

ELECTROCONDUCTIVE PASTE AND PROCESS FOR PRODUCING
ELECTROCONDUCTIVE METALLIZED CERAMICS USING THE SAME"

1 This invention relates to a highly electro-
conductive paste for forming wiring conductor layers
and a process for producing a highly electroconductive
metallized ceramic by applying said electroconductive
5 paste to sintered or unsintered alumina ceramic sub-
strates.

Heretofore, in order to form conductor layers
on the surfaces or interiors of alumina ceramic sub-
strates which are used in ceramic wiring boards and
10 packages, it has been necessary to print a conductive
paste, for example, by a thick film forming method
and to sinter it. In such a case, as a process for
forming wiring conductor layers, there has been used,
for example, a dry thick film wiring process in which
15 a silver-palladium (Ag-Pd) series conductive paste
mixed with glass frit as a binding agent is screen
printed on a sintered alumina ceramic substrate and
a conductor wiring layer is formed by melt binding the
conductive paste at high temperatures. But the dry
20 thick film wiring process has many disadvantages in
that adhesive strength to the substrate is not so good
because of melt binding by using a glass frit, wiring
conductors are easily peeled off during the usage
and some properties such as thermal shock properties
25 are insufficient when said process is applied to high

density wiring boards which require high adhesive strength, and said process is very expensive since noble metal conductors are used therein.

On the other hand, there have been proposed wiring
5 conductor forming processes for overcoming the disadvantages of the dry thick film wiring process. These processes are, for example, a molybdenum-manganese (Mo-Mn) metallizing process, a molybdenum (Mo) metallizing process, and a tungsten (W) metallizing process. The Mo-Mn metallizing
10 process is used for the metal-sealing of electron tubes and production of semiconductor products. However, according to this process, since sintered substrates are used, it is necessary to conduct a sintering step at least twice in order to form conductor layers. This
15 makes the procedure both complicated and costly. Further, it is difficult to apply this process to high density wiring boards, since dimensional accuracy is poor and reproducibility is low according to this process. In contrast, according to the Mo metallizing process and the
20 W metallizing process, a metal paste such as a Mo paste or a W paste is screen printed on an unsintered alumina ceramic substrate by a thick film forming method. The alumina ceramic substrate and the metal paste are fired simultaneously. According to these processes, strong
25 adhesion is obtained which cannot be expected when sintered alumina ceramic substrates are employed, since the alumina ceramic substrate and the metal paste readily diffuse mutually during the firing. But when these processes are

applied, for example, to highly pure alumina ceramics having an alumina purity of 90% or higher and which are generally used for high density wiring boards with excellent electrical properties, it is necessary to
5 meet properly the sintering temperature of the alumina ceramics and the sintering temperature of the metal paste in order to complete the sintering of the alumina ceramics and to obtain strong adhesion between the substrate and the conductor layer, since the content
10 of metal oxides which react with the metal paste and diffuse is small in the alumina ceramics. Therefore, as the metal paste, there has been used a paste obtained by mixing metal powders such as tungsten powders which are made dense and have a particle size of, e.g. 5 μm or
15 more and readily meeting the sintering temperature of the alumina ceramics, a binding agent and a solvent. But the electric resistance of the conductor layer of the wiring board produced by using such a paste is changed remarkably depending on the particle size of the
20 metal powder such as tungsten and on the sintering temperature. That is, according to the experiments carried out by the present inventors, the electrical resistance of the tungsten conductor layer formed on the alumina ceramic substrate and having good adhesive
25 strength thereto was 0.03 $\text{m}\Omega\text{cm}$ when a paste containing tungsten particle size of 1 μm was used, said value being remarkably high compared with the electrical resistance

value of metallic tungsten ($0.0055 \text{ m}\Omega \text{ cm}$), and $0.05 \text{ m}\Omega \text{ cm}$ when the tungsten particle size was $3.8 \text{ }\mu\text{m}$. Therefore, when said process is applied to multi-layer wiring boards having high wiring density or IC packages, there are many disadvantages in designing wiring in that distances between wiring should be made narrower, the number of layers should be increased for making multi-layer structure, and the like. On the other hand, when a tungsten paste obtained by using tungsten powders having a particle size of $0.5 \text{ }\mu\text{m}$ or less is used in order to improve the above-mentioned disadvantages and to obtain high electroconductivity, the formation of wiring conductor layer becomes difficult, since proper meeting with the sintering temperature of the alumina ceramics can hardly be obtained, which results in remarkable decrease in metallizing strength, generation of cracks on or peeling of the metallized layer after sintering.

It is an object of this invention to provide a highly electroconductive metal paste for metallizing and also useful for the Mo metallizing process, the Mo-Mn metallizing process and the like as well as the W metallizing process and a process for producing said metal paste. It is another object of this invention to provide a process for producing highly electroconductive metallized ceramics having high adhesive strength by applying said metal paste for metallizing to sintered or unsintered alumina ceramic substrates.

This invention provides an electroconductive paste for metallizing comprising:

(a) 100 parts by weight of a powder of a metal having a melting point of at least 1700°C,

5 (b) 0.1 to 3 parts by weight of an additive which can fill vacant spaces among particles of said metal powder and can shrink and increase the density of said metal powder without influencing the sintering rate of said metal powder,

10 (c) a binding agent, and
(d) a solvent.

According to the invention this paste is produced by uniformly dispersing components (a), (b), (c) and (d).

This invention also provides a process for producing an electroconductive metallized ceramic which comprises
15 coating said metal paste for metallizing on an alumina ceramic substrate and firing said metal paste to form a metallized layer.

The metal powder (a) (referred to herein as "high-
20 melting metal powder") used in this invention has a melting point of at least 1700°C such as W, Mo, Mo-Mn, Pt alone or a mixture thereof. In order to disperse the metal powders uniformly in the paste, those having a smaller particle size such as 0.3 to 8 μ m are preferably used.

25 The additive (b) should have such a function as filling vacant spaces among particles of said high-melting metal powder and shrink and increase the density of said high-melting metal powder without influencing the sinter-

ing rate of said high-melting metal powder. Examples of the additive are so-called sintering promoters for alumina and alumina ceramics such as magnesium oxide, calcium oxide, silicon dioxide, aluminum oxide, or a mixture
5 thereof.

The additive such as sintering promoters for alumina and alumina ceramics is used in an amount of 0.1 to 3.0 parts by weight per 100 parts by weight of the high-melting metal powder. If the amount of the
10 additive is outside the above-mentioned range, the object of this invention cannot be attained.

As the binding agent, there can be used cellulose derivative resins such as ethyl cellulose, nitrocellulose, etc, acrylic resins, alkyd and phenolic resins, vinyl
15 resins, epoxy resins, and the like. The binding agent is usually used in an amount of 2 to 20 parts by weight per 100 parts by weight of the high-melting metal powder.

As the solvent for making a paste, there can
20 be used aromatic solvents such as toluene, xylene, benzene, etc.; ester series solvents such as ethyl acetate, butyl acetate, butyric acid esters, propionic acid esters, etc.; ketone series solvents such as

1 methyl ethyl ketone, cyclohexanone, etc.; alcohol series
solvents such as ethyl alcohol, butyl alcohol, ethylene
glycol monobutyl ether, ethylene glycol derivatives,
and the like. These solvent should be able to dissolve
5 the binding agent.

The solvent is used in an amount sufficient
for uniformly dispersing and mixing the high-melting
metal powder, the additive and the binding agent. Con-
sidering the removal of the solvent at the time of
10 producing metallized ceramics, it is usually used in
an amount of 5 to 100 parts by weight per 100 parts
by weight of the high-melting metal powder.

The highly electroconductive metal paste for
metallizing can be prepared by mixing the high-melting
15 metal powder, the additive, the binding agent and
the solvent by using a mixing and grinding machine.
In addition, there can also be used a roll mill, a ball
mill, an impeller mill, an oscillating mill, or the
like depending on the viscosity of the metal paste.

20 Metallized ceramics are produced by coating
the above-mentioned metal paste for metallizing on
a substrate by a conventional process and firing the
paste to form a metallized layer strongly binded to
the substrate.

25 As the substrate, there can be used alumina
ceramics, particularly preferably unsintered alumina
ceramics. When very great adhesive strength is not
necessary or the requirement for dimensional accuracy

- 1 is not so strict, sintered alumina ceramic substrates usually used may be employed.

After coating the metal paste for metallizing on the alumina ceramic substrate by a conventional
5 process such as a printing process (screen printing, offset printing, etc.), if necessary, the metal paste is dried at a temperature from room temperature to 160°C, and it is fired at a temperature of 1400°C to 1700°C. It is preferable to carry out the firing under a weakly
10 reducing atmosphere such as a mixture of an inert or reductive gas e.g., H₂ gas, N₂ gas, or the like and H₂O. But when an anti-oxidative metal paste such as a Pt paste is used, it can be fired under an oxidative atmosphere such as air. Firing time is usually from
15 30 minutes to 5 hours.

This invention is illustrated by way of the following Examples, in which all parts are parts by weight.

Examples

- 20 To tungsten powders having particle sizes as shown in Table 1 in an amount of 100 parts, additives having a composition containing sintering promoters for alumina and alumina ceramics as shown in Table 2 are added in amounts of 0, 0.3, 1, 3 and 5 parts. Further,
25 6 parts of ethyl cellulose, 2 parts of nitrocellulose, and a mixed solvent containing equal amounts of ethyl acetate and ethyl alcohol were mixed with the above-

mentioned tungsten powders and additives in a mixing and grinding machine for 5 hours. After uniformly mixing the solvent was replaced by ethylene glycol monobutyl ether to give a W paste. Then the W paste 5 was screen printed on an unsintered alumina ceramic substrate having an Al purity of 96% and a thickness of 1.0 mm so as to make the film thickness 30 μm . After drying at 80°C for 15 minutes, the W paste was fired at temperatures as listed in Table 1 under a weakly 10 reductive atmosphere to form W metal conductor layers. Then the thickness, width and length of the W conductor layers on the alumina ceramic substrates were measured and volume resistivity was obtained by measuring electric resistance at 20°C. The results are as shown in Table 1.

Table 1

Compounded composition				
W powder		Additive (parts)	1400	
Particle size (μm)	(parts)		Adhesive strength (kg/mm^2)	Electric resistance ($\text{m}\Omega\cdot\text{cm}$)
0.4	100	0	2.0 - 3.0	0.040
		0.3	"	0.020
		1.0	"	"
		3.0	"	"
		5.0	"	0.038
0.9	100	0.1	1.5 - 2.5	0.045
		0.3	"	0.025
		1.0	"	"
		3.0	"	"
		5.0	"	0.040
1.8	100	0.1	0.5 - 1.5	0.050
		0.3	"	0.040
		1.0	"	"
		3.0	"	"
		5.0	"	0.052
3.7	100	0	0 - 0.5	0.065
		0.3	"	0.050
		1.0	"	0.055
		3.0	"	0.050
		5.0	"	0.065

- Cont'd -

Table 1 (Cont'd)

Firing Temperature (°C)			
1450		1500	
Adhesive strength (kg/mm ²)	Electric resistance (mΩ·cm)	Adhesive strength (kg/mm ²)	Electric resistance (mΩ·cm)
2.5 - 3.5	0.035	1.0 - 2.0	0.030
"	0.020	"	0.020
"	"	"	"
"	"	"	"
"	0.035	"	0.030
3.0 - 5.0	0.040	1.0 - 2.5	0.033
"	0.023	"	0.020
"	"	"	"
"	"	"	"
"	0.032	"	0.035
1.0 - 2.0	0.045	3.0 - 4.0	0.040
"	0.035	"	0.030
"	"	"	"
"	"	"	"
"	0.047	"	0.042
0 - 0.5	0.060	0.5 - 1.0	0.050
"	0.045	"	0.040
"	"	"	0.038
"	"	"	0.040
"	0.060	"	0.050

- Cont'd -

Table 1 (Cont'd)

1550		1600	
Adhesive strength (kg/mm ²)	Electric resistance (mΩ·cm)	Adhesive strength (kg/mm ²)	Electric resistance (mΩ·cm)
0.5 - 1.0	0.028	0 - 0.5	0.025
"	0.018	"	0.015
"	"	"	"
"	"	"	"
"	0.025	"	0.025
1.0	0.035	0 - 0.5	0.030
"	0.018	"	0.015
"	"	"	"
"	"	"	"
"	0.035	"	0.030
1.5 - 2.0	0.036	0 - 0.5	0.032
"	0.025	"	0.025
"	"	"	"
"	"	"	"
"	0.038	"	0.034
1.0 - 2.0	0.045	2.0 - 3.0	0.040
"	0.035	"	0.035
"	"	"	0.032
"	"	"	0.035
"	0.045	"	0.040

Table 2

Components	Compounding Ratio. (parts)	Mixing conditions
Al ₂ O ₃	5	Dry mixed powders were heat treated at 1350°C for 3 hours, ball-milled in water for 24 hours, dried at 100°C for 24 hours, and further ground finely.
SiO ₂	60	
MgO	15	
CaCO ₃	20	

- 1 As shown in Table 1, electric resistance of the W layers is decreased in proportion to the firing temperatures and increased in proportion to the W particle sizes. On the other hand, as to the pastes
- 5 obtained by adding sintering promoters to W powders, electric resistance is decreased with an increase of the addition amount of the sintering promoters to show a minimum value, and after which value, electric resistance is increased again with an increase of the addition
- 10 amount of the sintering promoters.

Heretofore, it has been considered that when insulating particles are mixed with electroconductive particles, electroconductivity of the resulting mixture is lowered, so that a resistant paste containing carbon

15 black or silver powder as a base is used practically. The phenomenon that the addition of a small amount of insulating particles comprising sintering promoters for alumina and alumina ceramics makes electroconductivity

1 increase as mentioned in the above Examples cannot be
expected from the common knowledge at all. The
reason for this is not clear, but it seems that the
additives such as sintering promoters for alumina
5 and alumina ceramics fill vacant spaces among high-melting
metal such as W powders and during the simultaneous
sintering of the ceramics there is generated firing
shrinkage, which causes shrinking and condensing of the
whole high-melting metal powders to increase the packing
10 density of W powders.

This invention is based on the finding of
such an unexpected phenomenon. According to the common
knowledge in this art, since electroconductivity of the
W conductor layer is increased in proportion to the
15 sintering temperature, it was necessary to use remarkably
high sintering temperature in order to obtain a conductor
layer having high electroconductivity, which resulted
in over-sintering of alumina ceramics sometimes, decrease
in mechanical strength and finally decrease in metallizing
20 strength. Therefore, it was very difficult to obtain
metallized wiring boards of high quality. But, such
difficulty is overcome by this invention, wherein the
additive such as one or more sintering promoters for
alumina and alumina ceramics in an amount of 0.1 to 3
25 parts by weight is mixed with 100 parts by weight of
high-melting metal powder. Since the specially mixed
metal paste is used in this invention, even if the
metal paste is fired at a temperature of 50 to 100°C

- 1 lower than the firing temperature of the conventional process, conductor layers having the same or higher electroconductivity compared with the conventional ones can be produced. Thus, it becomes possible to
- 5 make wires finer without damaging conductor resistance. Consequently, this invention is practically excellent not only in improving packaging density of wiring boards and performance but also in economical and technical production of metallized ceramics.



CLAIMS

1. An electroconductive paste for metallizing comprising:

(a) 100 parts by weight of a powder of a metal having a melting point of at least 1700°C,

5 (b) 0.1 to 3 parts by weight of an additive which can fill vacant spaces among particles of said metal powder and can shrink and increase the density of said metal powder without influencing the sintering rate of said metal powder,

10 (c) a binding agent, and

(d) a solvent.

2. A paste according to claim 1, wherein the metal powder (a) is tungsten, molybdenum, molybdenum-manganese, platinum or a mixture thereof.

15 3. A paste according to claim 1 or 2, wherein the additive (b) is one or more sintering promoters for alumina and alumina ceramics.

4. A paste according to claim 1 or 2, wherein the additive (b) is magnesium oxide, calcium oxide,
20 silicon oxide, aluminum oxide, or a mixture thereof.

5. A paste according to any one of the preceding claims, wherein the binding agent (c) is a cellulose derivative resin, an acrylic resin, an alkyd or phenolic resin, a vinyl resin, an epoxy resin, or a mixture thereof.



6. A paste according to any one of the preceding claims, wherein the solvent (d) is an aromatic hydrocarbon, an ester, a ketone, an alcohol or a mixture thereof.

7. An electroconductive paste according to claim 5 1 substantially as hereinbefore described with reference to any one of the Examples.

8. A process for producing an electroconductive paste for metallizing which comprises: dispersing uniformly,

(a) 100 parts by weight of a powder of a metal
10 having a melting point of at least 1700°C,

(b) 0.1 to 3 parts by weight of an additive which can fill vacant spaces among particles of said metal powder and can shrink and increase the density of said metal powder without influencing the sintering rate of
15 said metal powder, and

(c) a binding agent
in (d) a solvent.

9. A process according to claim 8, wherein the powder (a), additive (b), binding agent (c) and solvent (d)
20 is any one of those specified in any one of claims 2 to 6.

10. A process according to claim 8 substantially as hereinbefore described with reference to any one of the Examples.

11. A process for producing an electroconductive
25 metallized ceramic which comprises coating the surface of an alumina ceramic substrate with an electroconductive paste according to any one of claims 1 to 7 and firing the paste to form a metallized layer.



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12. A process according to claim 11, wherein the firing temperature is 1400°C to 1700°C.

13. A process according to claim 11 or 12, wherein the alumina ceramic substrate is an unsintered alumina ceramic.

14. A process according to any one of claims 11 to 13, wherein the firing is conducted in a weakly reductive atmosphere.

15. A process according to claim 11 substantially as hereinbefore described.

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