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(71) Applicant: Zexel Corporation
Tokyo 150-8360 (JP)

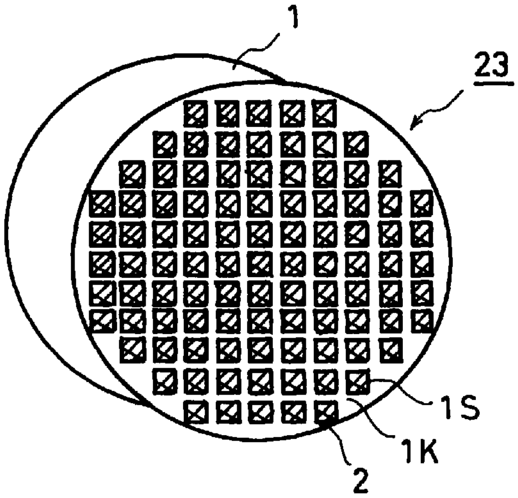
(72) Inventor: Takatsu, Katsumi
Higashimatsuyama-shi, Saitama-ken (JP)

(74) Representative:
Goddar, Heinz J., Dr.
FORRESTER & BOEHMERT
Franz-Joseph-Strasse 38
80801 München (DE)

(54) Absorbing layer for a high-frequency heating catalyst

(57) The high-frequency heating catalyst of the present invention comprises a high-frequency absorbing layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a high-frequency absorbing material and a catalyst such as Pd, Pd/Rh or Pt/Rh, carried by the high-frequency absorbing layer, for making clean harmful substances contained in exhaust gas. Since the high-frequency absorbing layer is made from a mixture of an electroconductive metal oxide and an insulating material having an impedance adjusted to the characteristic impedance of a medium through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more, the high-frequency wave can be absorbed and converted into heat energy effectively.

FIG. 1(a)



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Description

Background of the Invention

[Field of the Invention]

The present invention relates to a high-frequency heating catalyst used in an exhaust gas apparatus for an internal combustion engine or the like and, particularly, to a high-frequency heating catalyst for making clean harmful exhaust gas exhausted at the time of the start of the engine at low temperatures.

[Description of the Prior Art]

Exhaust gas from a car contains air pollutants such as hydrocarbon, carbon monoxide and nitrogen oxide. To make clean such harmful exhaust gas, there are available an engine combustion system and a post-processing system using a catalyst. The post-processing system using a catalyst comprises letting exhaust gas from a car pass through cleaning means having a three-element catalyst composed of a precious metal element alloy such as Pd/Rh or Pt/Rh to oxide hydrocarbon and carbon monoxide and reduce nitrogen oxide so as to change them into harmless carbonate gas, vapor and nitrogen and discharging them from the car.

However, in the exhaust gas apparatus of an internal combustion engine having a catalyst device of the prior art, a catalyst is heated by the exhaust gas of the internal combustion engine. Therefore, it takes time for the catalyst to reach a temperature at which its catalytic function can be effectively exerted and the catalyst cannot remove the above harmful substances completely at the time of the start of the internal combustion engine at low temperatures.

To remove harmful substances contained in exhaust gas even at the time of start at low temperatures, there is disclosed a method for heating a catalyst in the cleaning means quickly using a microwave (Japanese Laid-open Patent Application No. Hei 4-353208). As shown in Fig. 8, exhaust gas G supplied from a exhaust pipe 21a is let pass through cleaning means 23A provided in a heating chamber 22 to make clean the exhaust gas G, and then the clean exhaust gas G is discharged from an exhaust pipe 21b. The cleaning means 23A is held in the heating chamber 22 by a supporting member 24. A microwave generated by a high-frequency oscillator 25 is irradiated onto the cleaning means 23A through a waveguide path 26. As shown in Figs. 9(a) and 9(b), the cleaning means 23A comprises a substrate 1 which has a honeycomb structure and is made from a ceramic material such as alumina which rarely absorbs a high-frequency wave and a high-frequency heating catalyst 2A formed on the barrier 1K of the substrate 1 and having a three-element catalyst 2b such as Pd/Rh or Pt/Rh carried on a high-frequency absorbing material 2a such as ZnO which absorbs a microwave. The high-frequency absorbing material 2a converts the energy of the microwave radiation into heat energy to raise the temperature of the catalyst 2b to its operation temperature, thereby removing harmful substances contained in exhaust gas passing through through holes 1S in the substrate 1.

Figs. 10(a) and 10(b) are diagrams showing the structure of conventionally used cleaning means 23B which comprises (1) a substrate 1 composed of an insulating cordierite sintered body having a honeycomb structure, insulating properties and high thermal shock resistance and (2) a high-frequency heating catalyst 2B which comprises a high-frequency absorbing layer 2c formed on the surface of each barrier 1K of the substrate 1 and made from a high-frequency absorbing material and a wash coat layer 2d formed on the surface of the high-frequency absorbing layer 2c and carrying Pt/Rh dispersed therein. The Pt/Rh catalyst is dispersed and carried in the vicinity of the surface of the wash coat layer 2d. A microwave irradiated onto the cleaning means 23B is converted into heat by the above high-frequency absorbing layer 2c to raise the temperature of Pt/Rh dispersed and carried in the vicinity of the surface of the wash coat layer 2d to its operation temperature, whereby harmful substances contained in the exhaust gas passing through the cleaning means 23B are removed.

However, since the heat capacity of the wash coat layer 2d is large in the cleaning means 23B, the power of the input microwave must be made large to quickly heat Pt/Rh (catalyst) dispersed and carried in the vicinity of the surface of the wash coat layer 2d. Meanwhile, in the cleaning means 23A, since the high-frequency heating catalyst 2A is a mixture of a high-frequency absorbing material 2a and a three-element catalyst 2b, the heat propagation efficiency thereof is higher than that of the high-frequency heating catalyst 2B. However, since the characteristic impedance of propagation space which is determined by the frequency of high-frequency radiation (microwave) or a medium through which a high frequency wave propagates is not taken into account in the design of the impedances of the high-frequency heating catalysts 2A and 2B, the impedances of the high-frequency heating catalysts 2A and 2B do not match the characteristic impedance of the propagation space. Therefore, when the conventional high-frequency heating catalysts 2A and 2B are used, a high-frequency wave is reflected on the surfaces of the high-frequency heating catalysts 2A and 2B, thereby greatly reducing the absorption efficiency of the high-frequency wave.

To improve the catalytic activity of the conventional high-frequency heating catalyst 2A which is a mixture of a high-frequency absorbing material 2a such as ZnO or CoO and a three-element catalyst 2b, the content of the three-element catalyst 2b must be increased. However, when the content of the three-element catalyst is increased, the heating efficiency of the high-frequency heating catalyst 2A lowers.

Further, since the high-frequency heating catalysts 2A and 2B are carried on the surface or in the interior of the substrate 1 uniformly and a flow direction of the exhaust gas G is not taken into account, efficient high-frequency heating is impossible.

Moreover, when $La_{(1-x)}Sr_xCoO_3$ containing Co is used as the high-frequency absorbing material in conjunction with with the substrate 1 composed of a cordierite sintered body which is a composite metal oxide essentially composed of MgO and Al2O3, Al contained in the substrate 1 reacts with Co contained in the high-frequency absorbing layer 2c upon a rise in the temperature of the high-frequency heating catalyst 2B with the result that the composition ratio of the La(1-x)SrxCoO3 differs from the initial composition ratio, thereby deteriorating the heat conversion efficiency of the microwave. As a result, the temperature elevation rate of the catalyst lowers and the catalytic function efficiency of the high-frequency heating catalyst 2B deteriorates. Also when the high-frequency absorbing material contains Mn like La(1-x)SrxMnO3 and the material forming the substrate 1 contains Si like a composite oxide of SiO2 and MgO, the same reaction occurs with the result of a reduction in the catalytic function efficiency of the high-frequency heating catalyst 2B.

Summary of the Invention

It is therefore an object of the present invention which has been made in view of the above problems of the prior art to provide a high-frequency heating catalyst which can make clean harmful exhaust gas exhausted at the time of the start of an internal combustion engine at low temperatures by absorbing a high-frequency wave effectively to increase the temperature of a catalyst to its operation temperature at the time of the start at low temperatures.

According to a first aspect of the present invention, there is provided a high-frequency heating catalyst which comprises a high-frequency absorbing layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a high-frequency absorbing material and a catalyst such as Pd, Pd/Rh or Pt/Rh, carried by the high-frequency absorbing layer, for making clean harmful substances contained in exhaust gas, wherein the high-frequency absorbing layer is made from a mixture of an electroconductive metal oxide and an insulating material having an impedance adjusted to the characteristic impedance of a medium through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more.

According to a second aspect of the present invention, there is provided a high-frequency heating catalyst, wherein the insulating material is a metal oxide having co-catalytic activity such as ceria or ceria stabilized zirconia.

According to a third aspect of the present invention, there is provided a high-frequency heating catalyst, wherein the insulating material is a metal oxide having a large specific surface area such as g-alumina.

According to a fourth aspect of the present invention, there is provided a high-frequency heating catalyst which comprises a catalyst carrying layer, formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from either one or both of a metal oxide having co-catalytic activity and a metal oxide material having a large specific surface area, which a catalyst material such as Pd, Pd/Rh or Pt/Rh for making clean harmful substances contained in exhaust gas is uniformly dispersed in and carried by, and a high-frequency absorbing layer formed on part of the surface of the catalyst carrying layer and made from a mixture of an insulating material and an electroconductive metal oxide, wherein the high-frequency absorbing layer is formed on an upstream side of exhaust gas to be cleaned.

According to a fifth aspect of the present invention, there is provided a high-frequency heating catalyst, wherein the insulating material contains either one or both of a metal oxide having co-catalytic activity and a metal oxide material having a large specific surface area, which a catalyst such as Pd, Pd/Rh or Pt/Rh for making clean harmful substances contained in exhaust gas is uniformly dispersed in and carried by.

According to a sixth aspect of the present invention, there is provided a high-frequency heating catalyst which comprises a wash coat layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a heat resistant material such as g-alumina or ceria stabilized zirconia having a large specific surface area, and a high-frequency absorbing layer formed on part of the surface of the wash coat layer and made from a mixture of an electroconductive metal oxide and an insulating material and which has a catalyst such as Pt, Pt/Rh or Pd/Rh for making clean harmful substances contained in exhaust gas carried on the surfaces or in the vicinity of the surfaces of the wash coat layer and the high-frequency absorbing layer, wherein the high-frequency absorbing layer is formed on an upstream side of exhaust gas to be cleaned.

According to a seventh aspect of the present invention, there is provided a high-frequency heating catalyst, wherein the high-frequency absorbing layer contains a co-catalyst material such as ceria or ceria stabilized zirconia having co-catalytic activity and g-alumina or ceria stabilized zirconia having a large specific surface area.

According to an eighth aspect of the present invention, there is provided a high-frequency heating catalyst, wherein the material having co-catalytic activity and the heat resistant material do not contain an element which reacts with a metal element contained in the electroconductive metal oxide.

According to a ninth aspect of the present invention, there is provided a high-frequency heating catalyst, wherein an intermediate layer made from a metal oxide which does not contain a component reacting with a metal element component contained in the high-frequency absorbing layer at high temperatures is formed between the high-frequency absorbing layer and the substrate.

According to a tenth aspect of the present invention, there is provided a high-frequency heating catalyst, wherein when an electroconductive metal oxide containing Co is used as a high-frequency absorbing material, a metal oxide containing no Al, such as SiO2, ZrO2 or CeO2, or a composite metal oxide of two or more thereof is used to form the intermediate layer.

According to an eleventh aspect of the present invention, there is provided a high-frequency heating catalyst, wherein when an electroconductive metal oxide containing Mn is used as a high-frequency absorbing material, a metal oxide containing no Si, such as CaO, Al_2O_3 or CeO_2, or a composite metal oxide of two or more thereof is used to form the intermediate layer.

The above and other objectives, features and advantages of the invention will become more apparent from the following description when taken in conjunction with the accompanying drawings.

Brief Description of the Drawings

Figs. 1(a) to 1(c) are diagrams showing the structure of cleaning mean comprising a high-frequency heating catalyst according to Embodiment 1 of the present invention;

Fig. 2 is a diagram showing the constitution of an exhaust gas cleaning apparatus according to Embodiment 1 of the present invention;

Fig. 3 is a diagram showing the structure of cleaning means according to Embodiment 2 of the present invention;

Fig. 4 is a diagram showing the structure of cleaning means according to Embodiment 3 of the present invention;

Figs. 5(a) to 5(d) are diagram showing the structure of a high-frequency heating catalyst according to Embodiment 4 of the present invention;

Fig. 6 is a diagram showing the structure of another high-frequency heating catalyst according to Embodiment 4 of the present invention;

Fig. 7 is a diagram showing the structure of still another high-frequency heating catalyst according to Embodiment 4 of the present invention;

Fig. 8 is a diagram showing the constitution of an exhaust gas cleaning apparatus of the prior art;

Figs. 9(a) and 9(b) are diagrams showing the constitution of cleaning means of the prior art; and

Figs. 10(a) and 10(b) are diagrams showing the constitution of another cleaning means of the prior art.

Detailed Description of the Preferred Embodiments

Preferred Embodiments of the present invention will be described hereinunder with reference to the accompanying drawings.

In the following description, the same or corresponding elements as those of the prior art are given the same reference symbols.

Embodiment 1

Figs. 1(a), 1(b) and 1(c) are diagrams showing the structure of exhaust gas cleaning means 23 according to Embodiment 1 of the present invention. The cleaning means 23 comprises (1) a substrate 1 composed of a cordierite sintered body having a honeycomb structure, insulating properties and high thermal shock resistance and (2) a high-frequency heating catalyst 2 coated on the surface of each barrier 1K of the substrate 1. In these figures, reference symbol 1s denotes through holes formed in the substrate 1. As shown in Fig. 1(c), exhaust gas G is made clean by the high-frequency heating catalyst 2 while it passes through the through holes 1s in the cleaning means 23 and discharged.

The high-frequency catalyst 2 has Pt/Rh, a three-element catalyst, carried by a high-frequency absorbing layer made from a mixture of $La_{0.6}Sr_{0.4}MnO_3$ which is an electroconductive metal oxide and ceria stabilized zirconia which is an insulating material having co-catalytic activity and a large specific surface area. The mixing ratio of the electroconductive metal oxide and the insulating material is controlled to adjust the impedance of the high-frequency absorbing layer to the characteristic impedance of a transmission path through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more at an oscillation frequency of a microwave. The high-frequency absorbing layer is coated on the substrate 1 and then heated to be firmly fixed to the barrier 1K of the substrate 1.

The Pt/Rh three-element catalyst is carried on the surface or in the interior of the high-frequency absorbing layer by immersing the substrate 1 having the high-frequency absorbing layer formed thereon in a solution containing Pt/Rh and heating it. Since ceria stabilized zirconia which is an insulating material contained in the high-frequency absorbing layer has a large specific surface area, the Pt/Rh catalyst can be uniformly dispersed into the high-frequency absorbing layer.

Fig. 2 is a diagram showing the constitution of an exhaust gas cleaning apparatus equipped with the cleaning means 23 having the above high-frequency heating medium 2. A microwave generated by a high-frequency oscillator 25 passes through a waveguide path 26 and is transmitted to a cylindrical heating chamber 22 (cavity) whose impedance is adjusted to the impedance of the waveguide path 26 in a joint slot 28. The exhaust gas G is guided from an exhaust pipe 21 into the heating chamber 22 and discharged from an exhaust pipe 21b. Reflection plates 27a and 27b made from a punching metal are installed at both ends of the heating chamber 22, and the inner diameter and length of the heating chamber 22 are designed such that a microwave resonates in the heating chamber 22. In Fig. 2, reference letter P indicates the field strength of a standing wave in the heating chamber 22, and the high-frequency heating medium 2 is held by a supporting member 24 at a position of $\lambda g/4$ (λg is a wavelength in the waveguide) from the reflection plate 27b installed on a downstream side of exhaust gas G in the heating chamber 22, that is, a position where the amplitude of the standing wave is maximum.

Since the material of the high-frequency heating catalyst 2 is designed to adjust the impedance of the high-frequency absorbing layer of the high-frequency heating catalyst 2 to the characteristic impedance of the propagation path of the heating chamber 22 as described above, the reflection of a microwave by the cleaning means 23 is small and the energy of the microwave irradiated onto the high-frequency heating catalyst 2 is absorbed by the high-frequency absorbing layer efficiently. Therefore, the temperature of the catalyst contained in the high-frequency heating catalyst 2 can be sharply increased, the temperature of the catalyst can be raised to its operation temperature quickly even at the time of the start of an internal combustion engine at low temperatures, and harmful exhaust gas exhausted at the time of start at low temperatures can be made clean.

For example, when a microwave having an output power of 600 W and a frequency of 2.45 GHz generated by the high-frequency oscillator 25 was irradiated onto the cleaning means 23, it took about 20 seconds to increase the surface temperature of the conventional high-frequency heating catalyst 2B to 400°C. On the other hand, when the high-frequency heating catalyst 2 of Embodiment 1 was used, it took about 8 seconds to increase its surface temperature to 400°C. Since ceria stabilized zirconia which is an insulating material contained in the high-frequency heating catalyst 2 has co-catalytic activity, the catalytic function of the Pt/Rh catalyst is improved, whereby the cleaning function of harmful exhaust gas of the catalyst is further enhanced.

According to this Embodiment 1 of the present invention, the impedance of the high-frequency absorbing layer in the high-frequency heating catalyst 2 is adjusted to the characteristic impedance of the propagation path through which a microwave is transmitted such that reflection power ratio becomes 10 dB or more at an oscillation frequency of the microwave. Therefore, the reflection of the microwave by the high-frequency absorbing layer is small, the temperature of the catalyst can be raised sharply, and the temperature of the catalyst can be increased to its operation temperature quickly even at the time of the start of an internal combustion engine at low temperatures, thereby making it possible to make clean harmful exhaust gas exhausted at the time of start at low temperatures. Since ceria stabilized zirconia which is an insulating material contained in the high-frequency heating catalyst 2 has co-catalytic activity and a large specific surface area, the catalytic function of the Pt/Rh catalyst is improved, whereby the cleaning function of the harmful exhaust gas of the catalyst can be enhanced.

In this Embodiment 1, ceria stabilized zirconia is used as the insulating material. When a mixture of a metal oxide having a high specific surface area such as γ-alumina having a large specific surface area and ceria having co-catalytic activity is used, the same effect as above is obtained.

In the above embodiment, after the high-frequency absorbing layer is formed on the substrate 1, the Pt/Rh catalyst is carried on the surface or in the interior of the high-frequency absorbing layer. When a slurry of a mixture of the above electroconductive metal oxide and the insulating material is mixed with a solution containing a catalyst such as Pt/Rh and stirred to prepare a solution and the solution is coated on the substrate 1 to form the high-frequency heating catalyst 2, the catalyst such as Pt/Rh is uniformly dispersed into the high-frequency absorbing material. Therefore, the catalytic function of the high-frequency heating catalyst 2 can be further improved.

Embodiment 2

Fig. 3 is a diagram showing the structure of exhaust gas cleaning means 23 according to Embodiment 2 of the present invention. The cleaning means 23 comprises (1) a substrate 1 composed of a cordierite sintered body having a honeycomb structure, insulating properties and high thermal shock resistance, and (2) a high-frequency heating catalyst 2 formed on the surface of each barrier 1K of the substrate 1. The high-frequency heating catalyst 2 comprises a first catalyst carrying layer 3 comprising ceria stabilized zirconia and a Pd/Rh catalyst, and a second catalyst carrying layer 4, formed on part of the surface of the fist catalyst carrying layer 3, which is a high-frequency absorbing layer comprising $La_{0.6}Sr_{0.4}MnO_3$ and ceria stabilized zirconia having co-catalytic ability and a Pd catalyst. The second catalyst carrying layer 4 is formed on an upstream side of exhaust gas G to be cleaned.

The second catalyst carrying layer 4 is formed by preparing a slurry comprising $La_{0.6}Sr_{0.4}MnO_3$, an electroconductive metal oxide, and ceria stabilized zirconia, an insulating material, whose mixing ratio is controlled to adjust the impedance of the second catalyst carrying layer 4 to the characteristic impedance of a transmission path through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more and dip coating the slurry on the first catalyst carrying layer 3. The second catalyst carrying layer 4 can be formed on only one side of the substrate 1 by immersing only one side of the substrate 1 into the slurry.

The cleaning means 23 comprising the above high-frequency heating catalyst 2 was installed in an exhaust gas cleaning apparatus as shown in Fig. 2 like the above Embodiment 1, exhaust gas from an internal combustion engine while idling was caused to flow through the apparatus, and the cleaning means 23 was irradiated with a microwave generated from the high-frequency oscillator 25 and having an output power of 800 W and a frequency of 2.45 GHz. When the cleaning means 23A having the conventional high-frequency heating catalyst 2B was used, it took about 20 seconds to increase the surface temperature of the high-frequency heating catalyst 2B to its reaction start temperature (about 300°C). On the other hand, when the cleaning means 23 having the high-frequency heating catalyst 2 of Embodiment 2 in which the second catalyst carrying layer 4 was formed in a range of 10 mm on an upstream side of exhaust gas G was used, the start of a catalytic reaction was observed in about 10 seconds after the irradiation of a microwave.

This is because the reflection of a microwave by the cleaning means 23 is little and the energy of a microwave irradiated onto the high-frequency heating catalyst 2 is efficiently absorbed by the second catalyst carrying layer 4 which is a high-frequency absorbing layer as the material of the high-frequency heating catalyst 2 is designed to adjust the impedance of the second catalyst carrying layer 4 which is a high-frequency absorbing layer to the characteristic impedance of the propagation path in the heating chamber 22 such that reflection power ratio becomes 10 dB or more. Further, since the front (upstream side of exhaust gas G) of the high-frequency heating catalyst 2 is heated efficiently by the second catalyst carrying layer 4, the temperature of the supplied exhaust gas G rises and catalysts on a downstream side out of the catalysts contained in the cleaning means 23 are heated by the supplied exhaust gas G, thereby advancing the start time of a catalytic reaction.

Moreover, since the second catalyst carrying layer 4 contains ceria stabilized zirconia having co-catalytic activity and the Pd catalyst, heat is generated by the catalytic reaction in the front of the high-frequency heating catalyst 2 at the same time. Therefore, the temperature of the supplied exhaust gas G rises higher than when only the high-frequency absorbing layer is formed at the front of the cleaning means 23, thereby further quickening a rise in the temperature of the catalyst.

In the above Embodiment 2, ceria stabilized zirconia is used as the insulating material for the first catalyst carrying layer 3. The first catalyst carrying layer 3 may be formed by containing a catalyst such as Pt/Rh or Pd/Rh in γ-alumina or a mixture of γ-alumina and ceria. Ceria stabilized zirconia is used as the insulating material contained in the second catalyst carrying layer 4. When a metal oxide such as a mixture of γ-alumina having co-catalytic activity and a large specific surface and ceria is used as the insulating material, the same effect is obtained. It is needless to say that the start time of the catalytic reaction can be advanced even when a high-frequency absorbing layer composed of an insulating material and an electroconductive metal oxide is formed on an upstream side of exhaust gas in place of the second catalyst carrying layer 4 because the front of the high-frequency heating catalyst 2 is heated efficiently, the temperature of exhaust gas G rises, and catalysts on a downstream of the cleaning means are heated by the exhaust gas G.

Embodiment 3

Fig. 4 is a diagram showing the structure of exhaust gas cleaning means 23 according to Embodiment 3 of the present invention. The cleaning means 23 comprises (1) a substrate 1 composed of a cordierite sintered body having a honeycomb structure, insulating properties and high thermal shock resistance, and (2) a high-frequency heating catalyst 2 formed on the surface of each barrier 1K of the substrate 1. The high-frequency heating catalyst 2 comprises a wash coat layer 5 made from ceria stabilized zirconia, a high-frequency absorbing layer 6, formed on part of the surface of the wash coat layer, comprising $La_{0.6}Sr_{0.4}MnO_3$ and ceria stabilized zirconia, and a catalyst layer 7 formed from Pd/Rh carried in the vicinity of the surfaces of the wash coat layer 5 and the high-frequency absorbing layer 6. The high-frequency absorbing layer 6 is formed on an upstream side of exhaust gas G to be cleaned.

The above high-frequency absorbing layer 6 is formed by preparing a slurry comprising $La_{0.6}Sr_{0.4}MnO_3$, an electroconductive metal oxide, and ceria stabilized zirconia, an insulating material, whose mixing ratio is controlled to adjust the impedance of the high-frequency absorbing layer 6 to the characteristic impedance of a transmission path through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more and dip coating the slurry on the wash coat layer 5. The high-frequency absorbing layer 6 can be formed on only one side of the substrate 1 by immersing only one side of the substrate 1 into the slurry.

The catalyst layer 7 is carried on the surfaces and in the interiors of the surfaces of the wash coat layer 5 and the high-frequency absorbing layer 6 by immersing the substrate 1 having the wash coat layer 5 and the high-frequency absorbing layer 6 formed thereon in a solution containing Pd/Rh and heating. Since ceria stabilized zirconia which is an insulating material contained in the high-frequency absorbing layer 6 has a large specific surface area, the Pd/Rh catalyst is carried by the high-frequency absorbing layer 6 in high concentration.

The cleaning means 23 comprising the above high-frequency heating catalyst 2 was installed in an exhaust gas cleaning apparatus as shown in Fig. 2 like the above Embodiment 1, exhaust gas from an internal combustion engine while idling was caused to flow through the apparatus, and the cleaning means 23 having a diameter of 90 mm and a length of 30 mm was irradiated with a microwave generated from the high-frequency oscillator 25 and having an output power of 800 W and a frequency of 2.45 GHz. When the cleaning means 23B having the conventional high-frequency heating catalyst 2B was used, it took about 20 seconds to increase the surface temperature of the high-frequency heating catalyst 2B to its catalytic reaction start temperature (about 300°C). On the other hand, when the cleaning means 23 having the high-frequency heating catalyst 2 of Embodiment 3 in which the high-frequency absorbing layer 6 was formed in a range of 10 mm on an upstream side of exhaust gas G was used, the start of a catalytic reaction was observed in about 10 seconds after the irradiation of a microwave.

This is because the reflection of a microwave by the cleaning means 23 is little and the energy of a microwave irradiated onto the high-frequency heating catalyst 2 is efficiently absorbed by the high-frequency absorbing layer 6 as the material of the high-frequency heating catalyst 2 is designed to adjust the impedance of the high-frequency absorbing layer 6 to the characteristic impedance of the propagation path in the heating chamber 22 such that reflection power ratio becomes 10 dB or more.

Since the front of the high-frequency heating catalyst 2 is heated efficiently by the high-frequency absorbing layer 6, the temperature of the supplied exhaust gas G rises and the catalyst carried by the wash coat layer 17 on a downstream side of the cleaning means 23 is heated by the exhaust gas G, the start time of a catalytic reaction can be advanced. Further, since the Pd/Rh catalyst is carried in the vicinity of the surface of the high-frequency absorbing layer 6 in high concentration, a large amount of heat is generated by the catalytic reaction at the same time, thereby making it possible to further quicken a rise in the temperature of the catalyst. Further, since the use efficiency of the catalyst is high, the amount of a precious metal used in the catalyst can be reduced.

In the above Embodiment 3, ceria stabilized zirconia is used as the insulating material for the wash coat layer 5. γ-alumina or a mixture of γ-alumina and ceria may be used.

In the above Embodiments 1, 2 and 3, $La_{0.6}Sr_{0.4}MnO_3$ is used as the high-frequency absorbing material. When a composite metal oxide such as $La_{(1-x)}Sr_xCoO_3$, $La_{(1-x)}Sr_xCrO_3$, $La_{(1-x)}Sr_xMnO_3$, $La_{(1-x)}Sr_xCo_{(1-y)}Pd_yO_3$, $La_{(1-x)}Sr_xMn_{(1-y)}Pd_yO_3$, $La_{(1-x)}Ca_xCoO_3$ or $La_{(1-x)}Ca_xMnO_3$ ($0 < x < 1$, $0 < y < 1$) or a mixture thereof is used, the same effect is obtained.

When the above electroconductive metal oxide contains Mn, if the material forming the layer in contact with the layer containing the above high-frequency absorbing material, for example, the first catalyst carrying layer 3 of the above Embodiment 2 or the wash coat layer 5 of the above Embodiment, is a compound containing Si, Mn and Si react with each other at high temperatures with the result that the impedance of the high-frequency absorbing material forming the second catalyst carrying layer 4 or the high-frequency absorbing layer 6 changes, thereby greatly reducing the microwave absorption efficiency of the high-frequency heating catalyst 2. When the electroconductive metal oxide contains Co, the layer in contact with the layer containing the high-frequency absorbing material must be composed of a compound containing no Al.

For example, since $La_{0.6}Sr_{0.4}MnO_3$ is used as the high-frequency absorbing material and ceria stabilized zirconia is used as the material forming the second catalyst carrying layer 4 in the above Embodiment 2, even if the surface temperature of the cleaning means 23 rises, the above reaction does not occur and a change in the catalytic activity of the high-frequency heating catalyst 2 is not observed. Since $La_{0.6}Sr_{0.4}MnO_3$ is used as the high-frequency absorbing material and ceria stabilized zirconia is used as the material forming the wash coat layer 5 in the above Embodiment 3, even if the surface temperature of the cleaning means 23 rises, a change in the catalytic activity of the high-frequency heating catalyst 2 is not observed.

Embodiment 4

Figs. 5(a) to 5(d) are diagrams showing the structure of exhaust gas cleaning means 23 according to Embodiment 4 of the present invention. Fig. 5(a) is a diagram showing the outer appearance, Fig. 5(b) is a sectional view, and Fig. 5(c) is a partially enlarged front view of the cleaning means 23. Fig. 5(d) is a diagram typically showing the layer structure of the high-frequency heating catalyst 2. The cleaning means 23 comprises (1) a substrate 1 composed of a cordierite sintered body having a honeycomb structure, insulating properties and high thermal shock resistance, and (2) a high-frequency heating catalyst 2 which comprises an intermediate layer 8A made from ZrO_2 and coated on the surface of each barrier 1K of the substrate 1, a high-frequency absorbing layer 9A formed on the intermediate layer and made from a mixture of $La_{0.6}Sr_{0.4}CoO_3$ which is an electroconductive metal oxide and CeO_2 which is an insulating material, and a catalyst layer 10, formed on the high-frequency absorbing layer 9A and made from MgO carrying Pt/Rh.

When the above-structured cleaning means 23 was installed in the heating chamber 22 of an exhaust gas cleaning apparatus as shown in Fig. 2 and irradiated with a microwave generated from the high-frequency oscillator 25 and having an output power of 600 W and a frequency of 2.45 GHz, the surface temperature of the high-frequency heating catalyst 2 reached about 800°C in 30 seconds due to the energy of the microwave and heat generated by a catalytic reaction. At this point, the properties of the high-frequency absorbing layer 9A of the high-frequency heating catalyst 2 did not change and the temperature rise characteristics of the high-frequency heating catalyst 2 hardly changed even when its surface temperature was raised to about 800°C repeatedly under the above conditions. Further, the electric resistance of the high-frequency absorbing layer 9A did not change after the repeated temperature rise test.

Fig. 6 is a diagram showing the structure of the high-frequency heating catalyst 2 having a high-frequency absorbing layer made from an electroconductive metal oxide containing Mn. The high-frequency heating catalyst 2 comprises an intermediate layer 8B formed on the barrier 1K of the substrate 1 composed of a cordierite sintered body and made from Al_2O_3, a high-frequency absorbing layer 9B formed on the intermediate layer 8B and made from a mixture of $La_{0.6}Sr_{0.4}MnO_3$ which is an electroconductive metal oxide and CeO_2 which is an insulating material, and a catalyst layer 10, formed on the high-frequency absorbing layer 9B and made from MgO carrying Pt/Rh. When the same test as that of the above Embodiment 4 was carried out using the above-structured high-frequency heating catalyst 2, the properties of the high-frequency absorbing layer 9B of the high-frequency heating catalyst 2 did not change and the electric resistance of the high-frequency absorbing layer 9B did not change after the test as well.

According to this Embodiment 4, when the material forming the high-frequency absorbing layer 9A is $La_{0.6}Sr_{0.4}CoO_3$ containing Co, ZrO_2, a metal oxide containing no Al, is used to form the intermediate layer 8A between the high-frequency absorbing layer 9A and the substrate 1. When the material forming the high-frequency absorbing layer 9B is $La_{0.6}Sr_{0.4}MnO_3$ containing Mn, Al_2O_3, a metal oxide containing no Si is used to form the intermediate layer 8B. Therefore, even when the high-frequency heating catalyst 2 is heated to about 800°C by microwave radiation, the properties of $La_{0.6}Sr_{0.4}CoO_3$ or $La_{0.6}Sr_{0.4}MnO_3$ forming the high-frequency absorbing layer (9A or 9B) do not change and hence, the catalytic function of the high-frequency heating catalyst 2 does not deteriorate.

In the above Embodiment 4, the catalyst layer 22A or 22B is formed on the high-frequency absorbing layer 9A or 9B in the above Embodiment 4, and the intermediate layer 8A or 8B is formed between the substrate 1 and the high-frequency absorbing layer 9A or 9B. As shown in Fig. 7, also in the high-frequency heating catalyst having a high-frequency absorbing layer 9C made from a high-frequency absorbing material carrying a catalyst such as Pt/Rh, ZrO_2,a metal oxide containing no Al, is used to form an intermediate layer 8C between the barrier 1K of the substrate 1 and the high-frequency absorbing layer 9C when the material forming the high-frequency absorbing layer 9C is $La_{0.6}Sr_{0.4}CoO_3$ containing Co, and Al_2O_3, a metal oxide containing no Si, is used to form the intermediate layer 8C when the material forming the high-frequency absorbing layer 9C is $La_{0.6}Sr_{0.4}MnO_3$ containing Mn.

In the above Embodiment 4, $La_{0.6}Sr_{0.4}CoO_3$ containing Co or $La_{0.6}Sr_{0.4}MnO_3$ containing Mn is used as the material forming the high-frequency absorbing layer. $La_{(1-x)}Sr_xCoO_3$, $La_{(1-x)}Sr_xCrO_3$, $La_{(1-x)}Sr_xMnO_3$, $La_{(1-x)}Sr_xCo_{(1-y)}Pd_yO_3$ or $La_{(1-x)}Sr_xMn_{(1-y)}Pd_yO_3$ ($0 < x < 1$, $0 < y < 1$) may be used.

The intermediate layer may be made from a metal oxide such as MgO, SiO_2, CaO or CeO_2, or a composite oxide of two or more thereof in addition to the above ZrO_2. MgO, ZrO_2, CaO or CeO_2, or a composite metal oxide of two or more thereof may be used as the metal oxide containing no Si in addition to the above Al_2O_3.

As described above, the high-frequency heating catalyst according to the first aspect of the present invention comprises a high-frequency absorbing layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a high-frequency absorbing material and a catalyst such as Pd, Pd/Rh or Pt/Rh, carried by the high-frequency absorbing layer, for making clean harmful substances contained in exhaust gas, and the high-frequency absorbing layer is made from a mixture of an electroconductive metal oxide and an insulating material having an impedance adjusted to the characteristic impedance of a medium through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more. Therefore, the reflection of high-frequency radiation is little, the high-frequency wave can be absorbed and converted into heat energy effectively, and the temperature of the catalyst can be thereby increased to its operation temperature quickly at the time of the start of an internal combustion engine at low temperatures. Thus, harmful exhaust gas exhausted at the time of the start at low temperatures can be made clean.

In the high-frequency heating catalyst according to the second aspect of the present invention, the insulating material is a metal oxide having co-catalytic activity such as ceria. Therefore, the catalytic function of the high-frequency heating catalyst can be further improved.

In the high-frequency heating catalyst according to the third aspect of the present invention, the insulating material is a metal oxide having a large specific surface area such as ceria stabilized zirconia. Therefore, a catalyst such as Pd, Pd/Rh or Pt/Rh can be uniformly carried by the high-frequency absorbing layer, and differences in the function of the high-frequency catalyst at different sites can be eliminated.

The high-frequency heating catalyst according to the fourth aspect of the present invention comprises a catalyst carrying layer, formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from either one or both of a metal oxide having co-catalytic activity and a metal oxide material having a large specific surface area, which a catalyst material such as Pd, Pd/Rh or Pt/Rh for making clean harmful substances contained in exhaust gas is uniformly dispersed in and carried by, and a high-frequency absorbing layer formed on part of the surface of the catalyst carrying layer and made from a mixture of an insulating material and an electroconductive metal oxide, and the high-frequency absorbing layer is formed on an upstream side of exhaust gas to be cleaned. Therefore, since exhaust gas heated at an upstream heats a downstream portion of the high-frequency heating catalyst, the temperature of the catalyst can be increased to its operation temperature quickly.

In the high-temperature heating catalyst according to the fifth aspect of the present invention, the insulating material contains either one or both of a metal oxide having co-catalytic activity and a metal oxide material having a large specific surface area, which a catalyst such as Pd, Pd/Rh or Pt/Rh for making clean harmful substances contained in exhaust gas is uniformly dispersed in and carried by. Therefore, the exhaust gas is further heated by a catalyst reaction in the high-frequency absorbing layer at an upstream, thereby making it possible to increase the temperature of the catalyst to its operation temperature more quickly.

The high-frequency heating catalyst according to the sixth aspect of the present invention comprises a wash coat layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a heat resistant material such as γ-alumina or ceria stabilized zirconia having a large specific surface area, and a high-frequency absorbing layer formed on part of the surface of the wash coat layer and made from a mixture of an electroconductive metal oxide and an insulating material, a catalyst such as Pt, Pt/Rh or Pd/Rh for making clean harmful substances contained in exhaust gas is carried on the surfaces or in the vicinity of the surfaces of the wash coat layer and the high-frequency absorbing layer, and the high-frequency absorbing layer is formed on an upstream side of exhaust gas to be cleaned. Therefore, the exhaust gas at an upstream is also heated by heat generated by a catalytic reaction, thereby making it possible to increase the temperature of the catalyst to its operation temperature more quickly.

In the high-frequency heating catalyst according to the seventh aspect of the present invention, the high-frequency absorbing layer contains a co-catalyst material such as ceria or ceria stabilized zirconia having co-catalytic activity and γ-alumina or ceria stabilized zirconia having a large specific surface area. Therefore, the catalytic function of the high-frequency heating catalyst can be further improved.

In the high-frequency heating catalyst according to the eighth aspect of the present invention, the material having co-catalytic activity and the heat resistant material do not contain an element which reacts with a metal element contained in the electroconductive metal oxide. Therefore, the high-frequency catalyst can be used at a wide temperature range.

In the high-frequency heating catalyst according to the ninth aspect of the present invention, an intermediate layer made from a metal oxide which does not contain a component reacting with a metal element component contained in the high-frequency absorbing layer at high temperatures is formed between the high-frequency absorbing layer and the substrate. Therefore, even when the high-frequency absorbing material is heated to a high temperature by the absorption of a microwave, a reaction does not occur between the material forming the high-frequency absorbing layer and the material forming the substrate and the catalyst function does not deteriorate. Further, since there are no changes in the characteristics of the high-frequency heating catalyst after long-term use, the reliability of the high-frequency heating catalyst can be greatly improved.

In the high-frequency heating catalyst according to the tenth aspect of the present invention, when the high-frequency absorbing layer is made from a material containing Co, a metal oxide containing no Al is used to form the intermediate layer. Therefore, the composition of the intermediate layer can be limited in advance.

In the high-frequency heating catalyst according to the eleventh aspect of the present invention, when the high-frequency absorbing layer is made from a material Containing Mn, a metal oxide containing no Si is used to form the intermediate layer. Therefore, the composition of the intermediate layer can be limited in advance.

The features disclosed in the foregoing description, in the claims and/or in the accompanying drawings may, both separately and in any combination thereof, be material for realising the invention in diverse forms thereof.

Claims

1. A high-frequency heating catalyst comprising a high-frequency absorbing layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a high-frequency absorbing material and a catalyst such as Pd, Pd/Rh or Pt/Rh, carried by the high-frequency absorbing layer, for making clean harmful substances contained in exhaust gas, wherein

   the high-frequency absorbing layer is made from a mixture of an electroconductive metal oxide and an insulating material having an impedance adjusted to the characteristic impedance of a medium through which a high-frequency wave is transmitted such that reflection power ratio becomes 10 dB or more.

2. The high-frequency heating catalyst of claim 1, wherein the insulating material is a metal oxide having co-catalytic activity such as ceria or ceria stabilized zirconia.

3. The high-frequency heating catalyst of claim 1, wherein the insulating material is a metal oxide having a large specific surface area such as γ-alumina.

4. A high-frequency heating catalyst comprising a catalyst carrying layer, formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from either one or both of a metal oxide having co-catalytic activity and a metal oxide material having a large specific surface area, which a catalyst material such as Pd, Pd/Rh or Pt/Rh for making clean harmful substances contained in exhaust gas is uniformly dispersed in and carried by, and a high-frequency absorbing layer formed on part of the surface of the catalyst carrying layer and made from a mixture of an insulating material and an electroconductive metal oxide, wherein

the high-frequency absorbing layer is formed on an upstream side of exhaust gas to be cleaned.

5. The high-frequency heating catalyst of claim 4, wherein the insulating material contains either one or both of a metal oxide having co-catalytic activity and a metal oxide material having a large specific surface area, which a catalyst such as Pd, Pd/Rh or Pt/Rh for making clean harmful substances contained in exhaust gas is uniformly dispersed in and carried by.

6. A high-frequency heating catalyst which comprises a wash coat layer formed on the surface of a substrate made from a material which rarely absorbs a high-frequency wave and made from a heat resistant material such as γ-alumina or ceria stabilized zirconia having a large specific surface area, and a high-frequency absorbing layer formed on part of the surface of the wash coat layer and made from a mixture of an electroconductive metal oxide and an insulating material, and which has a catalyst such as Pt, Pt/Rh or Pd/Rh for making clean harmful substances contained in exhaust gas carried on the surfaces or in the vicinity of the surfaces of the wash coat layer and the high-frequency absorbing layer, wherein

the high-frequency absorbing layer is formed on an upstream side of exhaust gas to be cleaned.

7. The high-frequency heating catalyst of claim 4, wherein the high-frequency absorbing layer contains a co-catalyst material such as ceria stabilized zirconia or ceria having co-catalytic activity and γ-alumina or ceria stabilized zirconia having a large specific surface area.

8. The high-frequency heating catalyst of claim 4, wherein the material having co-catalytic activity and the heat resistant material do not contain an element which reacts with a metal element contained in the electroconductive metal oxide.

9. The high-frequency heating catalyst of claim 1, wherein an intermediate layer made from a metal oxide which does not contain a component reacting with a metal element component contained in the high-frequency absorbing layer at high temperatures is formed between the high-frequency absorbing layer and the substrate.

10. The high-frequency heating catalyst of claim 9, wherein when the high-frequency absorbing layer is made from an electroconductive metal oxide containing Co, a metal oxide containing no Al, such as SiO_2, ZrO2 or CeO_2, or a composite metal oxide of two or more thereof is used to form the intermediate layer.

11. The high-frequency heating catalyst of claim 9, wherein when the high-frequency absorbing layer is made from an electroconductive metal oxide containing Mn, a metal oxide containing no Si, such as CaO, Al_2O_3 or CeO_2, or a composite metal oxide of two or more thereof is used to form the intermediate layer.

FIG. 1(a)

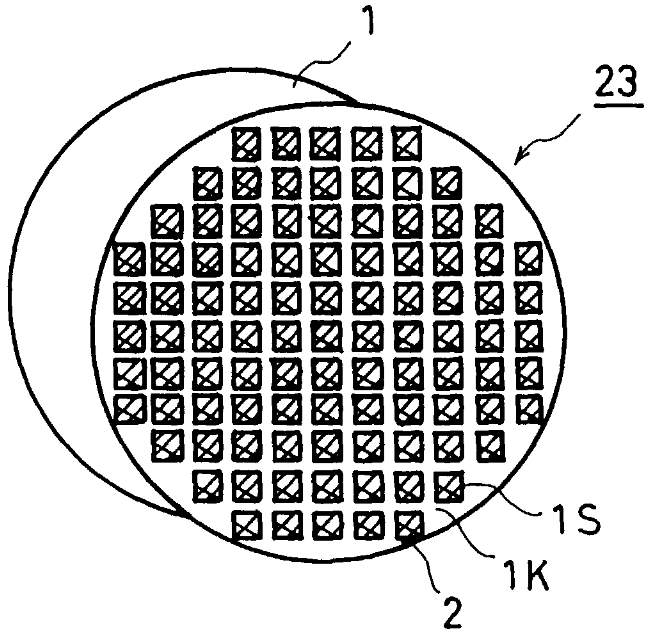

FIG.1(b)

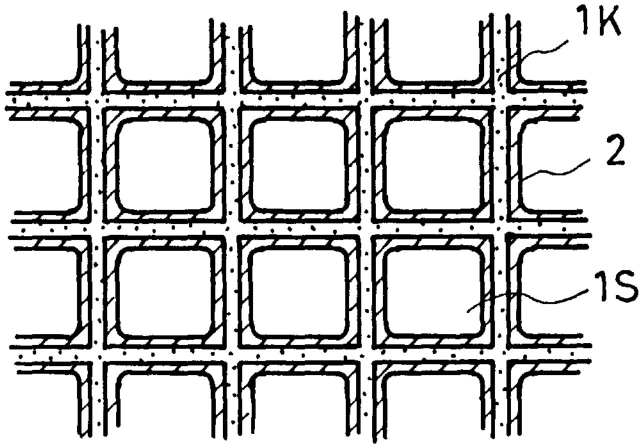

FIG.1(c)

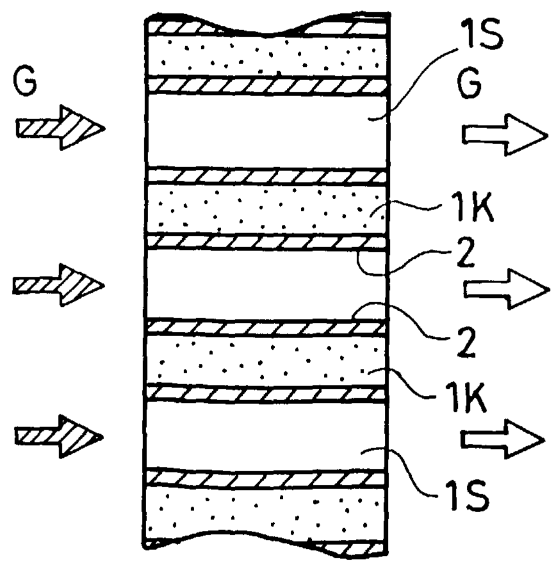

FIG. 2

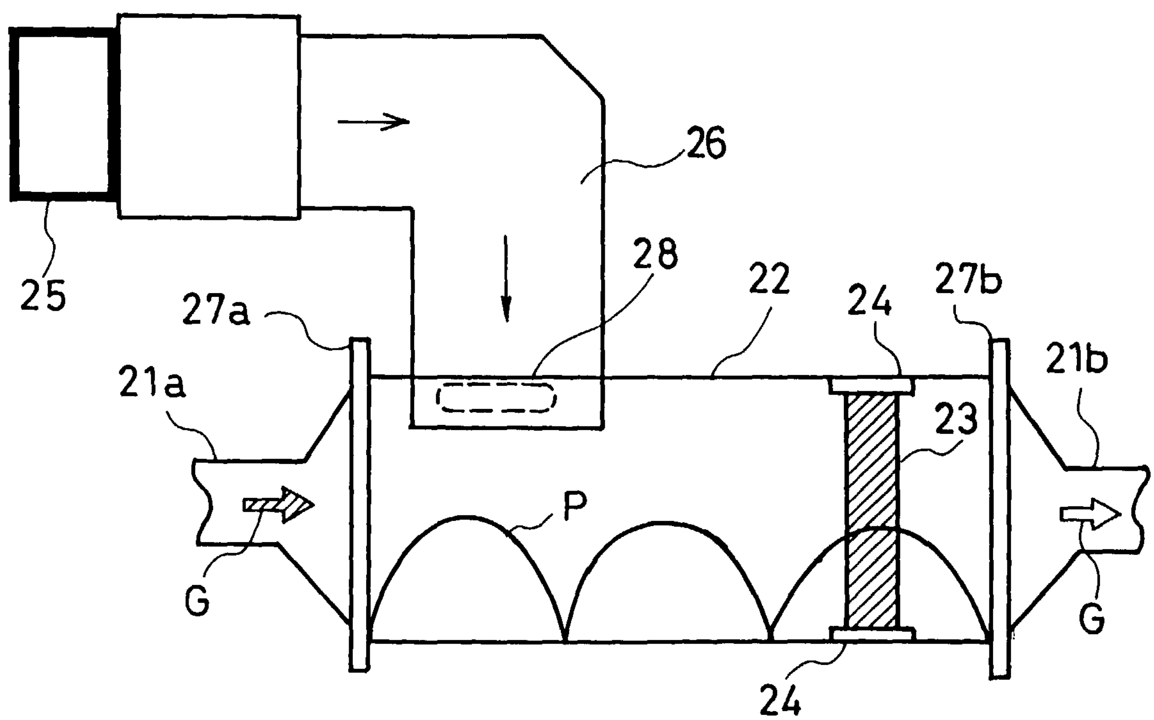

FIG.3

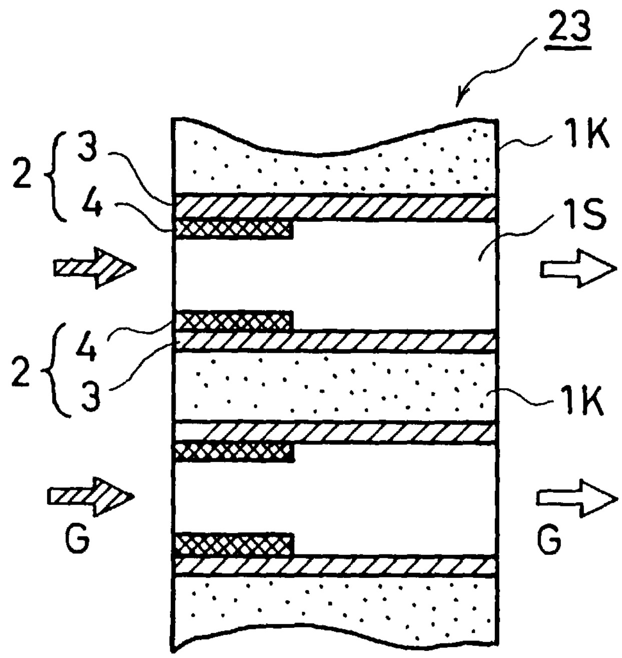

FIG. 4

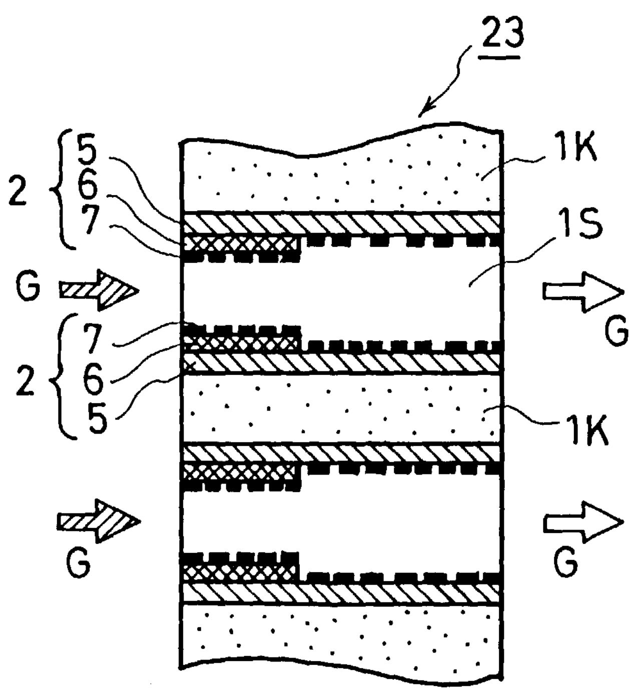

FIG.5(a)

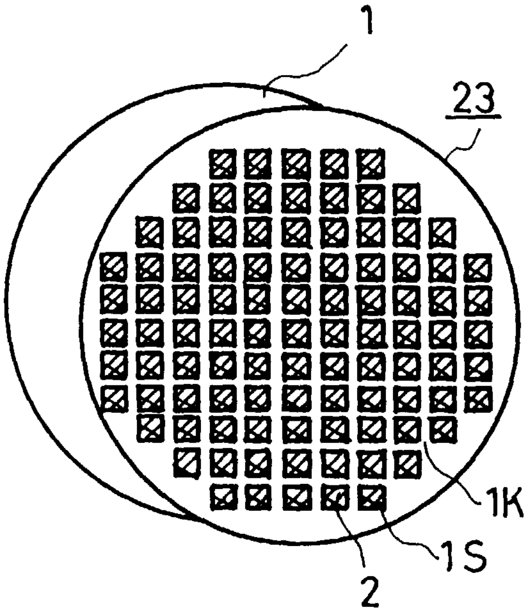

FIG.5(b)

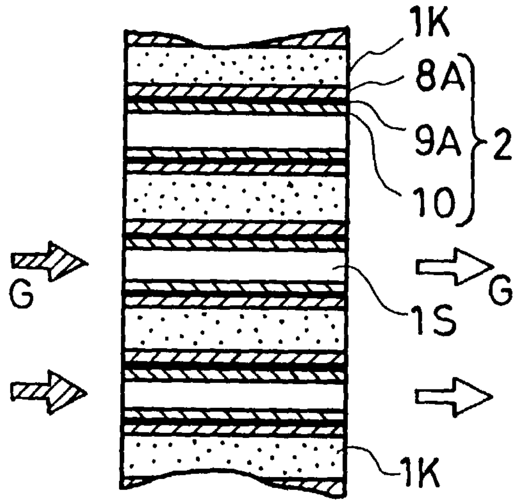

FIG.5(c)

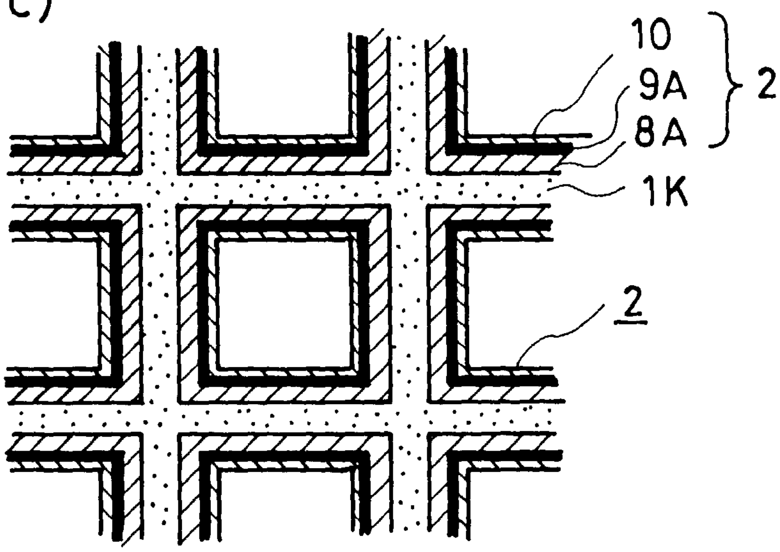

FIG.5(d)

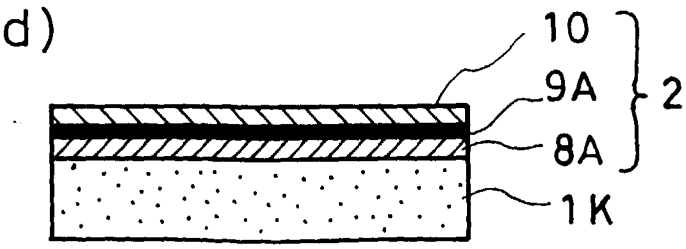

FIG.6

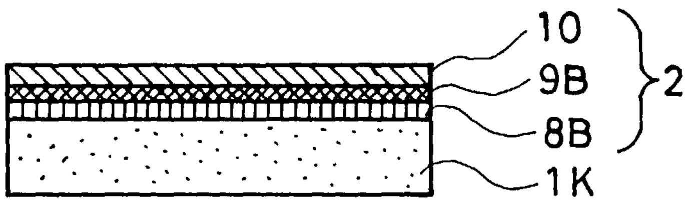

FIG.7

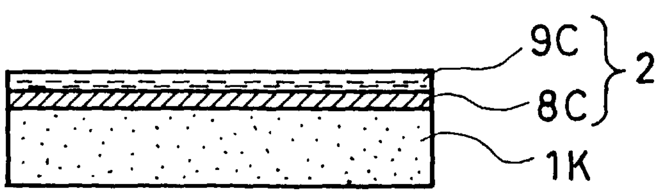

FIG.8 PRIOR ART

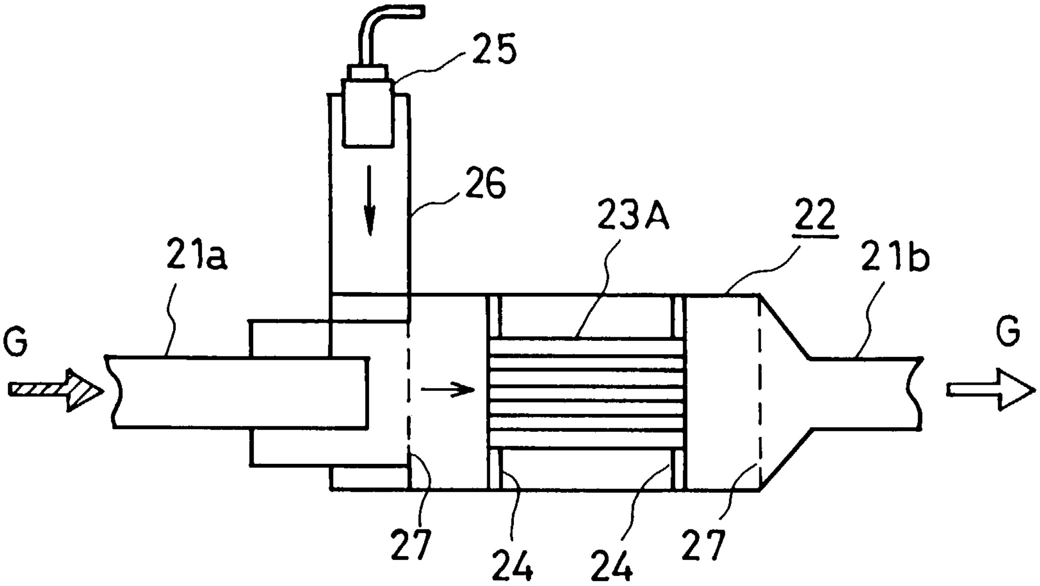

FIG.9(a) PRIOR ART

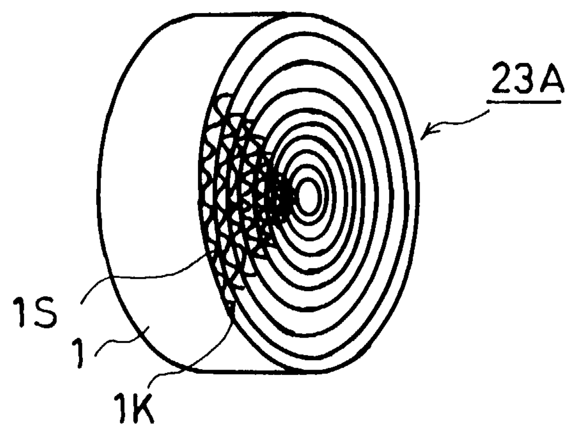

FIG.9(b) PRIOR ART

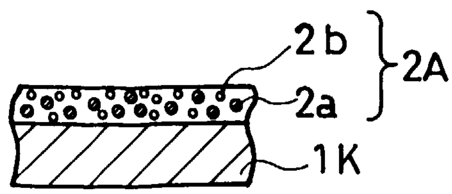

FIG. 10(a)
PRIOR ART

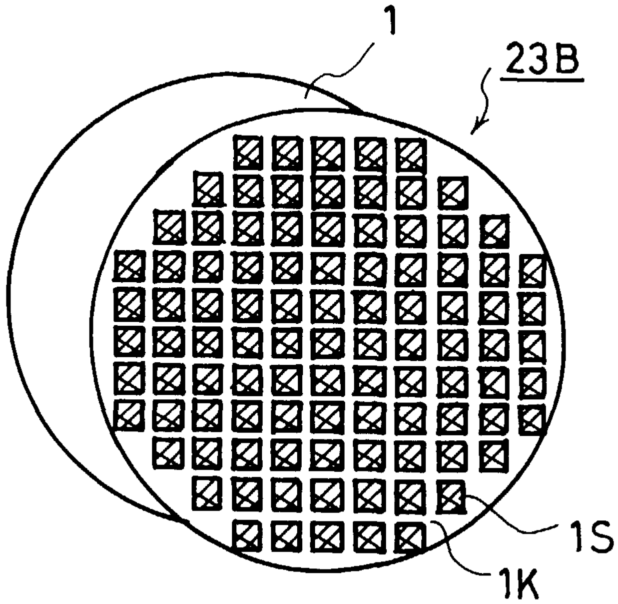

FIG. 10(b)
PRIOR ART