

[54] **OXYGEN ION TRANSPORT TYPE
THERMISTORS**

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[22] Filed: **June 14, 1974**

[21] Appl. No.: **479,472**

[30] **Foreign Application Priority Data**

June 21, 1973 Japan..... 48-70493

[52] U.S. Cl..... **338/22 R; 252/520; 252/521**

[51] Int. Cl.²..... **H01C 7/04**

[58] Field of Search 338/22, 23, 25; 29/612;
252/518, 520, 521

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Primary Examiner—C. L. Albritton
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[57] **ABSTRACT**

An oxygen ion transport type thermistor comprising an oxygen ion type solid solution consisting of 50–95 mol percent of an oxide of tetravalent metals and 5–50 mol percent of oxide(s) of divalent and/or trivalent metals and two metal lead wires embedded in said solid solution, in which said two metal wires are embedded and held oppositely in substantially the center line in the thickness direction of said solid solution, parallel and adequately space and that the porosity of said oxygen ion type solid solution is 7–55 percent.

2 Claims, 2 Drawing Figures

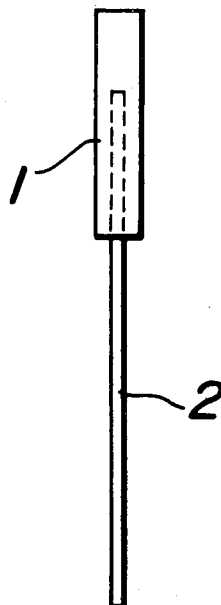


FIG. 1A

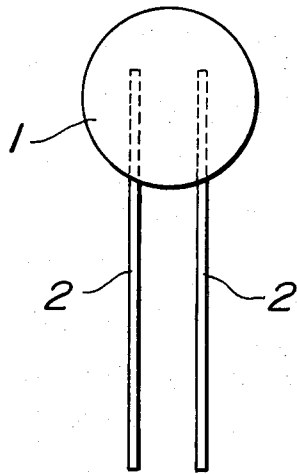
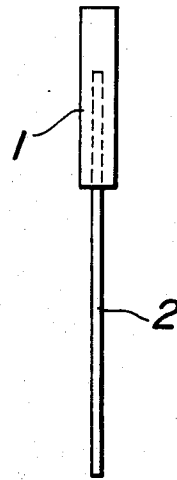


FIG. 1B



OXYGEN ION TRANSPORT TYPE THERMISTORS

The present invention relates to thermistors.

Oxygen ion transport type sintered oxide solid solutions having a stable crystal structure until a high temperature zone consisting of 50–95 mol percent of an oxide of tetravalent metals such as ZrO_2 , CeO_2 , HfO_2 and ThO_2 and 5–50 mol percent of oxide(s) of divalent alkaline earth metals and/or trivalent rare earth metals, such as CaO , MgO , SrO , La_2O_3 , Y_2O_3 , Yb_2O_3 , Sc_2O_3 , Gd_2O_3 and Nd_2O_3 decrease rapidly the electrical resistance at a temperature of 400°–1,200°C and have excellent properties as a high temperature resistor of a thermistor. Such a solid solution is generally composed of polycrystalline fluorite structures, which have oxygen vacancies to preserve lattice neutrality. Accordingly, these oxide sintered bodies have been used for parts for measuring or controlling temperature of a high temperature furnace and an apparatus for purifying an exhaust gas of an internal combustion engine. Such ceramic resistors are referred to as "oxygen transport type thermistors", because the electrical conductivity is shown to be due to the transport of oxygen ion of the oxide in the solid solution constituting the resistor. Heretofore, the electrodes of such oxygen ion transport type thermistors are provided by coating a platinum paste on both parallel main surfaces of the ceramic resistor fired in a disc form and arranging platinum wires to form lead wires thereon and bonding said wires to the resistors with the above described platinum paste and firing said paste at a temperature of 1,000°–1,500°C, but the adhesion at the portions where the lead wires get out of the ceramic resistor, is weak and further the working steps are many and troublesome.

The adhesion at the bonded portions of the lead wires is degraded with the raising of the temperature owing to softening of vitreous components in the platinum paste at a high temperature. Accordingly, it is impossible at a high temperature, for example, higher than 1,000°C to increase the bonding strength of the lead wires even by such oxidation resistant metal paste. Furthermore, the above described coated metal paste requires a moderate vapor permeability in order to make smooth the receiving and supply of oxygen ion in the atmosphere to be converted into electricity at the contact portion of the electrodes with the resistor, so that a thick coating exceeding a certain degree cannot be effected. Accordingly, the adhesion cannot be essentially improved.

While, the oxygen ion transport type thermistors according to the present invention which aim to obviate the above described drawbacks, are characterized in that as shown in FIG. 1, a molding is effected in such a manner that two fine metal wires 2, 2 composed of metals having a higher oxidation resistance, such as platinum or platinum-rhodium alloy are embedded in a resistor matrix leaving a space in parallel and the molded assembly is fired at an adequate temperature to form electrodes and lead wires which are embedded and held in a ceramic resistor 1 of the thermistor and that the porosity of the above described ceramic resistor 1 is made to be 7–55 percent, preferably 15–35 percent, more particularly 25 percent.

The conventional oxygen ion transport type thermistor in which the electrodes are provided on the surfaces

of the ceramic resistor, are very tightly sintered and the porosity is usually less than 2 percent.

The reason why the lower limit of the porosity of the ceramic resistor of the thermistor according to the present invention is defined to be 7 percent is as follows. When the oxygen ion transport type thermistor is supplied with a given direct current voltage of about 12V usually used between the electrodes, the oxygen molecule is absorbed from the atmosphere near the cathode in order that the oxygen ion O^{2-} which transports in the ceramic resistor and is concerned in the electric transmission mechanism, is supplied at the cathode side as $\frac{1}{2}O_2 + 2e \rightarrow O^{2-}$ and said oxygen molecule is discharged into the atmosphere near the anode in order that the above described oxygen ion is taken out at the anode side as $O^{2-} \rightarrow \frac{1}{2}O_2 + 2e$. But in the thermistor of the present invention, both the electrodes are provided by embedding the fine metal wires in the ceramic resistor, so that the contact area of the electrodes to the resistor is small and consequently if the porosity in the resistor is less than 7 percent, the diffusion movement of the oxygen molecule which is effected through pores in the resistor between air in the pores near the electrodes and the ambient atmosphere, becomes not free and particularly when the oxygen to be supplied at the cathode side is deficient, the oxygen ion in the crystal structure of the sintered body of oxides is used for the electric transmission after the electric current flows for a given time under a high temperature condition and the oxides are reduced and blackened and the resistor becomes a semiconductor having a very small resistance and loses the normal function. Accordingly, in order to prevent such a fact and to ensure the stable circulation mechanism of oxygen during use for a long time, the porosity must be not less than 7 percent. On the other hand, the above described upper limit of the porosity is defined for on the following reason. When the porosity is more than 55 percent, the variation of the electric resistance with the lapse of time in the ceramic resistor not only becomes larger but also the mechanical strength lowers and the electrodes are readily removed and cracks and breaks are apt to be caused. When the porosity is too large, the contact resistance between the electrodes and the resistor is large and further the adhesion is gradually lowered owing to the ion conversion at the electrode portions.

The present invention will be explained in more detail.

For a better understanding of the invention, reference is taken to the accompanying drawings, wherein:

FIG. 1A is a plan view of the oxygen ion transport type thermistor according to the present invention; and FIG. 1B is a side view of said thermistor.

The following examples are given for the purpose of illustration of this invention and are not intended as limitations thereof.

EXAMPLE 1

Each of mixtures of powdery ZrO_2 and $CaCO_3$ having compositions as shown in the following Tables 1–3 (83 mol percent of ZrO_2 +17 mol percent of $CaO(CaCO_3)$, 87 mol percent of ZrO_2 +13 mol percent of $CaO(-CaCO_3)$, 75 mol percent of ZrO_2 +25 mol percent of $CaO(CaCO_3)$) was added with 4 percent by weight of an emulsion consisting of equal weight amounts of stearic acid and water as a binder and pulverized in a wet process in a trommel for 20 hours. Each of the resulting

powdery mixtures was filled in a mold and two 0.4 mm platinum wires were held in the center portion and the filled mixture in the mold was pressed at a pressure of 2,000 Kg/cm² and the molded mixture was fired at various temperatures of about 1,400°–1,800°C in air to produce oxygen ion transport type disc-shaped thermistors having different porosities as shown in the attached drawing, which have an outer diameter of about 3.8 mm and a thickness of about 1.4 mm and in which a pair of platinum wires 2, 2 are embedded and fixed in parallel at the center line of the thickness direction at a spacing of about 2 mm. The resulting thermistor was applied with DC12V at 800°C between the two platinum electrodes for 1,000 hours. This test showed that in the thermistors having the porosity of less than 7 percent, the vicinity of the electrodes became grey or black and the run away phenomenon occurred, while the thermistors having the porosity of 7–55 percent ac-

cording to the present invention did not cause such a variation and further even after the test was continued for 10,000 hours, the resistance increases only slightly and satisfactory durability was attained. However, when the porosity exceeds 55 percent, the adhesion (pulling strength) of the platinum electrodes is insufficient and there is problem in practical use. The test results are shown in the following Tables 1–3 showing data from the. Process for testing the tension strength of the electrodes.

The two electrode wires are separately secured with clips at a distance of 3 mm from the ends of the ceramic resistor and pulled in such a direction that the two electrode wires are diverged, through a spring system tension gauge fixed between the two clips and the strength when the electrode wires are removed from the above described resistor, is determined and is shown by an average value of 10 samples.

Table 1

83 mol% of ZrO ₂ +17 mol% of CaO(CaCO ₃)							
Resistance 800°C, 12V							
Test No.	Firing temperature (°C)	Porosity (%)	Initial (KΩ)	After 10 hours (KΩ)	After 100 hours (KΩ)	After 1,000 hours (KΩ)	Tension strength between electrodes (Kg)
1	1,450	65	26	17	16	120	0.2
2	1,480	58	13	9.3	11	21	0.5
3	1,485	55	8.7	7.6	7.0	13	0.6
4	1,500	52	7.2	7.0	6.0	10	0.7
5	1,520	45	5.1	4.6	4.2	5.7	1.0
6	1,535	40	4.1	3.8	4.4	1.2	
7	1,550	35	3.5	3.5	3.5	3.8	1.4
8	1,570	30	3.0	3.3	3.3	3.7	1.6
9	1,600	25	2.8	3.1	3.5	3.7	1.8
10	1,650	20	2.6	3.0	3.2	3.7	2.1
11	1,665	15	2.5	3.0	3.2	3.6	2.1
12	1,680	10	2.5	2.9	3.2	3.3	2.2
13	1,700	6.3	2.5	1.4	0.2	run away	2.2
14	1,730	4.3	1.4	run away	—	—	2.2

Table 2

87 mol% of ZrO ₂ +13 mol% of CaO(CaCO ₃)							
Resistance 800°C, 12V							
Test No.	Firing temperature (°C)	Porosity (%)	Initial (KΩ)	After 10 hours (KΩ)	After 100 hours (KΩ)	After 1,000 hours (KΩ)	Tension strength between electrodes (Kg)
15	1,410	60	7.0	5.5	6.0	18	0.3
16	1,500	55	4.6	4.2	4.2	7.6	0.5
17	1,520	50	3.5	3.3	3.4	4.5	0.7
18	1,545	45	2.8	2.7	2.7	3.4	0.9
19	1,570	40	2.4	2.5	2.6	2.9	1.1
20	1,585	35	2.2	2.2	2.3	2.4	1.3
21	1,610	30	1.9	2.0	2.2	2.3	1.5
22	1,645	25	1.8	1.9	2.1	2.3	1.7
23	1,665	20	1.8	1.9	2.1	2.3	1.9
24	1,700	15	1.8	1.9	2.0	2.3	2.0
25	1,740	10	1.7	1.9	2.0	2.3	2.1
26	1,755	8	1.7	1.8	1.4	1.0	2.2
27	1,780	6	1.5	0.8	run away	—	2.2
28	1,800	4	1.0	run away	—	—	2.2

Table 3

75 mol% of ZrO ₂ +25 mol% of CaO(CaCO ₃)							
Resistance 800°C, 12V							
Test No.	Firing temperature (°C)	Porosity (%)	Initial (KΩ)	After 10 hours (KΩ)	After 100 hours (KΩ)	After 1,000 hours (KΩ)	Tension strength between electrodes (Kg)
29	1,470	55	44	37	38	88	0.4
30	1,485	50	28	27	28	34	0.6
31	1,500	45	22	21	22	26	0.8
32	1,515	40	19	18	18	21	1.0
33	1,535	35	17	17	17	18	1.2
34	1,550	30	15	15	16	16	1.4
35	1,570	25	14	14	15	16	1.6
36	1,600	20	13	14	15	16	1.8
37	1,620	15	13	13	14	16	1.9
38	1,630	12	14	14	15	17	2.0
39	1,645	10	14	15	15	17	2.1
40	1,665	8	14	15	15	17	2.1
41	1,690	5	12	8	5	1	2.2
42	1,710	3	10	0.1	run away	—	2.2

EXAMPLE 2

70 mol percent of a mixture of 12 mol percent of CaO and 88 mol percent of ZrO₂ was added with 30 mol percent of spinel composed of MgO and Al₂O₃ as a resistance controlling agent. The resulting mixture was calcined at 1,350°C for 2 hours and then added with 4 percent by weight of an emulsion consisting of equal weight amounts of stearic acid and water and pulverized in a wet process in a trommel for 20 hours. The pulverized mixture was treated in the same manner as described in Example 1 except that the heating temperature lower than 1,700°C to produce the oxygen ion transport type thermistors. DC 12V was applied to each of the thermistors at 800°C. The obtained results are shown in the following Table 4. As seen from this table, the thermistor having a porosity of 5 percent obtained by sintering at a temperature of 1,670°C showed "run away" after 100 hours and was not able to be practically used.

Table 4

70 mol% (12 mol% CaO+88 mol% ZrO ₂)+30 mol% (MgAl ₂ O ₄)							
Resistance 800°C, 12V							
Test No.	Firing temperature (°C)	Porosity (%)	Initial (KΩ)	After 10 hours (KΩ)	After 100 hours (KΩ)	After 1,000 hours (KΩ)	Tension strength between electrodes (Kg)
43	1,420	55	16	13	14	24	0.5
44	1,465	50	11	9.8	10	14	0.7
45	1,475	45	8.2	7.6	7.8	9.6	0.9
46	1,505	40	6.4	6.0	6.2	7.3	1.2
47	1,520	35	5.2	5.0	5.1	5.8	1.4
48	1,545	30	4.4	4.3	4.4	5.2	1.6
49	1,560	25	4.2	4.3	4.4	4.8	1.7
50	1,575	20	4.2	4.3	4.4	5.0	2.0
51	1,610	15	4.2	4.3	4.5	5.0	2.1
52	1,620	13	4.3	4.3	4.6	5.0	2.1
53	1,635	11	4.4	4.4	4.6	5.0	2.1
54	1,660	7	4.4	4.4	4.6	4.9	2.2
55	1,670	5	4.4	1.6	run away	—	2.2
56	1,695	3	2.7	run away	—	—	2.2

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EXAMPLES 3 AND 4

A mixture of 90 mol percent of ZrO₂ and 10 mol percent of Y₂O₃ and a mixture of 90 mol percent of ThO₂ and 10 mol percent of Y₂O₃ were calcined at 1,400°C for 2 hours respectively. Then each of the mixtures was added with 3.2 percent by weight of an emulsion consisting of equal weight amounts of stearic acid and water. The resulting mixture was pulverized in a wet process in a trommel for 8 hours. The pulverized mixture was treated in the same manner as described in Examples 1 and 2 at various temperatures as shown in the following Tables 5 and 6 by using 0.4 mm alloy wires having and consisting of 70 percent of platinum and 30 percent of rhodium as a pair of electrodes to produce oxygen ion transport type thermistors.

DC 12V was applied to the resulting thermistors and the results as shown in the following Tables 5 and 6 were obtained.

Table 5

90 mol% of ZrO ₂ +10 mol% of Y ₂ O ₃							
Resistance 800°C, 12V							
Test No.	Firing temperature (°C)	Porosity (%)	Initial (KΩ)	After 10 hours (KΩ)	After 100 hours (KΩ)	After 1,000 hours (KΩ)	Tension strength between electrodes (Kg)
57	1,420	60	2.6	2.3	2.5	5.4	0.3
58	1,480	55	2.2	1.9	2.1	3.7	0.5
59	1,520	50	1.8	1.7	1.8	2.8	0.7
60	1,540	45	1.6	1.4	1.5	2.2	0.9
61	1,570	40	1.4	1.2	1.3	1.8	1.1
62	1,590	35	1.2	1.1	1.1	1.5	1.3
63	1,620	30	1.0	1.0	1.0	1.2	1.5
64	1,640	25	0.90	0.88	0.9	1.0	1.6
65	1,675	20	0.86	0.85	0.88	0.98	1.7
66	1,710	15	0.85	0.86	0.89	0.98	1.8
67	1,750	10	0.86	0.86	0.92	0.98	1.9
68	1,790	7	0.87	0.87	0.92	0.40	2.0
69	1,805	5	0.87	0.80	0.20	run away	2.0
70	1,820	3	0.70	run away	—	—	2.1

Table 6

90 mol% of ThO ₂ +10 mol% of Y ₂ O ₃							
Resistance 800°C, 12V							
Test No.	Firing temperature (°C)	Porosity (%)	Initial (KΩ)	After 10 hours (KΩ)	After 100 hours (KΩ)	After 1,000 hours (KΩ)	Tension strength between electrodes (Kg)
71	1,590	60	72	64	75	156	0.4
72	1,615	55	65	61	69	112	0.5
73	1,630	50	58	55	60	71	0.7
74	1,655	45	44	41	45	56	0.9
75	1,670	40	36	34	35	40	1.1
76	1,695	35	27	26	27	30	1.3
77	1,720	30	22	22	23	26	1.5
78	1,730	25	20	20	21	24	1.8
79	1,745	20	19	19	20	22	2.0
80	1,760	15	17	18	18	20	2.0
81	1,780	11	16	17	17	19	2.1
82	1,805	8	15	17	17	17	2.1
83	1,840	5	14	16	13	run away	2.2
84	1,870	2	14	7	run away	—	2.2

In the oxygen ion transport type thermistors of the present invention as mentioned above, there is no fear that the electrodes will fall from the ceramic resistors, oxygen can be transported freely between both the electrodes, the variation of the resistance due to the reduction of the ceramic resistor can be prevented, the durability is improved and mass-production can be easily effected.

The above described examples are with respect to thermistors produced by a press molding but molding processes other than press molding, for example extrusion molding, cast molding and the like which are used for general moldings for ceramics, can be used.

We claim:

- 45 1. An oxygen ion transport type thermistor comprising an oxygen ion type solid solution consisting of 50–95 mol percent of at least one metal oxide selected from the group consisting of ZrO₂, CeO₂, HfO₂ and ThO₂, and 5–50 mol percent of at least one metal oxide selected from the group consisting of CaO, MgO, SrO, La₂O₃, Y₂O₃, Yb₂O₃, Sc₂O₃, Gd₂O₃ and Nd₂O₃, and two metal lead wires are embedded in said solution and held in an adequately spaced parallel relationship to each other and lying substantially in the center line in the thickness direction of said solution and that the porosity of said oxygen ion transport type solid solution is 7–55 percent.
- 50 2. The thermistor as claimed in claim 1, wherein said porosity is 15–35 percent.

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