

SPECIFICATION

[TITLE OF THE INVENTION]

POSITIVE TEMPERATURE COEFFICIENT THERMISTOR

5

AND THERMISTOR DEVICE UTILIZING THE SAME

[CLAIMS]

1. A positive temperature coefficient thermistor comprising:

10 a positive temperature coefficient thermistor element;

first electrode layers constituted of single or multi layers which contain silver layers and which are formed on both principal surfaces of the positive temperature coefficient thermistor element in such a way that edges thereof recede inward from outer peripheries of the positive temperature coefficient thermistor element; and

20 second electrode layers constituted of layers which contain aluminum as a principal component and which are formed so as to cover surfaces and sides of the first electrode layers.

2. The positive temperature coefficient thermistor as defined in claim 1, wherein the second electrode layers are constituted of thick-film printed layers containing 5 to 60 vol% conductive boron-compound and aluminum.

25 3. A positive temperature coefficient thermistor comprising:

a positive temperature coefficient thermistor element;

first electrode layers formed on both principal surfaces of the positive temperature coefficient thermistor element;

second electrode layers which contain silver as a principal component and which are formed in such a way that edges thereof recede inward from edges of the first electrode layers; and

third electrode layers constituted of aluminum layers and which are formed in such a way as to cover the second electrode layers.

4. A thermistor device comprising:

a positive temperature coefficient thermistor element;

a positive temperature coefficient thermistor including electrodes which are formed on both principal surfaces of the positive temperature coefficient thermistor element and in which outermost layers are aluminum layers; and

terminals that support the positive temperature coefficient thermistor on two sides,

wherein at least those areas of the terminals that are in contact with the positive temperature coefficient thermistor are made of a substance that does not form an aluminum alloy having a melting point of 300°C or lower.

5. The thermistor device as defined in claim 4, wherein the substance is one of nickel, silver, copper, aluminum,

titanium, or an alloy of two or more of them.

[DETAILED DESCRIPTION OF THE INVENTION]

[TECHNICAL FIELD]

5 The present invention relates to a positive temperature coefficient thermistor and a thermistor device in which the thermistor is used, and in particular to an electrode structure thereof.

10 [BACKGROUND ART]

Oxide semiconductors in which yttrium, neodymium, or the like has been added in an amount of 0.1 to 0.3 at % to BaTiO_3 , have a substantial positive temperature coefficient and are thus referred to as PTC thermistors.

15 Because such PTC thermistors allow temperature zones having a substantial positive temperature coefficient to be regulated by adding strontium, lead, or the like, they have come to be regarded as essential in a wide variety of fields, such as low temperature heaters and circuit
20 elements for degaussing color televisions, starting motors, preventing excess current, measuring temperatures, and the like.

As shown in Figure 21(a), such thermistors comprise a thermistor element 11 obtained by sintering an oxide,
25 carbonate, nitrate, chloride, or other compound of a metal such as barium, titanium, or neodymium, which is then formed into the shape of a thin cylinder or the like; first electrode layers 12a and 12b consisting of nickel-plated

layers formed on the upper and lower sides of the element 11; and second electrode layers 13a and 13b containing silver as a principal component formed on the electrode layers 12a and 12b.

5 Such a positive temperature coefficient thermistor is ordinarily used with the application of voltage between the second electrode layers 13a and 13b. This causes a so-called migration phenomenon, that is, causes the silver inside the second electrode layers to move and precipitate
10 in the direction of the electric field. A particular disadvantage is that when the outer peripheries of the second electrode layers are formed in such a way that they reach the outer peripheries of the positive temperature coefficient thermistor element 1, silver moves and
15 precipitates in the direction of the electric field at the outer peripheries of the positive temperature coefficient thermistor element 1, causing short circuits.

To address this problem, as shown in Figure 21(b), positive temperature coefficient thermistors have been
20 proposed in which the outer diameters of the second electrode layers are made smaller than the outer diameters of the first electrode layers.

A drawback of this structure, however, is that since the outer dimensions of the second electrode layers are
25 made smaller than the outer dimensions of the first electrode layers, the portions of the first electrode layers that are not covered by the second electrode layers are readily oxidized because of being directly exposed to

the atmosphere, and the contact resistance gradually increases.

In addition, because silver migration is a phenomenon involving movement in the direction of the electric field, the silver contained in the second electrode layers is exposed even when attempts are made to draw inward the peripheral portions of the second electrode layers alone, as is the case in conventional examples, with the result that migration, albeit small, occurs nonetheless, and the problem of short circuits can be alleviated but not solved completely.

In addition, electrodes for conventional positive temperature coefficient thermistors are formed using plating techniques, so these methods involve the penetration of the plating solution into the sintered compacts during the nickel plating in the course of electrode formation. Occasionally, this lowers the resistance value and causes other changes in the characteristics of the sintered compacts. These changes take the shape of characteristic changes and may appear immediately following formation or develop gradually over time. As described above, thermistor applications include temperature measurement and control, compensation, gain adjustment, power measurement, overcurrent prevention, motor starting, color TV degaussing, and the like. Each of these applications requires that the resistance value be controlled with high precision, and devices for which the condition $R_{1\alpha\%}$ is satisfied must be used. The changes in

the resistance value that are induced by the penetration of the plating solution have therefore become a serious problem.

Methods have also proposed in which the penetration
5 of plating solutions is prevented by forming aluminum or some other low-melting metal by metal spraying, and using the product as the electrode.

These methods, however, are still disadvantageous in that the abrupt temperature changes that occur during
10 electrode formation induce cracking in the thermistor elements or in electrodes themselves.

The inventors addressed this problem by proposing, in Japanese Laid-Open Patent Application 6-5403, a thermistor electrode structure obtained using vapor-
15 deposited films or printed electrodes containing aluminum as the principal component. No migration at all occurs in this structure because it contains aluminum as the principal component. In addition, the use of printed or vapor-deposited films improves durability without causing
20 cracking in the elements themselves. A serious disadvantage, however, is that because the first electrode is made of aluminum or the like, the electrode itself has substantial resistance and is unsuitable for circuits carrying comparatively large currents.

25 Another proposal (Japanese Laid-Open Patent Application 5-109503) involves an electrode structure in which migration is prevented by forming nickel electrodes as the first electrodes over the entire surfaces of the

both principal sides of a thermistor element, leaving gap areas around the electrodes, forming second electrodes containing silver as the principal component, and forming third electrodes containing aluminum and silicon to cover the gap areas. A serious disadvantage, however, is that when surface irregularities are formed in this structure and two superposed elements are used, it is impossible to obtain adequate thermal contact, and a considerable residual current flows.

To reduce the residual current, it was proposed to use a two-element type device in which a positive temperature coefficient thermistor for coil applications is heated by a positive temperature coefficient thermistor for heater applications, but in this case the thermal contact between the elements was poor when irregularities are formed on the electrode surfaces, making it impossible to lower the residual current.

[PROBLEMS TO BE SOLVED BY THE INVENTION]

A disadvantage of such a conventional electrode structure is that the contact resistance is increased when the use of silver is avoided and aluminum is used in an attempt to prevent migration.

In addition, a disadvantage of the structure in which gap areas are left in the outer periphery portions, electrodes containing silver as the principal component are formed, and these gap areas are covered with electrodes composed of aluminum and silicon is that because silver is

exposed in some areas, migration is not adequately prevented, and satisfactory thermal contact cannot be obtained when irregularities are formed on the surface and two superposed elements are used, thus increasing the residual current.

An object of the present invention, which was perfected in view of the above situation, is to provide a positive temperature coefficient thermistor which is easy to assemble, remains stable and highly reliable, allows migration to be completely prevented, and is suitable for circuits with large currents.

[MEANS TO SOLVE THE PROBLEMS]

In view of this, the first distinctive feature of the present invention is that it comprises first electrode layers containing silver layers which are formed on the both principal sides of a positive temperature coefficient thermistor element and in which the edges recede inward from the outer peripheries of the positive temperature coefficient thermistor element, and second electrode layers constituted of layers which contain aluminum as the principal component and which are formed in such a way that they cover the surfaces and sides of the first electrode layers.

Preferably, the second electrode layers are configured with thick-film printed layers containing 5 to 60 vol% conductive boron-compound ceramic and aluminum. In addition to TiB_2 , the conductive boron-compounds used in

this case may be one or more compounds (or combinations thereof) selected from the group consisting of diborides such as ZrB_2 , HfB_2 , VbB_2 , TaB_2 , CrB_2 , and MoB_2 ; the monoborides TiB , ZrB , HfB , VbB , TaB , CrB , MoB , WB , and NiB ; 5 and the compounds V_3B_4 , V_3B_2 , Nb_2B_3 , Nb_3B_4 , Ta_3B_2 , Ta_3B_4 , Cr_3B_4 , Mo_3B_2 , Mo_2B_5 , W_2B_5 , Ni_4B_3 , and B_4C .

The second distinctive feature of the present invention is that it comprises first electrode layers formed on the both principal sides of the positive 10 temperature coefficient thermistor element, second electrode layers constituted mainly of silver layers formed in such a way that the edges recede inward from the edges of the first electrode layers, and third electrode layers constituted of aluminum layers formed so as to cover the 15 second electrode layers.

The third distinctive feature of the present invention is that it comprises a positive temperature coefficient thermistor including electrodes which are formed on the both principal sides of a thermistor element 20 and in which the outermost layers are aluminum layers, and terminals that sandwichingly support the positive temperature coefficient thermistor; and that at least those areas of the terminals that are in contact with the positive temperature coefficient thermistor are configured 25 with a substance that does not form an aluminum alloy having a melting point of $300^\circ C$ or lower.

Preferably, a distinctive feature of this substance is that it is nickel, silver, copper, aluminum, titanium,

or an alloy thereof.

[FUNCTION]

5 The aforementioned structure involves using silver electrodes with satisfactory electrical conductivity and completely coating these silver electrodes with aluminum electrodes, thus excluding any danger that short circuits will be caused by migration.

10 The formation of the electrodes in the aforementioned structure may be effected by vapor deposition, thick-film printing, or other such dry process. It is therefore possible to form electrodes having superior bonding properties and low contact resistance while preventing solutions or the like from causing any changes
15 in characteristics due to the contamination of the exposed portions of the surfaces and rear sides of the thermistor element during electrode formation.

The aforementioned first structure involves forming first electrode layers containing silver layers that are
20 formed in such a way that the edges recede inward from the outer peripheries of the positive temperature coefficient thermistor element, and forming second electrode layers constituted of aluminum layers to cover the surfaces and sides of the aforementioned first electrode layers, making
25 it possible to maintain the electrical conductivity at a satisfactory level and to completely prevent the emergence of migration. It is desirable for the second electrode layers to be configured as thick-film printed layers

containing 5 to 60 vol% conductive boron-compound and aluminum, thereby preventing conductivity from being lowered even when oxygen is trapped during the baking of electrodes, and making it possible to maintain satisfactory electric contact properties even in those regions where the thermistor element and the second electrodes are in direct contact.

According to the second structure of the present invention, the formation of fractures or cracks in the thermistor element is reduced because the entire surface of the thermistor element is covered with the first electrode layers, and the second electrode layers are formed on the first electrode layers.

According to the third structure of the present invention, heat is evolved by the large currents flowing through the points of contact, that is, through the contact points, between the terminals and the electrodes every time the voltage is switched on, with the result that the temperature increases locally, reaching as high as about 200°C, but because the surfaces of at least those areas of the terminals that are in contact with the positive temperature coefficient thermistor are made of a material that does not form aluminum alloys of 300°C or lower, no separation occurs, and the existing state can be satisfactorily preserved. Materials that form high-melting aluminum alloys, such as nickel, silver, copper, aluminum, titanium, and alloys thereof, are desirable for use in the surface layers of such elastic terminals.

[EMBODIMENTS]

Embodiments of the present invention are described in detail below with reference to the figures.

5 Embodiment 1:

Figure 1 is a diagram illustrating the positive temperature coefficient thermistor of the first embodiment of the present invention.

This positive temperature coefficient thermistor
10 comprises a thermistor element 1 containing barium titanate as the principal component; first electrode layers 2a and 2b constituted of silver-zinc (Ag-Zn) layers formed by printing on the upper and lower sides of the thermistor element in such a way that the edges recede to positions
15 that are somewhat inside of the outer peripheries; second electrode layers 3a and 3b constituted of silver layers (Ag) formed by printing in such a way as to cover these first electrode layers 2a and 2b; and third electrode layers 4a and 4b constituted of aluminum-titanium boride
20 (Al-TiB₂) layers formed by printing in such a way as to cover these second electrode layers 3a and 3b. The film thickness of each electrode was made about 10 μ m.

The process for manufacturing this positive temperature coefficient thermistor will now be described.

25 Figures 2(a) and 2(b) are process diagrams illustrating the process for manufacturing the thermistor of the embodiment of the present invention.

First, as shown in Figure 2(a), TiO₂, BaCO₃, and

Nd_2O_3 powders are mixed in a prescribed ratio, compression-molded into a discoid by cold pressing, sintered at 1300°C , and molded into discoid thermistor element 1 with a diameter of 4.47 mm.

5 Then, as shown in Figure 2(b), first through third electrode layers are sequentially applied by screen printing to the end faces (electrode-formation sides) of the thermistor element 1. In this case the formation processes involve first performing screen printing using an
10 Ag-Zn paste and conducting a drying process for 10 minutes at 180°C , then performing screen printing using an Ag paste and conducting drying for 10 minutes at 180°C , and finally performing screen printing using an Al-TiB₂ paste, conducting drying for 10 minutes at 180°C , and carrying out
15 a baking process for 10 minutes at 550°C .

 The Al-TiB₂ paste used here is obtained by mixing an aluminum powder having a mean particle diameter of about 5 μm and a binder to make the integer into an aluminum paste, mixing the aluminum past and a TiB₂ ceramic powder
20 having a mean particle diameter of 3 μm in a compounding ratio of 7:3, and adjusting the viscosity.

 With the thermistor thus obtained, the silver-containing electrode layers are completely covered with the electrode layers containing, as the principal component,
25 aluminum non-ionizable in condensed water, with the result that the silver does not migrate even during a prolonged operation in a hot and humid environment, and reliability can be maintained. Satisfactory electrical contact is also

maintained between the thermistor element and the electrodes.

In addition, the electrodes can be applied to the entire surfaces of the both principal planes of the element because no aluminum migration occurs. The flow of a rush current entering the element is therefore rendered uniform, and in comparison with what was observed in the past, cracking or chipping is less likely to occur during the application of a surge current or voltage.

10 Embodiment 2:

Figure 3 is a diagram illustrating the positive temperature coefficient thermistor of the second embodiment of the present invention.

This positive temperature coefficient thermistor comprises a thermistor element 1 containing barium titanate as the principal component; first electrode layers 2m and 2m' constituted of nickel (Ni) layers that have film thicknesses of 0.3 to 2 μm and that are formed by vacuum vapor deposition over the entire upper and lower sides of the thermistor element; second electrode layers 3a and 3b constituted of silver layers (Ag) formed by screen printing in such a way that the edges recede to positions that are somewhat inside of the outer peripheries; and third electrode layers 4a and 4b constituted of aluminum-titanium boride (Al-TiB_2) layers formed by printing in such a way as to cover these second electrode layers 3a and 3b. The film thickness of each of the second and third electrode layers was made about 10 μm .

As far as formation is concerned, it was performed in the same manner as in Embodiment 1 above.

As with Embodiment 1 above, a thermistor thus obtained produced the effects described above.

5 For the sake of comparison, an electrode structure serving as Comparative Example 1 was obtained by forming the first electrode layers 2a and 2b as well as the second electrode layers 3a and 3b which are constituted of silver-zinc layers and silver layers, respectively, and which were
10 consecutively laminated by printing in such a way that the edges receded to positions that were somewhat inside of the outer peripheries of the same thermistor element 1 as that used in Embodiments 1 and 2 of the present invention (Figure 4).

15 In addition, Comparative Example 2 involved forming a thermistor in the same manner as the thermistor of Embodiment 2, but without the third electrode layers (Figure 5).

Next, to perform migration tests, 1000 cycles of a
20 250-V voltage (30 seconds "on," 30 seconds "off") were applied at an ambient temperature of 120°C and a humidity of 95 RH% using a testing apparatus such as that schematically shown in Figure 6. The sides of the tested element were subjected to an EPMA analysis to detect silver
25 migration. The results are shown in the table in Figure 7. As is evident from this table, no migration was observed in the structures of Embodiments 1 and 2 of the present invention, whereas small amounts of silver were detected on

the sides in Comparative Examples 1 and 2.

Next, to perform low-temperature, intermittent-load tests, 1000 cycles of a 250-V voltage (1 minute "on," 5 minutes "off") were applied at an ambient temperature of -20°C using a testing apparatus such as that schematically shown in Figure 8. The tested element was measured for the presence or absence of cracking and chipping and for the resistance change ratio. The results are shown in the table in Figure 9. As is evident from this table, no cracking or chipping occurred in any of the examples, the resistance change ratio was about -2.6 to -1.9%, and all the evaluation results were denoted with circle marks.

Next, to perform surge-current tests, a voltage that started at 250 V and was increased in successive steps of 50 V was applied at an ambient temperature of -20°C using a testing apparatus such as that schematically shown in Figure 10. The tested element was studied for cracking or chipping; the results are shown in Figure 11. As can be seen from these results, the element did not crack or chip at all following the completion of the tests.

Next, the thermistor of Embodiment 1 was mounted on terminals 10 such as those shown in Figure 12, and low-temperature, intermittent-load tests were performed to measure the terminal materials. As shown in the table in Figure 13, no electrode separation occurred following testing when the surface material of the terminals used was composed of a plated layer of nickel or silver. Separation

occurred, however, in the terminal contact portion when the terminals were formed using solder or tin. As used herein, the term "separation" refers to the separations R occurring on the electrode surfaces that correspond to the contact portions with the terminals 10. It is believed that local temperature increases occur, and aluminum and tin or solder form alloys because heat is evolved by the flow of a substantial current every time a voltage is applied during a low-temperature, intermittent-load test. These results also suggest that it is desirable to use nickel and silver, which do not form alloys with aluminum, as the materials for the terminal surfaces.

The melting points of alloys of aluminum with nickel, silver, and tin are shown in the table in Figure 15. In addition, Figures 16 through 18 are diagrams illustrating the relation between the melting point and the composition of an aluminum-tin alloy, and the relation between the melting point and the composition of a silver-aluminum alloy, respectively, as well as the relation between the melting point and the composition of aluminum-nickel.

Since heat is evolved by the large current that flows through a contact each time a voltage is switched on, local temperature increases occur, and the temperature rises up to about 200°C, so, to ensure safety, it is desirable to use a material that does not form aluminum alloys of 300°C or lower.

In addition, as shown in Figure 19, methods used to

form terminal configurations include full plating which involves forming the entire surfaces of the elastic or central terminals from nickel, copper, silver, aluminum, or other plating layers, and partial plating which involves forming only the areas in contact with the positive temperature coefficient thermistor from plating layers composed of metals such as those described above. It is also possible to employ commonly used tin terminals and to install layers that do not form alloys with tin at least in those portions of the aluminum electrode layers that are in contact with the terminals.

Embodiments 1 and 2 above concerned cases in which TiB_2 was added to aluminum. The amount in which TiB_2 was added was subsequently varied, and the relation between the element resistance and the maximum surge voltage causing no crack initiation was measured. The results are shown in Figure 20.

As is evident from these results, the effect appears at an addition of 5 vol% or greater, but baking becomes difficult at 70 vol% or higher. This suggests that the maximum surge voltage rises because the addition of TiB_2 improves the ohmic contact between the thermistor element and aluminum. In the structure described in Embodiment 2, the ohmic contact with the thermistor element was obtained using a nickel electrode, so the addition of TiB_2 produced hardly any effect on the maximum surge voltage.

These comparative examples also show that the present invention yields a more reliable thermistor having

a stabler resistivity.

As used with reference to the present invention, the term "aluminum layer" is not limited to pure aluminum and can also refer to a layer in which aluminum is the principal component.

[EFFECT OF THE INVENTION]

As described above, the present invention can yield a positive temperature coefficient thermistor which is unlikely to short-circuit because of migration, is easy to assemble, and has stable characteristics.

[BRIEF DESCRIPTION OF THE DRAWINGS]

Figure 1 is a diagram illustrating the thermistor of the first embodiment of the present invention.

Figures 2(a) and 2(b) are manufacturing process diagrams of the thermistor of the first embodiment.

Figure 3 is a diagram illustrating the thermistor of the second embodiment of the present invention.

Figure 4 is a diagram illustrating a conventional thermistor (comparative example).

Figure 5 is a diagram illustrating a conventional thermistor (comparative example).

Figure 6 is a diagram illustrating a test apparatus for migration testing.

Figure 7 is a diagram illustrating the results of a migration test performed using the apparatus shown in Figure 6.

Figure 8 is a diagram illustrating a test apparatus for low-temperature, intermittent-load testing.

Figure 9 is a diagram illustrating the results of a low-temperature, intermittent-load test performed using the apparatus shown in Figure 8.

Figure 10 is a diagram illustrating a testing apparatus for performing surge-current tests.

Figure 11 is a diagram illustrating the results of a surge-current test performed using the apparatus shown in Figure 10.

Figure 12 is a diagram illustrating a testing apparatus for measuring the dependence of the low-temperature, intermittent-load test results on the terminal material.

Figure 13 is a diagram illustrating the results of a low-temperature, intermittent-load test performed using the apparatus shown in Figure 12.

Figure 14 is a diagram illustrating how separation occurs in a low-temperature, intermittent-load test performed using the apparatus shown in Figure 12.

Figure 15 is a diagram illustrating the melting points of the alloys formed by aluminum with nickel, silver, and tin.

Figure 16 is a diagram illustrating the relation between the melting point and the composition of an aluminum-tin alloy.

Figure 17 is a diagram illustrating the relation between the melting point and the composition of a silver-

aluminum alloy.

Figure 18 is a diagram illustrating the relation between the melting point and the composition of aluminum-nickel.

5 Figure 19 is a diagram illustrating examples of terminal structures.

Figure 20 is a diagram illustrating the results obtained by measuring the relation between the element resistance and the maximum surge voltage.

10 Figures 21(a) and 21(b) are diagrams illustrating conventional thermistors.

[DESCRIPTION OF REFERENCE NUMBERS AND SYMBOLS]

- 1 ... Thermistor element
- 15 2a, 2b ... First electrode layers
- 3a, 3b ... Second electrode layers
- 11 ... Thermistor element
- 12a, 12b ... First electrode layers
- 13a, 13b ... Second electrode layers