powder as a filler is included in order to maintain the strength of the bond between the stack and the external electrode. The glass powder melts during the baking of the electrode and melted

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glass powder moves to the interface between the stack and the external electrode and acts as an adhesive.

Ag powder or Ag-Pd powder has been mainly used as the conducting powder, but recently inexpensive Cu powder has started to be used instead of Ag powder or Ag-Pd powder to reduce costs.

However, when Cu powder has been used as the conducting powder to promote cost reduction there have been the following kinds of problem:

(1) Because Cu is easily oxidized, baking must be carried out in a non-oxidizing atmosphere; however, in this case the rate of decomposition of the resin component in the organic vehicle is slow, resin component remains until the temperature at which the glass starts to melt is reached and consequently gas produced by the decomposition of the resin component forms bubbles in the melted glass.

As a result, a phenomenon occurs wherein parts of the external electrode, called blisters, swell up. Such blisters are also caused by gas produced by the ceramic and the glass reacting with each other at high temperatures. That is, these blisters tend to form at high temperatures at which sintering of the surface of the Cu electrode has progressed and there is no way for produced gas to escape.

The strength of the bond between the stack and the external electrode is sometimes reduced by these blisters.

(2) Because during baking in a non-oxidizing atmosphere the glass powder is reduced and its properties deteriorate, when the plating is carried out glass powder in the electrode tends to dissolve in the plating liquid.

Consequently, in the middle of the plating process the plating liquid dissolves glass in the external electrode and reaches as far as the internal electrodes, as a result of this the strength of the bonds between the internal electrodes and the ceramic dielectric layers of the laminated ceramic capacitor falls, peeling occurs at these interfaces and cracks occur in the ceramic dielectric itself.

(3) Also, because a large quantity of glass powder is included, when baking is carried out at a high temperature and in a non-oxidizing atmosphere, glass covers the surface of the external electrode, a plating layer cannot be formed, and the solder wettability of the surface falls.

Summary of the invention

An object of this invention is to provide a conducting thick film composition, a thick film electrode, a ceramic electronic component and a laminated ceramic capacitor with which it is possible to improve electrical reliability by improving the strength of a bond between a ceramic substrate and a thick film electrode and improve the adherence of solder to a thick film electrode.

To achieve the above object and other objects, the invention provides a conducting thick film composition containing Cu powder, glass powder and an organic vehicle wherein the Cu powder comprises spherical powder and scaly powder.

By means of this constitution, the invention makes it possible to prevent blistering of a thick film electrode occurring while the electrode is being formed, increase the strength of a bond between a ceramic element and a thick film electrode and improve the adherence of solder to a thick film electrode.

That is, because sintering of the spherical powder starts and the sintered density becomes high in the range 700 to 800°C, which is the temperature region in which blistering occurs, with only spherical powder the void rate of the thick film electrode during sintering is insufficient and consequently blisters form on the surface of the thick film electrode and the strength of the bond between the ceramic element and the thick film electrode is low.

With only scaly powder, on the other hand, because the strength with which it bonds with glass is small, it peels off relatively easily and the bonding strength of the thick film electrode is low.

Accordingly, in this invention, scaly powder is blended with spherical powder. Because sintering of this

scaly powder does not start fully in the temperature region in which blistering occurs, the void rate of the thick film electrode during sintering increases, passages through which produced gas can escape are formed and this prevents the occurrence of blistering of the thick film electrode surface. As a result it is possible to raise the strength of the bond between the ceramic element and the thick film electrode.

Also, because by this method it is possible to reduce the blended amount of glass powder, which had been included in large quantities in order to maintain the strength of the bond between the ceramic element and the thick film electrode, deterioration of the plating adherence caused by glass melting and covering the surface of the thick film electrode can be prevented and soldering can be improved.

Also, the invention provides a conducting thick film composition including Cu powder, glass powder and an organic vehicle wherein the glass powder comprises borosilicate zinc glass and borosilicate barium glass.

By means of this constitution, the invention makes it possible to prevent cracking of a ceramic element occurring during electrode formation, raise the strength of the bond between a ceramic element and a thick film electrode and improve the adherence of solder to the thick film electrode.

That is, because plating liquid does not readily

dissolve borosilicate zinc glass or borosilicate barium glass when these are compared with others in dissolving tests and the like, reduction in the strength of the bond between the ceramic element and the thick film electrode caused by plating liquid permeating into the inside of the thick film electrode can be suppressed and cracking of the ceramic element can be prevented.

Because the softening point of borosilicate zinc glass is about 570°C to 700°C and borosilicate zinc glass readily sinters at over about 600°C, which is the temperature at the time of electrode formation, at this temperature it becomes too fluid and glass comes out onto the surface of the thick film electrode during baking of the conducting thick film composition. As a result, the plating liquid does not adhere well.

With borosilicate barium glass only, on the other hand, because it does not readily melt during baking of the conducting thick film composition, it hinders sintering of the conducting powder.

For this reason, in this invention, borosilicate zinc glass and borosilicate barium glass are blended together. Because the softening point of this borosilicate barium glass is over about 770°C, higher than that of borosilicate zinc glass, and it does not sinter readily at the temperature of the time of electrode formation, its fluidity

at that temperature is low. Making use of this, it is possible to adjust the fluidity of the glass with borosilicate barium glass and prevent glass from coming out onto the surface of the thick film electrode.

Accordingly, by blending borosilicate zinc glass and borosilicate barium glass it is possible to make a conducting thick film composition to which plating liquid readily adheres, with which the strength of the bond between a ceramic element and a thick film electrode is high and which plating liquid does not readily dissolve.

Also, because by this method it is possible to reduce the blended amount of glass powder, which had been included in large quantities in order to maintain the strength of the bond between the ceramic element and the thick film electrode, deterioration of the plating film adherence caused by glass melting and covering the surface of the thick film electrode can be prevented and soldering can be improved.

Also, the invention provides a conducting thick film composition including Cu powder, glass powder and an organic vehicle wherein the Cu powder comprises spherical powder and scaly powder and the glass powder comprises borosilicate zinc glass and borosilicate barium glass.

By means of this constitution, the invention makes it possible to prevent blistering of a thick film electrode and

cracking of a ceramic element occurring during electrode formation, further raise the strength of the bond between the ceramic element and the thick film electrode and further improve the adhesion of solder to the thick film electrode.

That is, because as a result of the Cu powder comprising spherical powder and scaly powder the occurrence of blistering of the surface of the thick film electrode is prevented, it is possible to raise the strength of the bond between the ceramic element and the thick film electrode.

Also, as a result of the glass powder comprising borosilicate zinc glass and borosilicate barium glass, plating liquid adheres well to the conducting thick film composition and does not readily dissolve it and consequently it is possible to make a conducting thick film composition with which the strength of the bond between the ceramic element and the thick film electrode is high.

Furthermore, because by this method it is possible to reduce the blended amount of glass powder, which had been included in large quantities in order to maintain the strength of the bond between the ceramic element and the thick film electrode, deterioration of the plating adherence caused by glass melting and covering the surface of the thick film electrode can be prevented and soldering can be improved.

In the invention, preferably, the Cu powder and the

glass powder in total are contained in the amount of 65 to 85wt% of the 100wt% of the conducting thick film composition and the organic vehicle is contained in the amount of 15 to 35wt% of the 100wt% of the conducting thick film composition. More preferably, the Cu and glass constitute about 65 to 78wt%.

That is, when the total amount of the Cu powder and the glass powder is over 65wt% of the conducting thick film composition, the viscosity of the conducting thick film composition is high, the levelability of the conducting thick film composition after it is coated is good and sagging and the like does not occur. Also, when the total amount of the Cu powder and the glass powder is under 85wt% of the conducting thick film composition, because the conducting thick film composition is pastelike, it is easy to coat. The amount of the organic vehicle is the remainder of the conducting thick film composition excluding the Cu powder and the glass powder.

In the invention, preferably, the glass powder is about 3 to 15wt%, more preferably about 5 to 10wt% of 100wt% of the conducting thick film composition.

That is, when the glass powder constitutes over 3wt% of the conducting thick film composition, a high bonding strength between a ceramic element and a thick film electrode formed after baking of the conducting thick film composition can be obtained. Also, when the glass powder

constitutes less than 15wt% of the conducting thick film composition, glass does not separate out onto the surface of the thick film electrode and the Ni/Sn plating adherence improves.

In the invention, preferably, the Cu powder comprises spherical powder and scaly powder and the average particle diameter of the spherical powder is 0.3 to 5.0 μ m.

That is, when the average particle diameter is over 0.3 μ m, because the particles are large they are not readily oxidized. When the average particle diameter is 5.0 μ m or less, because the sintered density is high the composition becomes fine and the moisture resistance improves.

In the invention, more preferably, the Cu powder comprises spherical powder and scaly powder and the average particle diameter of the spherical powder is 0.3 to 1.5 μ m.

The reason for this is that an average particle diameter of the spherical powder in the range 0.3 to 1.5 μ m is optimum.

In the invention, preferably, the Cu powder comprises spherical powder and scaly powder and the spherical powder comprises a fine spherical powder of which the average particle diameter is 0.3 to 1.5 μ m and a coarse spherical powder of which the average particle diameter is in the range 2.0 to 5.0 μ m.

That is, by mixing a scaly powder with a fine

spherical powder of which the average particle diameter is 0.3 to 1.5 μ m and then further mixing with this a coarse spherical powder of which the average particle diameter is 2.0 to 5.0 μ m, the coating form further improves.

Also, in the invention, preferably, the Cu powder comprises a spherical powder and a scaly powder and the average length of the scaly powder is 10.0 to 40.0 μ m.

That is, when the average length is over 10.0 μ m, an ample effect of retarding the sintering can be obtained. When the average length is under 40.0 μ m, the Cu powder is easy to coat onto the ceramic element itself, which is small, and its surface can be made smooth.

Preferably, the scaly powder is contained in the amount of 10wt% to 70wt% of the total 100wt% of the fine spherical powder, the coarse spherical powder and the scaly powder.

The reason for this is that when the contained amount of the scaly powder is over 10wt%, because it does not become very fine during sintering of the conducting thick film composition the amount of glass flowing out onto the surface of the thick film electrode is small and as a result plating adheres easily to the surface of the thick film electrode. When the contained amount of the scaly powder is below 70wt%, the coatability of the thick film electrode is good and the sintered density is high and consequently the

conducting thick film composition resists the penetration of plating liquid.

In the invention, preferably, the glass powder comprises borosilicate zinc glass and borosilicate barium glass and the borosilicate zinc glass is more than about 50wt% of 100wt% of the glass powder. Preferably, it constitutes about 50 to 80wt% of the glass.

That is, when borosilicate zinc glass constitutes over 50wt% of the 100wt% of the glass powder sintering is rapid because the blended amount of borosilicate zinc glass is large and the blended amount of borosilicate barium glass is small, at the same temperature the composition becomes finer and the sintered density is higher and consequently the composition has a better heat shock property. When the borosilicate zinc glass is made 100wt%, excessive fluidity causes a glass layer to form on the surface and cover the Cu powder and consequently the plating process becomes difficult. Therefore, because the plating adherence is impaired, a borosilicate zinc glass content of 100wt% is not preferable.

In the invention, preferably, the glass powder comprises a borosilicate zinc glass and a borosilicate barium glass and the borosilicate zinc glass contains about 3 to 35wt% of ZnO in 100wt% of the borosilicate zinc glass.

That is, when the amount of the ZnO is greater than 3wt%, the composition has better Ni/Sn plating adherence

characteristics. When the amount of ZnO is less than 35wt%, the composition has better insulating and heat shock characteristics.

In the invention, preferably, the glass powder comprises a borosilicate zinc glass and a borosilicate barium glass and the borosilicate barium glass contains 10 to 40wt% of BaO in the 100wt% of the borosilicate barium glass.

That is, when the amount of the BaO is greater than 10wt%, the composition has better insulating, Ni/Sn plating adherence and heat shock characteristics. When this amount is less than 40wt%, the composition has better insulating and heat shock characteristics.

Also, in the invention, preferably, the glass powder comprises a borosilicate zinc glass and a borosilicate barium glass and the borosilicate zinc glass and the borosilicate barium glass contain at least one of alumina, an alkali metal oxide and an alkali earth metal oxide.

The reason for this is that when alumina is added the acid resistance of the composition is improved and when an alkali metal oxide or an alkali earth metal oxide is added the softening point of the borosilicate zinc glass and the borosilicate barium glass is lowered and the glass powder is made to melt more readily.

The invention also provides a thick film electrode

formed on a ceramic element of a ceramic electronic component, the thick film electrode comprising a sintered film made by sintering a conducting thick film composition according to the invention.

That is, a sintered film to constitute a thick film electrode can be formed by sintering the above-mentioned conducting thick film composition by heating the conducting thick film composition at a specific temperature for example in the range 600°C to 800°C.

The invention also provides a ceramic electronic component comprising a ceramic element and a terminal electrode formed on the ceramic element the terminal electrode comprising a thick film electrode according to the invention.

That is, it is possible to prevent blistering of a thick film electrode and cracking of a ceramic element occurring during formation of a terminal electrode of a ceramic electronic component, improve the strength of the bond between the ceramic element and the terminal electrode and improve the adhesion of solder to the terminal electrode.

Also, the invention provides a laminated ceramic capacitor comprising a stack made up of a ceramic dielectric layer and internal electrodes disposed facing each other with the ceramic dielectric layer therebetween and external

electrodes each having one end connected to one of the internal electrodes, the external electrodes consisting of thick film electrodes according to the invention.

That is, it is possible to prevent blistering of a thick film electrode and cracking of a stack occurring during formation of an external electrode of a laminated ceramic capacitor, improve the strength of the bond between the stack and the external electrode and improve the adherence of solder to the external electrode.

Brief Description of the Drawings

Fig. 1 is a sectional view of a preferred embodiment of the invention; and

Fig. 2 is a sectional view of another preferred embodiment of the invention.

Detailed Description of the Preferred Embodiments

A preferred embodiment of a thick film electrode consisting of a sintered film made by sintering a conducting thick film composition according to the invention will now be described with reference to cases wherein such thick film electrodes are used in a platelike ceramic capacitor and a laminated ceramic capacitor, which are ceramic electronic components.

Fig. 1 is a sectional view of a platelike ceramic capacitor.

As shown in Fig. 1, this platelike ceramic capacitor

has a platelike ceramic dielectric 1 which is a ceramic element, a pair of terminal electrodes 3 disposed facing each other on the main flat surfaces of the ceramic dielectric 1, lead terminals 4 soldered to the terminal electrodes 3, and covering resin 2.

The ceramic dielectric 1 is made for example of a porcelain material such as barium titanate or lead niobate, the terminal electrodes 3 are formed on opposite main flat surfaces of the ceramic dielectric 1 and the covering resin 2 covers the ceramic dielectric 1 and the terminal electrodes 3.

The lead terminals 4 are provided for connecting the terminal electrodes 3 to a circuit board not shown in the drawing and each have one end embedded in the covering resin 2 and connected to one of the terminal electrodes 3 and the other end projecting from the covering resin 2 and connected to the circuit board.

Fig. 2 is a sectional view of a laminated ceramic capacitor.

As shown in Fig. 2, this laminated ceramic capacitor has a rectangular parallelepiped shaped stack 5 and a pair of external electrodes 7a, 7b disposed facing each other on the ends of the stack 5.

Here, the stack 5 is made by sintering and thereby integrating a laminated plurality of ceramic sheets 6 which

are ceramic dielectric layers consisting of for example a porcelain material such as barium titanate or lead niobate.

Pluralities of internal electrodes 9a, 9b are disposed alternately inside the stack 5.

The internal electrodes 9a are connected to the external electrode 7a disposed on one side of the stack 5 and are insulated from the external electrode 7b disposed on the other side of the stack 5.

The internal electrodes 9b are connected to the external electrode 7b and are insulated from the external electrode 7a. The internal electrodes 9a, 9b are disposed in parallel with each other.

The terminal electrodes 3 of the platelike ceramic capacitor and the external electrodes 7a, 7b of the laminated ceramic capacitor described above are thick film electrodes consisting of sintered films formed by baking a conducting thick film composition according to the invention.

Next, conducting thick film compositions according to the invention will be described in detail.

(First Preferred Embodiment)

Conducting thick film compositions according to this invention all contain a Cu powder, a glass powder and an organic vehicle.

In this preferred embodiment, the Cu powder and the

glass powder together are blended in the amount of 65 to 85wt% of the 100wt% of the conducting thick film composition and the glass powder is blended in the amount of 3 to 15wt% of the 100wt% of the conducting thick film composition.

As the Cu powder, a mixture of a spherical powder and a scaly powder having different particle shapes is used.

This spherical powder consists of substantially spherical Cu particles and is made up of a fine spherical powder A of average particle diameter 0.3 to 1.5 μ m and a coarse spherical powder B of average particle diameter 2.0 to 5.0 μ m.

The scaly powder is a scaly powder C consisting of flake-shaped particles of about several μ m in thickness and average length 10.0 to 40.0 μ m.

As the glass powder, borosilicate zinc glasses and borosilicate barium glasses set forth in a second preferred embodiment described below are used.

That is, the borosilicate zinc glass is glass powder containing ZnO-SiO₂-B₂O₃ and bonded with other components such as alumina, alkali metal oxides such as Li₂O and alkali earth metal oxides such as CaO.

The borosilicate barium glass is glass powder containing BaO-SiO₂-B₂O₃ and bonded with other components such as alumina, alkali metal oxides such as Li₂O and alkali earth metal oxides such as CaO, BaO.

The borosilicate zinc glass in the glass powder is blended in the amount of 50wt% or more of the 100wt% of the glass powder.

Here the borosilicate zinc glass contains ZnO in the amount of 3 to 35wt% of the 100wt% of the borosilicate zinc glass and the borosilicate barium glass contains BaO in the amount of 10 to 40wt% of the 100wt% of the borosilicate barium glass.

As the organic vehicle, an acrylic resin base resin, dissolved in butyl cellosolve, which is an organic solvent, is used.

Table 1 shows for conducting thick film compositions of preferred embodiments 1-1 to 1-16 the Cu powder blend ratio (the respective blend proportions of the fine spherical powder A, the coarse spherical powder B and the scaly powder C of the 100wt% of the total of these three), an Ni/Sn plating film adherence evaluation, the electrode bond strength, the presence or absence of blisters and an overall evaluation.

Table 1

	Cu powder blend ratio			Ni/Sn plating film adherence	electrode bond strength (N)	blisters	overall evaluation
embodiment	A	B	C				
1-1	90	0	10	○	45	○	○
1-2	80	0	20	○	42	○	○
1-3	80	10	10	○	43	○	○
1-4	70	20	10	○	45	○	○
1-5	70	10	20	○	41	○	○
1-6	60	30	10	○	43	○	○
1-7	60	20	20	○	45	○	○
1-8	60	10	30	○	40	○	○
1-9	50	30	20	○	45	○	○
1-10	50	40	10	○	42	○	○
1-11	50	10	40	○	38	○	○
1-12	40	40	20	○	40	○	○
1-13	40	20	40	○	36	○	○
1-14	30	50	20	○	43	○	○
1-15	20	70	10	○	41	○	○
1-16	10	20	70	○	34	○	○
	Cu powder blend ratio			Ni/Sn plating film adherence	electrode bond strength (N)	blisters	overall evaluation
reference example	A	B	C				
1-1	100	0	0	x	40	x	x
1-2	0	100	0	x	40	x	x
1-3	0	0	100	○	26	○	x

For reference, Table 1 also shows an Ni/Sn plating film adherence evaluation, the electrode bond strength, the presence or absence of blisters and an overall evaluation for three compositions, reference example 1-1 to reference example 1-3, each containing one of the fine spherical powder A, the coarse spherical powder B and the scaly powder C as 100wt% of the Cu powder.

Next, measurement methods and measurement results of the evaluations of the Ni/Sn plating film adherence, the electrode bond strength and the presence or absence of blisters will be described as will the overall evaluations based on these results.

To evaluate the Ni/Sn plating film adherence, first, external electrodes were formed on both ends of a laminated ceramic capacitor chip by baking at about 800°C in a nitrogen atmosphere and Ni/Sn plating was carried out. Then, the film thickness of the Ni/Sn plating film was measured with a fluorescence X-ray film thickness meter and when the film thickness was greater than 1μm the film was deemed good as indicated with a ° in Table 1 and when it was less than 1μm the film was deemed defective as indicated with a x in Table 1.

In both reference example 1-1 and reference example 1-2 the film thickness of the Ni/Sn plating film was less than 1μm, it could also be seen from the external appearance that

the Cu electrode was exposed, and the plating adherence was therefore defective.

In the case of reference example 1-1 the reason for this is probably that because only the spherical powder A was blended as the Cu powder the void rate of the thick film electrode during sintering was insufficient and consequently deterioration in the Ni/Sn plating film adherence caused by glass melting and covering the surface of the thick film electrode occurred.

In the case of reference example 1-2 the reason is probably that because only the spherical powder B was blended as the Cu powder deterioration in the Ni/Sn plating film adherence occurred in the same way as in reference example 1-1.

Accordingly, from the evaluation of the Ni/Sn plating film adherence it can be seen that not only just the spherical powder A or just the spherical powder B but also the scaly powder C which increases the void rate of the thick film electrode is necessary in the Cu powder.

With respect to the electrode bond strength, first a wire was soldered to the end surface of the thick film electrode, both ends of the thick film electrode were pulled and the size of the force (units: N) at the time when the thick film electrode and the wire parted is shown in Table 1; the electrode bond strength was deemed to be good when

the force was greater than 30N and deemed to be defective when the force was less than 30N.

In reference example 1-3 the electrode bond strength (N) was, at 26N, less than 30N and therefore deemed to be defective, and the thick film electrode had peeled off at its interface with the chip.

The reason for this is probably that in reference example 1-3 because only the scaly powder C was blended as the Cu powder the bonding force with glass was small and the thick film electrode consequently peeled off relatively easily and the electrode bond strength had therefore decreased.

The presence or absence of blisters was determined from the external appearance of a thick film electrode of a laminated ceramic capacitor formed by the manufacturing method described above. When air bubbles formed at the surface of the thick film electrode and irregularities had formed in the thick film electrode it was deemed that blistering had occurred and this was shown by a x in Table 1, and when not this was shown with a $\circ$ in Table 1.

Blistering occurred in both reference example 1-1 and reference example 1-2.

In the case of reference example 1-1 the reason for this is probably that because only the spherical powder A was blended as the Cu powder the void rate of the thick film

electrode during sintering was insufficient and consequently there was no way for produced gas to escape and blistering occurred as a result.

In the case of reference example 1-2 the reason is probably that because only the spherical powder B was blended as the Cu powder the void rate of the thick film electrode during sintering was insufficient and consequently there was no way for produced gas to escape and blistering occurred as a result as it did in the case of reference example 1-1.

Accordingly, because preferred embodiment 1-1 to preferred embodiment 1-16 were deemed good in Ni/Sn plating film adherence, electrode bond strength and the presence or absence of blistering, this is indicated by a ° in Table 1. Because reference example 1-1 to reference example 1-3 were deemed to be defective in Ni/Sn plating film adherence, electrode bond strength or the presence or absence of blistering this is indicated by a x in Table 1.

The conducting thick film composition of the present invention is not limited to the preferred embodiment described above and various changes can be made within the scope of the invention.

For example, although in the preferred embodiment described above borosilicate zinc glass and borosilicate barium glass set forth in the second preferred embodiment

described below were used as the glass powder, just borosilicate zinc glass may be used or just borosilicate barium glass may be used. Alternatively, some other glass may be used. In any case the objects of the invention can be achieved.

Also, for example, although in the preferred embodiment described above an acrylic resin base resin dissolved in butyl cellosolve, which is an organic solvent, is used as the organic vehicle, a cellulose resin or a butyral resin or the like may be used as the base resin and terpeneol may be used as the organic solvent.

(Second Preferred Embodiment)

Conducting thick film compositions according to this invention all contain a Cu powder, a glass powder and an organic vehicle.

In this preferred embodiment, the Cu powder and the glass powder together are blended in the amount of 65 to 85wt% of the 100wt% of the conducting thick film composition and the glass powder is blended in the amount of 3 to 15wt% of the 100wt% of the conducting thick film composition.

As the glass powder, borosilicate zinc glass and borosilicate barium glass are used.

That is, the borosilicate zinc glass is a glass powder containing $\text{ZnO-SiO}_2\text{-B}_2\text{O}_3$ and bonded with other components such as alumina, alkali metal oxides such as Li_2O and alkali

earth metal oxides such as CaO.

The borosilicate barium glass is a glass powder containing $\text{BaO-SiO}_2\text{-B}_2\text{O}_3$ and bonded with other components such as alumina, alkali metal oxides such as Li_2O and alkali earth metal oxides such as CaO, BaO.

As the Cu powder, the same Cu powder as that set forth in the first preferred embodiment was used.

That is, as the Cu powder, a mixture of a spherical powder and a scaly powder having different particle shapes is used.

This spherical powder consists of substantially spherical Cu particles and is made up of a fine spherical powder A of average particle diameter 0.3 to $1.5\mu\text{m}$ and a coarse spherical powder B of average particle diameter 2.0 to $5.0\mu\text{m}$.

The scaly powder is a scaly powder C consisting of flake-shaped particles of several μm in thickness and average length 10.0 to $40.0\mu\text{m}$.

As the organic solvent, an acrylic resin dissolved in butyl cellosolve was used.

Table 2 shows for conducting thick film compositions of preferred embodiments 2-1 to 2-10 frit numbers showing composition ratios of respective borosilicate zinc glasses (Zn type) and borosilicate barium glasses (Ba type), the wt% of the glass powder with respect to the 100wt% of the

conducting thick film composition, the wt% of the borosilicate zinc glass with respect to the 100wt% of the glass powder, the insulation resistance NG count, the Ni/Sn plating film adherence, the heat shock property and an overall evaluation based on these.

Table 2

	frit number		amount of glass powder added (wt%)	wt% of Zn type glass	insulation resistance NG count (n=20)	Ni/Sn plating film adherence	heat shock property $\Delta T=375^{\circ}\text{C}$	overall evaluation
embodiment	Zn type	Ba type						
2-1	B	H	4.0	70	0	○	○	○
2-2	B	H	9.0	50	0	○	○	○
2-3	B	H	9.0	70	0	○	○	○
2-4	B	H	9.0	90	0	○	○	○
2-5	B	H	9.0	100	0	○	○	○
2-6	B	H	13.0	70	0	○	○	○
2-7	B	G	9.0	70	0	○	○	○
2-8	B	I	9.0	70	0	○	○	○
2-9	A	H	9.0	70	0	○	○	○
2-10	C	H	9.0	70	0	○	○	○
	frit number		amount of glass powder added (wt%)	wt% of Zn type glass	insulation resistance NG count (n=20)	Ni/Sn plating film adherence	heat shock property $\Delta T=375^{\circ}\text{C}$	overall evaluation
reference example	Zn type	Ba type						
2-1	B	H	1.0	70	15	○	x	x
2-2	B	H	9.0	20	0	○	x	x
2-3	B	H	20.0	70	0	x	○	x
2-4	B	F	9.0	70	10	x	x	x
2-5	B	J	9.0	70	3	○	x	x
2-6	D	H	9.0	70	10	○	x	x
2-7	E	H	9.0	70	0	x	○	x
2-8	B	H	2.0	60	15	○	x	x
2-9	B	H	17.0	50	0	x	○	x

For reference, reference examples 2-1 to 2-9 are also shown in Table 2.

Also, in Table 3 are shown composition ratios (units are wt%) of frit numbers A, B, C which are preferred examples of borosilicate zinc glasses, composition ratios (units are wt%) of frit numbers G, H, I which are preferred examples of borosilicate barium glasses, composition ratios (units are wt%) of frit numbers D, E which are reference examples of borosilicate zinc glasses, and composition ratios (units are wt%) of frit numbers F, J which are reference examples of borosilicate barium glasses.

Table 3

embodiment		ZnO	BaO	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Li ₂ O	CaO
borosilicate zinc glass	A	4	-	50	30	2	10	4
	B	20	-	20	50	2	5	3
	C	35	-	35	20	0	5	5
borosilicate barium glass	G	-	15	10	50	10	6	4
	H	-	30	45	15	0	6	4
	I	-	40	10	30	10	6	4
reference example		ZnO	BaO	SiO ₂	B ₂ O ₃	Al ₂ O ₃	Li ₂ O	CaO
borosilicate zinc glass	D	50	-	10	30	0	5	5
	E	2	-	50	40	2	5	1
borosilicate barium glass	F	-	5	40	30	10	6	4
	J	-	55	10	15	10	6	4

Next, measurement methods and measurement results of the evaluations of the insulation resistance NG count, the Ni/Sn plating film adherence and the heat shock property will be described and then the overall evaluations based on these results will be discussed.

To evaluate the insulation resistance NG count, first, external electrodes were formed on both ends of a laminated ceramic capacitor chip by baking at about 800°C in a nitrogen atmosphere and Ni/Sn plating was carried out. Then, the insulation resistance across the two electrodes was measured and deemed to be NG when the resistance value was below $1 \times 10^9 \Omega$. This measurement was carried out for 20 laminated ceramic capacitors and the number of NG capacitors shown in Table 2. When there were no NG laminated ceramic capacitors the example was deemed to be good, but if there was even one NG laminated ceramic capacitor the example was deemed to be inferior.

In reference example 2-1 there were 15 NG laminated ceramic capacitors out of 20 and the example was therefore inferior.

The reason for this is that because the added amount of glass powder was small, at 1.0wt%, deterioration in insulation resistance occurred due to cracking occurring in the laminated ceramic capacitor and shorting occurring and the like.

In reference example 2-4 there were 10 NG laminated ceramic capacitors out of 20 and the example was therefore inferior.

The reason for this is that because in the composition ratios of the frit number F borosilicate barium glass the proportion of BaO was low, at 5wt%, with respect to the 100wt% of the glass powder, deterioration in insulation resistance occurred due to cracking occurring in the laminated ceramic capacitor and shorting occurring and the like.

In reference example 2-5 there were 3 NG laminated ceramic capacitors out of 20 and the example was therefore inferior.

The reason for this is that because in the composition ratios of the frit number J borosilicate barium glass the proportion of BaO was high, at 55wt%, with respect to the 100wt% of the glass powder, deterioration in insulation resistance occurred due to cracking occurring in the laminated ceramic capacitor and shorting occurring and the like.

In reference example 2-6 there were 10 NG laminated ceramic capacitors out of 20 and the example was therefore inferior.

The reason for this is that because in the composition ratios of the frit number D borosilicate zinc glass the

proportion of ZnO was high, at 50wt%, with respect to the 100wt% of the glass powder, deterioration in insulation resistance occurred due to cracking occurring in the laminated ceramic capacitor and shorting occurring and the like.

In reference example 2-8 there were 15 NG laminated ceramic capacitors out of 20 and the example was therefore inferior.

The reason for this is that because the added amount of glass powder was small, at 2.0wt%, deterioration in insulation resistance occurred due to cracking occurring in the laminated ceramic capacitor and shorting occurring and the like.

Accordingly, it can be seen that in insulation resistance NG count it is preferable that the added amount of glass powder be above 3.0wt%.

It can also be seen that it is preferable that the BaO in the borosilicate barium glass composition constitute more than 10wt% of the 100wt% of the glass powder.

It can also be seen that it is preferable that the BaO in the borosilicate barium glass composition constitute less than 40wt% of the 100wt% of the glass powder.

It can also be seen that it is preferable that the ZnO in the borosilicate zinc glass composition constitute less than 35wt% of the 100wt% of the glass powder.

To evaluate the Ni/Sn plating film adherence, first, external electrodes were formed on both ends of a laminated ceramic capacitor chip by baking at about 800°C in a nitrogen atmosphere and Ni/Sn plating was carried out. Then, the film thickness of the Ni/Sn plating film was measured with a fluorescence X-ray film thickness meter and when the film thickness was greater than 1μm the film was deemed to be good as indicated with a ° in Table 2 and when it was less than 1μm the film was deemed inferior as indicated with a x in Table 2.

In reference example 2-3 the film thickness of the Ni/Sn plating film was less than 1μm, it could also be seen from the external appearance that the Cu electrode was exposed, and the plating adherence was therefore inferior.

The reason for this is that because the added amount of glass powder was high, at 20.0wt%, glass separated out onto the surface of the thick film electrode and the Ni/Sn plating film adherence consequently fell.

In reference example 2-4 the film thickness of the Ni/Sn plating film was less than 1μm, it could also be seen from the external appearance that the Cu electrode was exposed, and the plating adherence was therefore inferior.

The reason for this is that because in the composition ratios of the frit number F borosilicate barium glass the proportion of BaO was low, at 5wt% with respect to the

100wt% of the glass powder, the Ni/Sn plating film adherence was low.

In reference example 2-7 the film thickness of the Ni/Sn plating film was less than $1\mu\text{m}$, it could also be seen from the external appearance that the Cu electrode was exposed, and the plating adherence was therefore inferior.

The reason for this is that because in the composition ratios of the frit number D borosilicate zinc glass the proportion of ZnO was low, at 2wt% with respect to the 100wt% of the glass powder, the Ni/Sn plating adherence was low.

In reference example 2-9 the film thickness of the Ni/Sn plating film was less than $1\mu\text{m}$, it could also be seen from the external appearance that the Cu electrode was exposed, and the plating adherence was therefore inferior.

The reason for this is that because the added amount of glass powder was high, at 17.0wt%, glass separated out onto the surface of the thick film electrode and the Ni/Sn plating adherence consequently fell.

Accordingly, it can be seen that in Ni/Sn plating film adherence it is preferable that the added amount of glass powder be 15.0wt% or less.

It can also be seen that it is preferable that the BaO in the composition of the borosilicate barium glass constitute more than 10wt% of the 100wt% of the glass

powder.

It can also be seen that it is preferable that the ZnO in the composition of the borosilicate zinc glass constitute more than 3wt% of the 100wt% of the glass powder.

To evaluate heat shock property, first, external electrodes were formed on both ends of a laminated ceramic capacitor chip by baking at about 800°C in a nitrogen atmosphere and Ni/Sn plating was carried out. Then, this laminated ceramic capacitor was dipped in a 400°C solder tank for about two seconds.

When at this time cracking occurred in the laminated ceramic capacitor it was deemed to be inferior and this was indicated by a x in Table 2. When cracking did not occur the laminated ceramic capacitor was deemed to be good and this was indicated by a o in Table 2. In Table 2, $\Delta T = 375^\circ\text{C}$ means $\Delta T = (400^\circ\text{C solder tank} - 25^\circ\text{C room temperature})$.

In reference example 2-1 cracking occurred in the laminated ceramic capacitor and it was therefore deemed to be inferior.

The reason for this was that cracking occurred because the added amount of glass powder was small, at 1.0wt%.

In reference example 2-2 cracking occurred in the laminated ceramic capacitor and it was therefore deemed to be inferior.

The reason for this cracking occurring was that the wt% of the borosilicate zinc glass was low, at 20wt%.

In reference example 2-4 cracking occurred in the laminated ceramic capacitor and it was therefore deemed to be inferior.

The reason for this cracking occurring was that in the composition ratios of the frit number F borosilicate barium glass the proportion of BaO was small at 5wt% with respect to the 100wt% of the glass powder.

In reference example 2-5 cracking occurred in the laminated ceramic capacitor and it was therefore deemed to be inferior.

The reason for this cracking occurring was that in the composition ratios of the frit number J borosilicate barium glass the proportion of BaO was large at 55wt% with respect to the 100wt% of the glass powder.

In reference example 2-6 cracking occurred in the laminated ceramic capacitor and it was therefore deemed to be inferior.

The reason for this cracking occurring was that in the composition ratios of the frit number D borosilicate barium glass the proportion of ZnO was large at 50wt% with respect to the 100wt% of the glass powder.

In reference example 2-8 cracking occurred in the laminated ceramic capacitor and it was therefore deemed to

be inferior.

The reason for this cracking occurring was that the added amount of glass powder was small, at 2.0wt%.

Accordingly, it can be seen that in heat shock property it is preferable that the added amount of glass powder be over 3.0wt%.

It can also be seen that it is preferable that the borosilicate zinc glass constitute more than 50wt% of the 100wt% of the glass powder.

It can also be seen that it is preferable that the BaO in the composition of the borosilicate barium glass constitute more than 10wt% of the 100wt% of the glass powder.

It can also be seen that it is preferable that the BaO in the composition of the borosilicate barium glass constitute less than 40wt% of the 100wt% of the glass powder.

It can also be seen that it is preferable that the ZnO in the composition of the borosilicate zinc glass constitute less than 35wt% of the 100wt% of the glass powder.

Accordingly, the overall evaluations show that the reference examples 2-1 to 2-9 were inferior in one or more of the characteristics insulation resistance NG count, Ni/Sn plating adherence or heat shock property and were inferior to the preferred embodiments 2-1 to 2-10.

Although here the overall evaluations of the reference examples 2-1 to 2-9 are x indicating that they are less preferable than the preferred embodiments 2-1 to 2-10, these reference examples are all satisfactory compared with conventional examples and can achieve the objects of the invention.

The conducting thick film composition of the present invention is not limited to the preferred embodiment described above and various changes can be made within the scope of the invention.

For example, although in this preferred embodiment the Cu powder set forth in the first preferred embodiment was used, as long as the Cu powder comprises a spherical powder and a scaly powder the particle diameter or length need not be particularly limited. Also, just a spherical powder or just a scaly powder can be used if the particle diameter or length is adjusted. Furthermore, the particle shape need not be particularly limited. In any case the objects of the invention can be achieved.

Also, for example although in this preferred embodiment an acrylic resin constituting a base resin dissolved in butyl cellosolve, which is an organic solvent, is used as the organic vehicle, a cellulose resin or a butyral resin or the like may be used as the base resin and terpeneol may be used as the organic solvent.

In a conducting thick film composition according to the present invention, as a result of the Cu powder comprising a spherical powder and a scaly powder it is possible to prevent blistering of the surface of a thick film electrode and consequently it is possible to improve the strength of a bond between a ceramic element and a thick film electrode.

Also, because by this method it is possible to reduce the blended amount of glass powder, which had been included in large quantities in order to maintain the strength of the bond between the ceramic element and the thick film electrode, deterioration of the plating adherence caused by glass melting and covering the surface of the thick film electrode can be prevented and soldering can be improved, and therefore it is possible to improve the electrical reliability of a ceramic electronic component.

In the invention, as a result of the Cu powder comprising a borosilicate zinc glass and a borosilicate barium glass, plating liquid readily adheres and plating liquid does not readily dissolve and consequently reduction in the strength of the bond between the ceramic element and the thick film electrode caused by plating liquid permeating into the inside of the electrode can be suppressed and cracking of the ceramic element can be prevented.

Also, because by this method it is possible to reduce

the blended amount of glass powder, which had been included in large quantities in order to maintain the strength of the bond between the ceramic element and the thick film electrode, deterioration of the plating adherence caused by glass melting and covering the surface of the thick film electrode can be prevented and soldering can be improved, and therefore it is possible to improve the electrical reliability of a ceramic electronic component.

In the invention, as a result of the Cu powder comprising a spherical powder and a scaly powder and the glass powder comprising a borosilicate zinc glass and a borosilicate barium glass it is possible to prevent the occurrence of blistering of the surface of the thick film electrode and cracking of the ceramic element and consequently it is possible to further improve the strength of the bond between the ceramic element and the thick film electrode.

Also, because by this method it is possible to reduce the blended amount of glass powder, which had been included in large quantities in order to maintain the strength of the bond between the ceramic element and the thick film electrode, deterioration of the plating adherence caused by glass melting and covering the surface of the thick film electrode can be prevented and soldering can be improved, and therefore it is possible to improve the electrical

reliability of a ceramic electronic component.

In the invention, preferably, the Cu powder and the glass powder in total are contained in the amount of 65 to 85wt% of the 100wt% of the conducting thick film composition and the organic vehicle is contained in the amount of 15 to 35wt% of the 100wt% of the conducting thick film composition.

By this method it is possible to increase the conducting thick film composition levelability and improve its coatability.

In the invention, preferably, the glass powder is contained in the amount of 3 to 15wt% of the 100wt% of the conducting thick film composition.

By this method, by further increasing the strength of the bond between the ceramic element and the thick film electrode and increasing the plating adherence it is possible to further increase the solder adherence.

In the invention, preferably, the Cu powder comprises spherical powder and scaly powder and the average particle diameter of the spherical powder is 0.3 to 5.0 μ m.

By this method it is possible to prevent oxidization of the conducting thick film composition and improve its moisture resistance.

In the invention, more preferably, the Cu powder comprises a spherical powder and a scaly powder and the

average particle diameter of the spherical powder is 0.3 to 1.5 μ m.

By this method, a more optimal average particle diameter is adopted.

In the invention, preferably, the Cu powder comprises a spherical powder and a scaly powder and the spherical powder comprises a fine spherical powder of which the average particle diameter is 0.3 to 1.5 μ m and a coarse spherical powder of which the average particle diameter is 2.0 to 5.0 μ m.

By this method, it is possible to further improve the coatability of the conducting thick film composition.

Also, in the invention, preferably, the Cu powder comprises a spherical powder and a scaly powder and the average length of the scaly powder is 10.0 to 40.0 μ m.

By this method it is possible to increase the effect of the scaly powder of retarding the sintering and shapewise also improve the coatability and make the surface smooth.

In the invention, preferably, the glass powder comprises borosilicate zinc glass and borosilicate barium glass and the borosilicate zinc glass is contained in the amount of over 50wt% of the 100wt% of the glass powder.

By this method it is possible to improve the heat shock property of the conducting thick film composition.

In the invention, preferably, the glass powder

comprises a borosilicate zinc glass and a borosilicate barium glass and the borosilicate zinc glass contains 3 to 35wt% of ZnO with respect to the 100wt% of the borosilicate zinc glass.

By this method it is possible to improve the plating adherence, insulation characteristics and heat shock property of the composition.

In the invention, preferably, the glass powder comprises a borosilicate zinc glass and a borosilicate barium glass and the borosilicate barium glass contains 10 to 40wt% of BaO with respect to the 100wt% of the borosilicate barium glass.

By this method it is possible to improve the insulation characteristics, plating adherence and heat shock property of the composition.

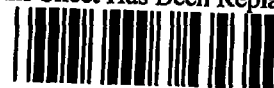
Also, in the invention, preferably, the glass powder comprises a borosilicate zinc glass and a borosilicate barium glass and the borosilicate zinc glass and the borosilicate barium glass contain at least one of alumina, an alkali metal oxide and an alkali earth metal oxide.

By this method, improvement of the acid resistance of the composition by the addition of alumina and improvement of the softening of the glass powder by the addition of an alkali metal oxide or an alkali earth metal oxide are possible.

With a thick film electrode according to the invention it is possible to form a sintered film to constitute a thick film electrode by sintering the above-mentioned conducting thick film composition and consequently a thick film electrode for a ceramic electronic component can be manufactured easily.

With a ceramic electronic component according to the invention it is possible to prevent blistering of a thick film electrode and cracking of a ceramic element occurring when terminal electrodes of the ceramic electronic component are being formed and improve the strength of the bond between the ceramic element and the terminal electrodes and improve the adherence of solder to the terminal electrodes.

With a laminated ceramic capacitor according to the invention it is possible to prevent blistering of a thick film electrode and cracking of a stack occurring when external electrodes of the laminated ceramic capacitor are being formed and improve the strength of the bond between the stack and the external electrodes and improve the adherence of solder to the external electrodes.

WHAT IS CLAIMED:

1. A conducting thick film composition comprising Cu powder, glass powder and organic vehicle wherein the Cu powder comprises spherical powder and scaly powder and the glass powder comprises borosilicate zinc glass and borosilicate barium glass.
2. A conducting thick film composition according to claim 1 wherein the Cu powder and the glass powder in total are contained in the amount of 65 to 85wt% of the 100wt% of the conducting thick film composition and the organic vehicle is contained in the amount of 15 to 35wt% of the 100wt% of the conducting thick film composition.
3. A conducting thick film composition according to any of claims 1 through 2 wherein the glass powder is contained in the amount of 3 to 15wt% of the 100wt% of the conducting thick film composition.
4. A conducting thick film composition according to any of claims 1 through 3 wherein the Cu powder comprises spherical powder and scaly powder and the average particle diameter of the spherical powder is 0.3 to 5.0 μ m.
5. A conducting thick film composition according to any of claims 1 through 4 wherein the Cu powder comprises spherical powder and scaly powder and the average particle diameter of the spherical powder is 0.3 to 1.5 μ m.





6. A conducting thick film composition according to any of claims 1 through 4 wherein the Cu powder comprises spherical powder and scaly powder and the spherical powder comprises fine spherical powder of which the average particle diameter is 0.3 to 1.5 μ m and coarse spherical powder of which the average particle diameter is 2.0 to 5.0 μ m.

7. A conducting thick film composition according to any of claims 1 through 6 wherein the Cu powder comprises spherical powder and scaly powder and the average length of the scaly powder is 10.0 to 40.0 μ m.

8. A conducting thick film composition according to any of claims 1 through 7 wherein the glass powder comprises borosilicate zinc glass and borosilicate barium glass and the borosilicate zinc glass is contained in the amount of over 50wt% of the 100wt% of the glass powder.

9. A conducting thick film composition according to any of claims 1 through 8 wherein the glass powder comprises borosilicate zinc glass and borosilicate barium glass and the borosilicate zinc glass contains 3 to 35wt% of ZnO with respect to the 100wt% of the borosilicate zinc glass.

10. A conducting thick film composition according to any of claims 1 through 9 wherein the glass powder comprises borosilicate zinc glass and borosilicate barium glass and the borosilicate barium glass contains 10 to 40wt% of BaO with respect to the 100wt% of the borosilicate barium glass.





11. A conducting thick film composition according to any of claims 1 through 10 wherein the glass powder comprises borosilicate zinc glass and borosilicate barium glass and the borosilicate zinc glass and the borosilicate barium glass contain at least one of alumina, an alkali metal oxide and an alkali earth metal oxide.

12. A thick film electrode formed on a ceramic element of a ceramic electronic component, the thick film electrode comprising a sintered film made by sintering a conducting thick film composition according to any of claims 1 through 11.

13. A ceramic electronic component comprising a ceramic element and a terminal electrode provided on the ceramic element, the terminal electrode comprising a thick film electrode according to claim 12.

14. A laminated ceramic capacitor comprising a stack made up of a ceramic dielectric layer laminated with internal electrodes disposed facing each other with the ceramic dielectric layer therebetween and external electrodes disposed facing each other on both ends of the stack each connected to one end of the internal electrodes, the external electrodes comprising thick film electrodes according to claim 12.

