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(72) Inventeurs/Inventors:
LARSEN, PETER HALVOR, DK;
HENDRIKSEN, PETER VANG, DK;
LINDEROTH, SOREN, DK;
MOGENSEN, MOGENS, DK

(73) Propriétaire/Owner:
TECHNICAL UNIVERSITY OF DENMARK, DK

(74) Agent: BORDEN LADNER GERVAIS LLP

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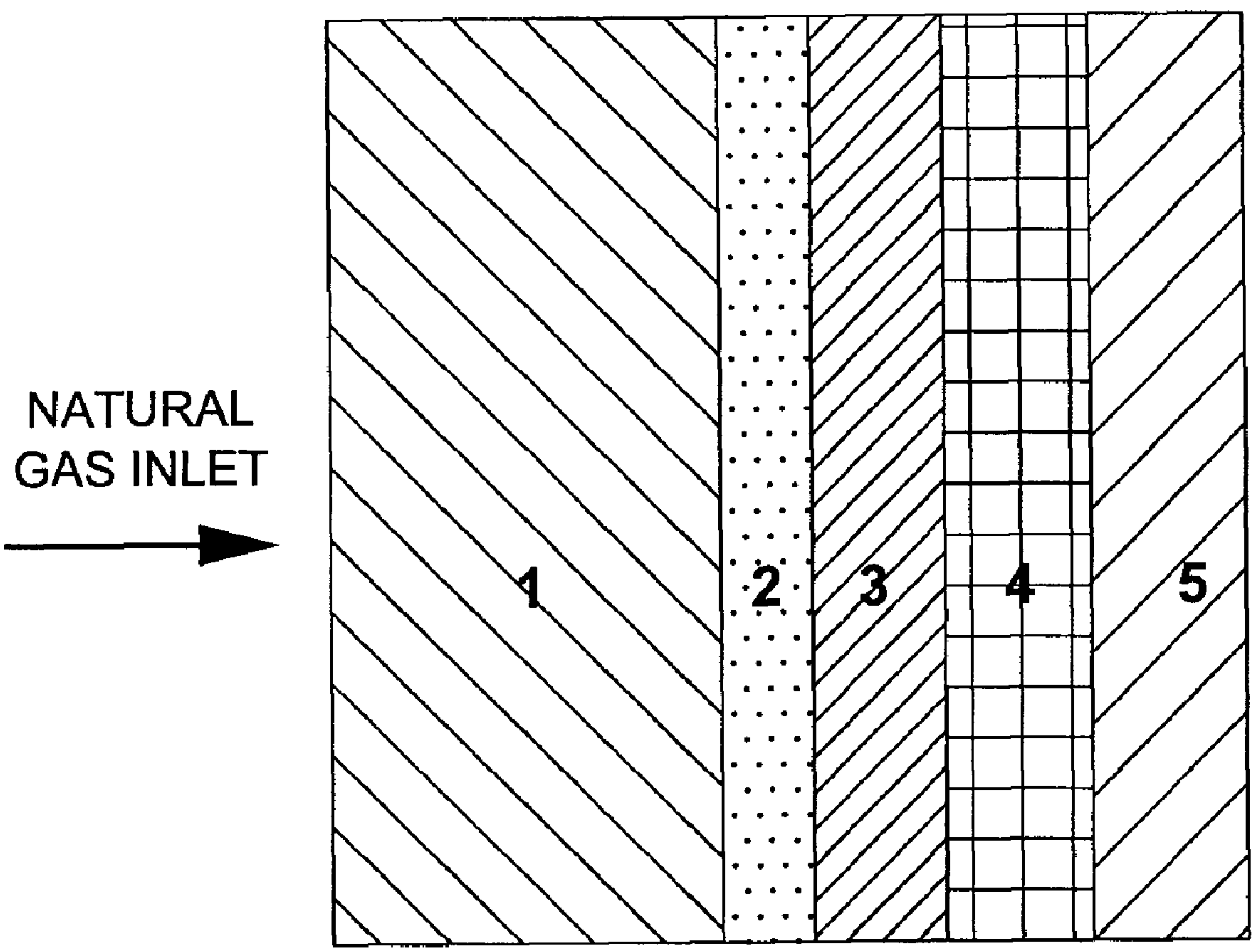


(57) Abrégé/Abstract:
The present invention provides a graded multilayer structure, comprising a support layer (1) and at least 10 layers (2, 3), wherein each of the at least 10 layers (2, 3) is at least partially in contact with the support layer (1), wherein the at least 10 layers (2, 3) differ

(57) Abrégé(suite)/Abstract(continued):
from each other in at least one property selected from layer composition, porosity and conductivity, and wherein the at least 10 layers (2, 3) are arranged such that the layer composition, porosity and/or conductivity horizontally to the support layer (1) forms a gradient over the total layer area.

Abstract

The present invention provides a graded multilayer structure, comprising a support layer (1) and at least 10 layers (2, 3), wherein each of the at least 10 layers (2, 3) is at least partially in contact with the support layer (1),

wherein the at least 10 layers (2, 3) differ from each other in at least one property selected from layer composition, porosity and conductivity, and

wherein the at least 10 layers (2, 3) are arranged such that the layer composition, porosity and/or conductivity horizontally to the support layer (1) forms a gradient over the total layer area.

Horizontally graded structures for electrochemical and electronic devices

Field of the invention

The present invention relates to a horizontally graded multilayer structure suitable for use as an electrode in electrochemical devices and to a method for producing same. Other applications of the graded multilayer structure include protective coatings for corrosion or mechanical wear.

Background of the invention

In a normal Ni-yttria stabilized zirconia (YSZ) anode of a solid oxide fuel cell (SOFC), which is operated on externally reformed methane, there is a temperature distribution over the cell in the order of about 150°C at an operational temperature of 850°C. Such a gradient has a detrimental effect on the mechanical as well as the chemical durability of the cell, and can for instance cause mechanical failure or enhanced chemical reactions in the warmest regions, as discussed, for example, in N. Q. Minh, and T. Takahashi, *Science and Technology of Ceramic Fuel Cells*, (Elsevier Science B. V., Amsterdam NL, 1995), and High Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications, Eds. S.C. Singhal and K. Kendall. This will in return inevitably result in a performance decrease of the cell over time. It is therefore desired to level the temperature gradient, as this will result in an overall increase in cell performance because the temperature of the colder parts of the cell is increased.

In the case of an internal reformation of wet natural gas, such as methane, in the cell, the temperature gradient will be even steeper than described above due to the endothermic reforming process at the inlet, and will thus be more damaging to the cell (and stack), as disclosed, for example, in Hendriksen, P. V., Model studies of internal steam reforming in SOFC stacks, Proceedings - Electrochemical Society (1997), 97-40 (Solid Oxide Fuel Cells V).

However, if dry natural gas is employed instead, the formation of carbon will result in a fast blocking of the active sites in the anode structure. This may be prevented by using, e.g. an all-ceramic anode for direct conversion of natural gas to CO, CO_2 and water at the inlet which further down the stream may be replaced by Ni-containing electrode for a more efficient conversion. Carbon formation may also be prevented by a slower conversion at the inlet.

It has been suggested to use electrodes for SOFC or other electrochemical devices which are graded vertically to optimise the ionic and electronic conductivity of the electrodes. US patent 5,543,239 discloses an improved electrode design for solid state devices, wherein a porous layer of electrolyte material is incorporated over the dense electrolyte, and wherein an electrocatalyst which is also continuous is incorporated into the porous layer.

EP-A-1701402 relates to systems and methods for minimizing temperature differences and gradients in solid oxide fuel cells. A manifold heat exchanger is used, which reduces thermal stress and increases cell life. Air passes from a periphery of a cell towards the cell centre, absorbs the heat, and proceeds to the manifold heat exchanger adjacent to the cell, where it absorbs further heat. Fuel is directed counter current to the air, which keeps hot spots away from the cell stack seals and directs hot air towards intense reforming areas on the cell to mitigate quenching effects of internal reforming.

US patent 6,228,521 concerns a high power density solid oxide fuel cell having a cathode, electrolyte and graded porous anode. The anode is formed from NiO and zirconium oxide doped with yttrium oxide and exhibits a graded density which allows thicker and thus stronger anodes without sacrificing electrochemical performance.

US patent 4,329,403 relates to an electrolyte-electrode assembly for high temperature fuel cells in which the electrolyte member is adapted to exhibit a more gradual transition in coefficient of thermal expansion in going from the anode electrode to the inner electrolyte region and in going from the cathode electrode to the inner electrolyte region.

US patent 5,171,645 discloses a graded metal oxide electrolyte comprising gradiations of zirconia and bismuth oxide across the cross-section of the electrolyte. The gradiation of the compositional content across the wall thickness of the electrolyte from a substantially pure zirconia surface zone to a substantially pure bismuth oxide-yttria surface zone minimizes the stress at the interfaces between the various compositional zones.

US-A1-2005/0092597 relates to a method of forming a thin-film fuel cell electrode, comprising the provision of a substrate and at least one deposition device; developing a deposition characteristic profile having at least one porous layer based on predetermined desired electrode properties; and forming a film in accordance with said deposition material from said deposition device while varying a relative position of said substrate in relation to said deposition device with respect to at least a first axis.

As the deposition device, sputter guns are used. However, said sputter guns result in varying thickness as the overlapping areas are thicker than the surrounding areas, which leads to unwanted variations of the layer properties in a horizontal direction.

J.A. Labrincha et al., "Evaluation of deposition techniques of cathode materials for solid oxide fuel cells", Mat. Res. Bull., Vol. 28, pp. 101-109, 1993, discusses specific cobaltates and manganates as cathode materials for solid oxide fuel cells, wherein the cathode layer was applied on an electrolyte layer by sputter deposition.

EP-A-1441406 discloses a method for making a fuel cell anode, comprising the steps of:

- depositing a first film on a first end region of a substrate, wherein the first film is preferentially catalytically active towards substantially unreformed hydrocarbon fuel; and
- depositing a second film on a second end region of the substrate, the second end region opposed to the first end region, wherein the second film is preferentially catalytically active towards at least one of substantially reformed or partially reformed hydrocarbon fuel, by-products thereof and mixtures thereof.

US-A-2004/0086633 discloses a method for the fabrication and evaluation of electrode and electrolyte materials for use in solid oxide fuel cells, the method comprising:

- providing a non-sintered or partially-sintered substrate; and
- delivering the electrode and electrolyte materials to a plurality of regions of the substrate using a plurality of liquid spraying devices, wherein the plurality of liquid spraying devices are arranged at appropriate angels to the substrate and to each other such that the spray plumes of the spraying devices overlap to form a gradient array.

Z. Wang et al., "A study of multilayer tape casting method for anode-supported planar type solid oxide fuel cells", Journal of Alloys and Compounds 437 (2007) 264-268, relates to a multilayer tape casting and co-sintering process to fabricate a large area anode-supported electrolyte film for reduced temperature solid oxide fuel cells.

However, there is still a need for graded multilayer structures, which may be used as anodes in solid oxide fuel cells, which have a sufficient horizontal grading without the layer having any thickness variations, having an improved life time, and which can be produced in a cost efficient way without much waste material in view of the desires and requirements for industrial large scale production.

Object of the present invention

In view of the difficulties of the prior art as outlined above, it was the problem underlying the present invention to provide a graded multilayer structure suitable as an anode in solid oxide cells which has an improved performance and improved lifetime.

Summary of the invention

The above object is achieved by a graded multilayer structure, comprising a support layer (1) and at least 10 layers (2, 3), wherein each of the at least 10 layers (2, 3) is at least partially in contact with the support layer (1),

wherein the at least 10 layers (2, 3) differ from each other in at least one property selected from layer composition, porosity and conductivity, and

wherein the at least 10 layers (2, 3) are arranged such that the layer composition, porosity and/or conductivity horizontally to the support layer (1) forms a gradient over the total layer area.

The object is further achieved by a method for producing the above graded multilayer structure, comprising the steps of:

providing a support layer (1);

applying a first layer (2) on top of said support layer (1);

applying a second layer (3) such that the second porous layer (3) is at least partially in contact with the support layer (1);

applying a third to tenth layer such that the each of said layers is at least partially in contact with the support layer (1);

optionally applying at least one further layer such that the further layer is at least partially in contact with the support layer (1); and

laminating the multilayer structure;

wherein the application of each of the layers is carried out by tape-casting or screen printing.

Brief description of the drawings

Figure 1 illustrates different grading patterns.

Figure 2 illustrates one preferred embodiment of the present invention, wherein the layers overlap; only a part of all layers is shown.

Figure 3 illustrates another preferred embodiment of the present invention, wherein the layers do not overlap; only a part of all layers is shown.

Figure 4 illustrates a graded structure in accordance with the invention for direct conversion of natural gas; only a part of all layers is shown.

Figure 5 illustrates a cross graded cathode in accordance with the present invention for cross flow configuration of air and fuel; only a part of all layers is shown.

Figure 6 illustrates a graded structure in accordance with the invention wherein the gas flow is going from the centre to the edge; only a part of all layers is shown.

Figure 7 illustrates a segmented fuel cell module in accordance with the invention; only a part of all layers is shown.

Figure 8 illustrates a tube shaped structure in accordance with the invention with one active layer along the tube; only a part of all layers is shown.

Figure 9 illustrates another graded structure in accordance with the invention which has a roof tile form; only a part of all layers is shown.

Figure 10 illustrates another graded structure in accordance with the invention wherein the gradient is diagonally; only a part of all layers is shown.

Detailed description of the invention

The present invention relates to a graded multilayer structure, comprising a support layer (1) and at least 10 layers (2, 3), wherein each of the at least 10 layers (2, 3) is at least partially in contact with the support layer (1),

wherein the at least 10 layers (2, 3) differ from each other in at least one property selected from layer composition, porosity and conductivity, and

wherein the at least 10 layers (2, 3) are arranged such that the layer composition, porosity and/or conductivity horizontally to the support layer (1) forms a gradient over the total layer area.

Examples of grading patterns are given in Figure 1, including a gradient along the edges, diagonal or circular gradients; only a part of all layers is shown for better illustration of the principle. Such structures are suitable for use especially as electrodes in electrochemical devices where differences in performance or properties across a layer are advantageous. This is particularly the case for solid oxide cells (SOC) and membrane cells for oxygen or hydrogen separation, where an accurate control of the local electrochemical activity enhances the overall efficiency and durability. Other applications include protective coatings for corrosion or mechanical wear.

The gradient may apply to all properties of the layer in question, and may for instance comprise one or more of the following properties: composition, porosity, impurity level, conductivity, density, abrasiveness, mechanical strength, materials cost etc.

The graded layer comprises at least 10 layers. The general principle is illustrated in Figure 2 wherein the graded multilayer structure comprises seven illustrated layers forming a horizontal grading. Layer 1 has property 1 and layer 7 has property 2. The layers in between can be fine tuned to change linearly or by any other gradient from property 1 to property 2 between layer 1 and layer 2. In Figure 2, the layers next to each other are depicted as overlapping layers. This is however not necessary, as illustrated in Figure 3, where the layers are adjacent to each other. As may also be taken from Figure 1, the grading does not necessarily have to change from one limit to the other going from edge to edge, but may undergo local maxima and/or minima instead.

In a preferred embodiment, the at least 10 layers (2,3) of the graded structure are at least partially in contact with the support layer (1) and in contact with at least one other layer. It is also preferred that the surface of the at least 10 layers (2,3) which is contact with the support layer (1) also contacts the surface of at least one of the at least 10 layers (2,3).

The number of layers may be finetuned to any number of layers, depending on the desired application. However, at least 10 layers are required to provide sufficient grading over the whole layer. In view of the overall costs of the process for obtaining the graded multilayer structure, a preferred number of layers is at least 20, more preferred at least 30, and even more preferred at least 40. Of course, the more layers are employed, the better the smooth and continuous grading of the respective property may be adjusted. Depending on the desired application, the suitable number of layers may be chosen.

An additional layer (4) is preferably present on top of the at least 10 layers (2, 3). The additional layer contact all of the at least 10 layers (2, 3).

In one preferred embodiment, the at least 10 layers (2, 3) are porous layers. The layers being porous is advantageous for applications such as solid oxide cells, including solid oxide fuel cells and solid oxide electrolysis cells.

Suitable materials being preferred for at least one of the layers of the at least 10 layers (2, 3) being intended as a fuel electrode for solid oxide cells (SOFC's/SOEC'S) include compositions comprising doped zirconia, doped ceria, doped gallates, doped chromium manganites, doped titanites and/or a metal oxide. Specific examples of suitable materials include LSCM $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, yttria stabilized zirconia (YSZ), scandia yttria stabilized zirconia (SYSZ), STN $Sr_s(Ti_{1-y}Nb_y)O_{3-\delta}$, and CGO $Ce_{1-x}Gd_xO_{2-\delta}$, with $0 < x/y \leq 1$ and $0 < \delta \leq 1$.

Suitable materials being preferred for at least one of the layers of the at least 10 layers (2, 3) being intended as an air electrode for solid oxide cells (SOFC's/SOEC'S) include compositions comprising doped zirconia, doped ceria, doped gallates, doped manganites and/or doped ferrite/cobaltites. Specific examples of suitable materials include, LSC $(La_{1-x}Sr_x)_sCoO_{3-\delta}$, $(La_{1-x}Sr_x)_sMnO_{3-\delta}$, yttria stabilized zirconia (YSZ), scandia yttria stabilized zirconia (SYSZ), CGO $Ce_{1-x}Gd_xO_{2-\delta}$, LSCF $(La_{1-x}Sr_x)_s(Co_{1-y}Fe_y)O_{3-\delta}$, and the like, with $0 < x/y \leq 1$ and $0 < \delta \leq 1$.

Suitable materials being preferred for at least one of the layers of the at least 10 layers (2, 3) being intended as an electrode for separation membranes include compositions comprising doped zirconia, doped ceria, doped gallates and/or Ru. Specific examples of suitable materials include MgO, CGO $Ce_{1-x}Gd_xO_{2-\delta}$, Ru, LSCr $(La_{1-x}Sr_x)CrO_{3-\delta}$, LSCrF $(La_{1-x}Sr_x)_s(Cr_{1-y}Fe_y)O_{3-\delta}$, yttria stabilized zirconia (YSZ), scandia yttria stabilized zirconia (SYSZ), CGO $Ce_{1-x}Gd_xO_{2-\delta}$, and LSC $(La_{1-x}Sr_x)_sCoO_{3-\delta}$, with $0 < x/y \leq 1$ and $0 < \delta \leq 1$.

Suitable materials being preferred for at least one of the layers of the at least 10 layers (2, 3) being intended as a protective coating include compositions comprising doped manganite/cobaltites and metal oxides, LSC $(La_{1-x}Sr_x)_sCoO_{3-\delta}$, with $0 < x \leq 1$ and $0 < \delta \leq 1$, and/or Al_2O_3 and the like.

Other suitable materials being preferred for at least one of the layers of the at least 10 layers (2, 3) are disclosed in EP-A-1760817 and EP-A-06024339.

The thickness of each layer is preferably from about 5 µm to 200 µm, more preferably from about 10 µm to 150 µm, measured in the green state, i.e. prior to sintering. It is also preferred that the thickness over the whole graded structure is identical, i.e. the overall thickness does not vary from layer to layer, resulting in a uneven structure.

The porosity of the layers (2, 3), in case the layers are porous layers, is preferably from 5% to 60%, more preferably from 10% to 40%, and even more preferably from 15% to 30%. In case the porosity forms a gradient, of course the porosity of each layer is different from each other. In case the gradient is formed by different conductivity or layer composition, the porosity of each layer may be the same or be different, or the layers may not be porous at all, depending on the desired application.

The present invention further provides a solid oxide fuel cell, comprising the above graded multilayer structure. Advantageously, the SOFC exhibits a reduced temperature gradient across the cell, and thus an improved lifetime. Preferably, the graded multilayer structure of the present invention forms an electrode layer in said SOFC. The accurate control of the local electrochemical activity due to the fine tuning of the grading and thereby influencing the layer properties enhances the overall efficiency and durability of the cell.

The present invention also provides a method for producing the above graded multilayer structure, comprising the steps of:

providing a support layer (1);

applying a first layer (2) on top of said support layer (1);

applying a second layer (3) such that the second layer (3) is at least partially in contact with the support layer (1);

applying a third to tenth layer such that the each of said layers is at least partially in contact with the support layer (1); optionally applying at least one further layer such that the further layer is at least partially in contact with the support layer (1); and

laminating the multilayer structure;

wherein the application of each of the layers is carried out by tape-casting or screen printing.

Preferably, the second layer (3) is applied such that the second and each further layer (3) is at least partially in contact with the support layer (1) and in contact with the first and each further layer, respectively (2); and the optional at least one further layer is applied such that the further layer is at least partially in contact with the support layer (1) and in contact with at least one layer.

It is also preferred that the second layer (3) is applied such that the second porous layer (3) is at least partially in contact with the support layer (1) and in contact with the first layer (2), and the least 10 layers and the optional layer being in contact with the support layer (1) also contact the surface of at least one of the at least 10 layers (2, 3).

Advantageously, tape casting or screen printing results in an even height of the applied layers. Especially preferred is tape-casting in view of the small amount of waste produced, and in view of the simple manufacture requirements. This allows for a more cost efficient apparatus and in return for a large scale production of the multilayer structures. Especially sputtering as a process is however disadvantageous and not cost effective for producing multilayer structures in an industrial scale.

The lamination is generally carried out at elevated temperatures, with a temperature of at least 100°C being preferred, and a temperature of at least 120°C being more preferred.

The at least 10 layers (2, 3) are preferably porous layers as mentioned above.

The present invention finally provides a graded multilayer structure, comprising a support layer (1) and at least 10 layers (2, 3), wherein each of the at least 10 layers (2, 3) is at least partially in contact with the support layer (1),

wherein the at least 10 layers (2, 3) differ from each other in at least one property selected from layer composition, porosity and conductivity, and

wherein the at least 10 layers (2, 3) are arranged such that the layer composition, porosity and/or conductivity horizontally to the support layer (1) forms a gradient over the total layer area,

the graded multilayer structure being obtainable by the above process.

In another embodiment of the present invention, the graded multilayer structure is used in a solid oxide cell.

The above described horizontal grading may be achieved by, but is not limited to, the following preferred methods:

- manufacture of individual layers by tape-casting. After drying, the individual layers are placed on a support and laminated or 2) alternatively the individual layers are placed directly on to final substrate. A sintering step is normally required to consoli-

date the particles in the layers, but in case of contact layers for SOC this may not be necessary.
- screen printing, manufacture of horizontal grading due to the high precision in the printing process, where individual layers may be deposited with an accuracy of around 1 micrometer.

The horizontally graded structure may be employed as an electrode in solid oxide cells, such as solid oxide fuel cells including both, SOFCs for reformed natural gas and for direct conversion of natural gas, solid oxide eletrolysis cells, further in membranes, for example membranes for syngas production, membranes for oxygen production, or as a graded corrosion protection coating.

In the following, the invention will be illustrated by Examples. It is however not intended to limit the invention thereto.

Examples

Example 1 (formation of a SOFC anode for reformed natural gas– LSCM/Ni)

An SOFC anode for reformed natural gas having a graded composition parallel to the direction of the anode gas flow is obtained. The compositions of each of the layers are formed such that an increased electrochemical activity from right to left (gas inlet to outlet) is achieved. The multilayer structure is illustrated in Figure 2; not all layers are shown.

Layer 1 consists of LSCM, $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, and layer 7 consists of 95 vol% NiO and 5 vol% LSCM. is obtained in seven steps. Layers 2 to 6 consist of a linear grading with Layer 4 having a 1:1 ratio. The electrochemical conversion for H_2 is low for LSCM, and high for Ni.

In the first step, seven tapes are produced. Suspensions for tape-casting are manufactured by means of ball milling of powders with polyvinyl pyrrolidone (PVP), polyvinyl butyral (PVB) and EtOH + MEK as additives. The suspensions are tape-cast using a double doctor blade system and the tapes are subsequently dried.

Layer 1: The suspension comprised LSCM. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Layer 2: The suspension comprised 83 vol% LSCM and 17 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 3: The suspension comprised 75 vol% LSCM and 25 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 4: The suspension comprised 66 vol% LSCM and 34 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 5: The suspension comprised 58 vol% LSCM and 42 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 6: The suspension comprised 50 vol% LSCM and 50 vol% NiO. The green thickness of the tape-cast layer was about 45 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 7: The suspension comprised 34 vol% LSCM and 66 vol% NiO. The green thickness of the tape-cast layer was about 45 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 8: The suspension comprised 25 vol% LSCM and 75 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 9: The suspension comprised 17 vol% LSCM and 83 vol% NiO. The green thickness of the tape-cast layer about 50 µm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 10: The suspension comprised 5 vol% LSCM and 95 vol% NiO. The green thickness of the tape-cast layer was about 50 µm. The porosity of this layer was about 30% after sintering and reduction of NiO.

In the second step, the tapes were placed onto a Mylar foil as a support layer, as illustrated in Figure 2, and laminated by employing heated rolls in a double roll set-up, wherein the lamination took place in one pass. The temperature was about 140°C and the pressure was about 1 bar.

The obtained laminated graded anode was ready to be build into any type of SOC cell.

Example 2 (formation of a SOFC anode for reformed natural gas – YSZ-LSCM/Ni)

An SOFC anode for reformed natural gas having a graded composition parallel to the direction of the anode gas flow is obtained. The compositions of the layers are formed such that there is an increased electrochemical activity going from right to left (gas inlet to outlet). The Example is illustrated in Figure 2; not all layers are shown.

Layer 1 consists of 40 vol% yttria stabilized zirconia (YSZ) and 60 vol% LSCM, $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, and layer 7 consists of 40 vol% YSZ, 50 vol% NiO and 5 vol% LSCM. Layers 2 to 6 consist of a linear grading with Layer 4 having a 1:1 ratio of LSCM and NiO, The YSZ is kept constant at 45 vol% and LSCM and NiO sums to 55 vol%. The electrochemical activity for conversion of H_2 is low for LSCM and high for Ni.

In the first step, seven tapes are produced. Suspensions for tape-casting are manufactured by means of ball milling of powders with polyvinyl pyrrolidone (PVP), polyvinyl butyral (PVB) and EtOH + MEK as additives. The suspensions are tape-cast using a double doctor blade system and the tapes are subsequently dried.

Layer 1: The suspension comprised 40 vol% YSZ and 55 vol% LSCM. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Layer 2: The suspension comprised 40 vol% YSZ, 50 vol% LSCM and 10 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 3: The suspension comprised 40 vol% YSZ, 45 vol% LSCM and 15 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 4: The suspension comprised 40 vol% YSZ, 40 vol% LSCM and 20 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 5: The suspension comprised 40 vol% YSZ, 35 vol% LSCM and 25 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 6: The suspension comprised 40 vol% YSZ, 30 vol% LSCM and 30 vol% NiO. The green thickness of the tape-cast layer was about 45 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 7: The suspension comprised 40 vol% YSZ, 25 vol% LSCM and 35 vol% NiO. The green thickness of the tape-cast layer was about 40 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 8: The suspension comprised 40 vol% YSZ, 20 vol% LSCM and 40 vol% NiO. The green thickness of the tape-cast layer was about 45 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 9: The suspension comprised 40 vol% YSZ, 10 vol% LSCM and 50 vol% NiO. The green thickness of the tape-cast layer was about 50 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

Layer 10: The suspension comprised 40 vol% YSZ, 5 vol% LSCM and 55 vol% NiO. The green thickness of the tape-cast layer was about 50 μm. The porosity of this layer was about 30% after sintering and reduction of NiO.

In the second step, the tapes were placed onto a Mylar foil (support layer) as illustrated in Figure 2 and laminated by employing heated rolls in a double roll set-up, wherein the lamination took place in one pass. The temperature was about 140°C and the pressure was about 1 bar.

The laminated graded anode was ready to be build into any type of SOC cell.

Example 3

The anode obtained in Example 1 was built in an anode supported solid oxide cell. In the first step, two tapes were produced: an anode support tape (AS) and an electrolyte tape (E). Suspensions for tape-casting are manufactured and cast as described in Example 1.

AS-layer: The suspension comprised 45 vol% yttria stabilized zirconia (YSZ) and about 55 vol% NiO powder. The green thickness of the tape-cast layer was about 400 μm. The porosity of this layer was about 30% after sintering and reduction.

E-layer: The suspension comprised scandia yttria stabilized zirconia (SYSZ) the green thickness of the tape-cast layer was about 15 μm.

In the second step, the AS and E tapes were laminated together with a graded tape manufactured as described in Example 1. The order of lamination was: AS/graded anode/E. Lamination is performed by employing heated rolls in a double roll set-up. The temperature was about 140°C and the pressure was about 1 bar.

In the third step, the laminated tapes were cut into the desired shapes. This was done by knife punching resulting in areas of 12x12 cm^2 after sintering.

In the fourth step, the half-cell was sintered. The half-cell was placed in a furnace and sintered at about 1300°C and left for about 12 hours before cooling to room temperature.

In the fifth step, a cathode was deposited on the sintered half-cell by screen printing an ink comprising a 1:1 weight ratio mixture of $La_{0.75}Sr_{0.25}MnO_{3-\delta}$ and SYSZ on the surface of the electrolyte layer (E). The thickness of the printed layer was 30 μm before sintering.

The sixth step was the sintering of the cell in a furnace at about 1100°C for 2 hours before cooling to room temperature so as to obtain the SOC.

Example 4 (formation of an anode for direct conversion of natural gas)

An SOFC anode for non-reformed natural gas having a graded composition parallel to the direction of the gas flow was obtained. The compositions of the layers were made such that there was an increased electrochemical activity going from right to left (gas inlet to outlet), as illustrated in Figure 4; not all layers are shown for illustrative purposes.

The compositions of the ten layers were as follows:

Layer 1: STN, $Sr_s(Ti_{1-y}Nb_y)O_{3-\delta}$;
Layer 2: 80 vol% STN, 20 vol% CGO, $Ce_{1-x}Gd_xO_{2-\delta}$;
Layer 3: 75 vol% STN, 20 vol% CGO and 5 vol% NiO;
Layer 4: 65 vol% STN, 20 vol% CGO and 15 vol% NiO;
Layer 5: 55 vol% NiO and 45 vol% STN;
Layer 6: 50 vol% NiO and 50 vol% STN;
Layer 7: 45 vol% NiO and 55 vol% STN;
Layer 8: 40 vol% NiO and 60 vol% STN;

Layer 9: 35 vol% NiO and 65 vol% STN;
Layer 10: 30 vol% NiO and 70 vol% STN.

The tapes were manufactured and laminated as described in Example 1.

Example 5

The anode obtained in Example 4 was built in an electrolyte supported cell. The SOFC anode for non-reformed natural gas had a graded composition parallel to the direction of the gas flow. The compositions of the layers were made such that there was an increased electrochemical activity going from right to left (gas inlet to outlet), as illustrated in Figure 4; however, not all layers are shown.

The first step was the manufacture of five screen printing inks having the compositions as given above.

The second step was the deposition of the layers side by side by screen printing.

The cell was completed as outlined in Example 3.

Example 6 (SOC cathode – LSM/LSCF)

In order to achieve further balance of the temperature distribution in an SOFC cell stack, the electrochemical activity of the cathode is balanced in this example. In case of cross flow of the air and fuel in the stack, the temperature in the four stack corners will under normal operational conditions be of a lower temperature as compared to the center of the stack as follows: T (air out -H_2 in) > T (air in - H_2 in) > T (air out-H_2 out) >T (air in-H_2 out).

The temperature distribution on the cathode side is levelled/controlled by having a cross gradient as illustrated in Figure 5; not all layers are shown. The compositions of the layers are as follows:

Layer 1: 50 vol% CGO + 50 vol% LSM 25;
Layer 2: 50 vol% CGO + 38 vol% LSM + 12 vol% LSCF;
Layer 3: 50 vol% CGO + 35 vol% LSM + 15 vol% LSCF;
Layer 4: 50 vol% CGO + 25 vol% LSM + 25 vol% LSCF;
Layer 5: 50 vol% CGO + 22 vol% LSM + 28 vol% LSCF;
Layer 6: 50 vol% CGO + 20 vol% LSM + 30 vol% LSCF;
Layer 7: 50 vol% CGO + 18 vol% LSM + 32 vol% LSCF;
Layer 8: 50 vol% CGO + 15 vol% LSM + 25 vol% LSCF;
Layer 9: 50 vol% CGO + 12 vol% LSM + 38 vol% LSCF;
Layer 10: 50 vol% CGO + 50 vol LSCF.

The tapes are manufactured and laminated as described in Example 1.

Example 7 (SOC cathode – LSM/LSCF)

Further balance of the temperature distribution in an SOFC cell stack may be achieved by controlling the electrochemical activity of the cathode. In case of cross flow of the air and fuel in the stack the temperature in the four stack corners will under normal operational conditions be in decreasing order of temperature: T (air out -H_2 in) > T (air in - H_2 in) > T (air out-H_2 out) >T (air in-H_2 out).

The temperature distribution on the cathode side is levelled/controlled by having a cross gradient as illustrated in Figure 5. The compositions of the layers are as follows:

Layer 1: 50 vol% CGO + 50 vol% LSCF 25;
Layer 2: 50 vol% CGO + 45 vol% LSCF + 5 vol% LSC;
Layer 3: 50 vol% CGO + 38 vol% LSCF + 12 vol% LSC;
Layer 4: 50 vol% CGO + 35 vol% LSCF + 15 vol% LSC;
Layer 5: 50 vol% CGO + 30 vol% LSCF + 20 vol% LSC;
Layer 6: 50 vol% CGO + 28 vol% LSCF + 22 vol% LSC;
Layer 7: 50 vol% CGO + 25 vol% LSCF+ 25 vol% LSC;
Layer 8: 50 vol% CGO + 20 vol% LSCF + 30 vol% LSC;
Layer 9: 50 vol% CGO + 12 vol% LSCF + 38 vol% LSC;
Layer 10: 50 vol% CGO + 50 vol LSC.

The tapes are manufactured and laminated as described in Example 1 in order to obtain the SOC cathode.

Example 8 (manufacture of a cell with a circular design)

A SOFC with a circular design for dry or pre-reformed natural gas being exposed to the anode was obtained. The inlet of the fuel gas was in the centre of the cell and the outlet at the edge. The anode had a graded composition from the inlet to the outlet. The compositions of the layers were made such that there was an increased electrochemical activity going from centre to edge (gas inlet to outlet), as illustrated in Figure 6; not all layers are shown.

Layer 1 consisted of LSCM, $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, layer 7 consisted of 80 vol% NiO and 5 vol% LSCM; and layer 10 consisted of 100 vol% NiO. Layers 2 to 9 consisted of a linear grading with Layer 6 having a 1:1 ratio. The electrochemical activity for conversion of H_2 is low for LSCM and high for Ni.

In the first step, seven inks were manufactured. Suspensions for screen printing were produced by means of ball milling of powders with polyvinyl pyrrolidone (PVP), polyvinyl butyral (PVB) and EtOH + MEK as additives. The suspensions were screen printed onto the cell with the composition varying in a controlled manner from the center and outwards. The layers were subsequently dried.

Ink 1: The suspension comprised LSCM. The green thickness of the printed layer was about 40 µm. The porosity of this layer was about 30% after sintering.

Ink 2: The suspension comprised 90 vol% LSCM and 10 vol% NiO. The green thickness of the printed layer was about 40 µm. The porosity of this layer was about 30% after sintering.

Ink 3: The suspension comprised 83 vol% LSCM and 17 vol% NiO. The green thickness of the printed layer was about 40 µm. The porosity of this layer was about 30% after sintering.

Ink 4: The suspension comprised 75 vol% LSCM and 25 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 5: The suspension comprised 66 vol% LSCM and 34 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 6: The suspension comprised 50 vol% LSCM and 50 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 7: The suspension comprised 34 vol% LSCM and 66 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 8: The suspension comprised 17 vol% LSCM and 83 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 9: The suspension comprised 5 vol% LSCM and 95 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink10: The suspension comprised NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

The cell was subsequently sintered at 1150°C in air.

Example 9 (manufacture of a cell with a tubular design)

A tubular or flat-tubular SOFC was obtained, where the composition of the anode was graded along the tube. The grading was made such that the composition of the electrode at the inlet was the least reforming active, and with the activity increasing towards the outlet (other end) of the tube, as illustrated in Figure 7; not all layers are shown.

Layer 1 consisted of LSCM, $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, and layer 7 consisted of 95 vol% NiO and 5 vol% LSCM. Layers 2 to 6 consisted of a linear grading with Layer 4 having a 1:1 ratio. The electrochemical activity for conversion of H_2 is low for LSCM and high for Ni.

In the first step, seven slurries were produced. Suspensions for spraying were manufactured by means of ball milling of powders with polyvinyl pyrrolidone (PVP), polyvinyl butyral (PVB) and EtOH + MEK as additives. The suspensions were sprayed onto the tube with the composition varying in a controlled manner along the tube. The layers were subsequently dried.

Slurry 1: The suspension comprised LSCM. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 2: The suspension comprised 90 vol% LSCM and 10 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 3: The suspension comprised 83 vol% LSCM and 17 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 4: The suspension comprised 75 vol% LSCM and 25 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 5: The suspension comprises 66 vol% LSCM and 34 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 6: The suspension comprised 50 vol% LSCM and 50 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 7: The suspension comprised 34 vol% LSCM and 66 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry 8: The suspension comprised 17 vol% LSCM and 83 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry9: The suspension comprised 5 vol% LSCM and 95 vol% NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Slurry10: The suspension comprised NiO. The green thickness of the sprayed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

The tube was then sintered at 1100-1400°C in air.

Example 10 (segmented cell design)

A flat-tubular SOFC design was obtained, where the composition of the anode was graded along the segmented-flat-tube cell. The grading was obtained by the composition of the individual segments changing from segment to segment such that the inlet was the least reforming active, and with activity increasing towards the outlet of the module/cell, as illustrated in Figure 8.

Layer 1 consisted of LSCM, $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, and layer 7 consisted of 95 vol% NiO and 5 vol% LSCM. Layers 2 to 6 consisted of a linear grading with Layer 4 having a 1:1 ratio.

The first step was the manufacture of seven inks. Suspensions for screen printing were manufactured by means of ball milling of powders with polyvinyl pyrrolidone (PVP), polyvinyl butyral (PVB) and EtOH + MEK as additives. The suspensions were screen printed onto the cell with the composition varying in a controlled manner from the center and outwards. The layers were subsequently dried.

Ink 1: The suspension comprised LSCM. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 2: The suspension comprised 90 vol% LSCM and 10 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 3: The suspension comprised 83 vol% LSCM and 17 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 4: The suspension comprised 75 vol% LSCM and 25 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 5: The suspension comprised 66 vol% LSCM and 34 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 6: The suspension comprised 50 vol% LSCM and 50 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 7: The suspension comprised 34 vol% LSCM and 66 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 8: The suspension comprised 17 vol% LSCM and 83 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 9: The suspension comprised 5 vol% LSCM and 95 vol% NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

Ink 10: The suspension comprised NiO. The green thickness of the printed layer was about 40 μm. The porosity of this layer was about 30% after sintering.

The cell was subsequently sintered at 1150°C in air.

The electrolyte layers, cathode and sealants were afterwards deposited and the whole assembly sintered in air at 1250°C.

Example 11 (production of a membrane for syngas production with a graded anode)

A device for the production of synthesis gas was obtained. Methane was fed to one side of a membrane, and air to the other. The membrane was a mixed oxide ion/electronic conductor with a thickness of about 10 micrometer. To provide sufficient strength, the membrane was placed on an inert support structure with a thickness of several hundred micrometer.

On the side exposed to air an oxygen reduction catalyst layer was applied, and on the side exposed to methane, a cracking/steam reforming catalyst was applied. When in operation, oxygen permeates from the air side through the membrane to the methane side, where a partial oxidation takes placed resulting in generation of a mixture of CO and hydrogen. The temperature will change in the direction of the gas-flows as will the chemical environment on both sides of the membrane. Hence, it is beneficial to have the possibility to vary the composition of the catalyst layers on both sides of the membrane in the direction of the gas flow as to achieve a local optimisation by varying the composition horizontally to reflect the changing requirements set by the changing temperature and the changing chemical environment.

In step 1, a support tape (CGO or MgO) with a thickness of 400 micrometer was obtained.

In step 2, a graded structure "anode or catalyst layer" as outlined in example 1 was produced. Said layer was made by combining 10 tapes of different composition:

Tape 1 comprised 50 vol% support material and 50 vol% Ru-based catalyst particles;
Tape 2 comprised 50 vol% support material and 45 vol% Ru-based catalyst particles; and 5 vol% Ni based catalyst particles;
Tape 3 comprised 50 vol% support particles, 40 vol% Ru based catalyst particles, and 10 vol% Ni based catalyst particles;
Tape 4 comprised 50 vol% support material and 35 vol% Ru-based catalyst particles; and 15 vol% Ni based catalyst particles;
Tape 5 comprised 50 vol% support material, 30 vol% Ru-based catalyst particles, 20 and vol% Ni;
Tape 6 comprised 50 vol% support material and 25 vol% Ru-based catalyst particles; and 25 vol% Ni based catalyst particles;
Tape 7 comprised 50 vol% support material, 20 vol% Ru-based catalyst particles, and 30 vol% Ni;
Tape 8 comprised 50 vol% support material and 15 vol% Ru-based catalyst particles; and 35 vol% Ni based catalyst particles;
Tape 9 comprised 50 vol% support material, 10 vol% Ru-based catalyst particles, and 40 vol% Ni;
Tape 10 comprised 50 vol% support material, and 50 vol% Ni.

The tapes were placed on a mylar support and laminated as outlined in Example 1.

In step 3, the catalyst layer tape was laminated together with the manufactured support tape.

In step 4, the support and catalyst layer tape were laminated with a 25 micrometer thick membrane tape which was based on CGO.

In step 5 the laminate was sintered at 1300°C for 5 hours.

In step 6, an oxygen reduction catalyst was applied on the membrane surface. Said layer was applied by screen printing a slurry of LSC.

In step 7, the cathode was sintered.

When operating the air and methane are fed in co-flow with side comprising the Ru catalyst of the membrane at the methane inlet. In the above structure, a more active and expensive Ru catalyst is replaced by a cheap Ni catalyst where gas composition and temperature allows for said replacement.

Example 12 (Membrane for syngas production with a horizontally graded cathode)

A membrane for the same purpose as described in example 11 and manufactured in the same way was obtained. However, for the cathode application, a horizontal grading is achieved such that the composition changes in the direction of the air flow. At the inlet $La_{0.2}Sr_{0.8}CoO_3$ is used, and down stream the air side materials with less and less Sr doping are applied.

Example 13 (Membrane for oxygen production with a horizontally graded electrode)

A membrane for oxygen production operating at high temperature between pressurized air and a pure oxygen permeate stream was obtained. The electrode composition varies down stream of the pressurized air such that the Sr content is gradually reduced going down stream the pressurized air 1) $SrCoO_{2.5}$, 2) $La_{0.3}$ $Sr_{0.7}CoO_3$, 3) $La_{0.6}Sr_{0.4}CoO_3$. The membrane was obtained as described in example 11.

Example 14 (Supported membrane with graded composition in the membrane (co-firing route))

A membrane with a composition gradient in the gas flow direction was obtained. At the methane inlet $La_{0.6}Sr_{0.4}Fe_{0.8}Cr_{0.2}O_3$ was used. In the middle section, $(La,Sr)FeO_3$ and in the outlet section, $(La,Sr)Fe_{0.8}Co_{0.2}O_3$ was applied.

In the first step, the support tape was obtained.

In the second step, the catalyst, a Ru based supported catalyst was tape cast.

Step 3 was the manufacture of a graded tape for later lamination. Tape 1 consisted of $La_{0.6}Sr_{0.4}Fe_{0.8}Cr_{0.2}O_3$, tape 2 consisted of $La_{0.6}Sr_{0.4}Fe_{0.9}Cr_{0.1}O_3$, tape 3 consisted of $La_{0.6}Sr_{0.4}FeO_3$, and tape 4 consisted of $La_{0.6}Sr_{0.4}Fe_{0.9}Co_{0.1}O_3$.

Step 4 was the lamination of the obtained tapes on each other.

Step 5 was the sintering of the obtained laminate.

In step 6, the cathode was applied on the sintered structure so as to obtain the membrane. The obtained membrane design is especially suitable for use in a counter flow device. Methane enters (and air exits) at the LSFCr side (hot and very reducing). Syngas exits and air is fed at the LSFeCo side (cold but less reducing).

Example 15 (Supported membrane with stepwise change in the membrane composition, screen printing)

A device was obtained as described in example 11, with the exception that the membrane composition changes stepwise and the membrane layers are made by screen printing.

Step 1 was the manufacture of a MgO support by extrusion or tape casting.

In step 2, the support was sintered for two hours at about 1300°C.

In step 3, the catalyst was applied by dip coating the support in a very thin slurry comprising ultrafine catalyst particles in form of a suspension.

Step 4 was the application of membrane layers in a sequence of printings, where first of all, the upstream segment was printed, consisting of ($La_{0.6}Sr_{0.4}Fe_{0.8}Cr_{0.2}O_3$), and subsequently four more segments were printed such that a small overlap at the border between neighbouring segments is ensured. The composition varied from segment to segment in the same manner as outlined in example 11.

In step 5, the component was sintered at 1325°C for four hours.

In step 6, a porous catalyst layer was applied on top of the membrane layer by spraying so as to obtain the supported membrane.

Example 17 (Supported membrane with stepwise change in the membrane composition, vacuum plasma spraying)

The membrane was obtained as outlined for example 15, with the exception that step 4 is replaced by a membrane application step by vacuum plasma spraying. The grading is achieved using several guns connected to different feeds.

Example 18 (Patterned and graded corrosion protection coating manufactured by "ink jet printing")

To achieve long term durability, ferritic Fe/Cr steels used as interconnects must be provided by suitable protective coatings. Both (La,Sr)CoO_3 and Al_2O_3 are excellent protection material for prolonging the lifetime of steels like Crofer22APU. In a stack where electrical contact is only needed over a fraction of the area it is desirable to apply an Al_2O_3 rich coating over the none current carrying areas and an (La,Sr)CoO_3 rich coating over the current carrying areas. A corrugated plate is considered where the cross section has the shape of a sinusoidal.

The plate is provided with a protective coat applied in strips (See Fig. 9). At the wave tops where contact is established to the cathode a coating of Al_2O_3 20 % and (La,Sr) CoO_3 80% was applied by printing (layer A, Fig 9). At the "bottom of the waves" (non current carrying area) a 80% Al_2O_3 and 20 % (La,Sr)CoO_3 coating was applied by printing (layer B, Fig. 9) using an ink-jet-type printing device specially suited for application of particulate slurries of the type described here. The jet was fed from two different cartridges containing the two slurries here preferred. The coat was applied in a line to line printing operation where the feed changes whenever jet moves in and out of the contact zones (see Figure 9).

Example 19 (Graded corrosion protection coating manufactured by air spraying)

The temperature in a stack varies in the air flow direction, as outlined above. This results in the air exit region being the most critical for corrosion protection. In this example, the interconnect is protectedby a sprayed coating where the composition varied from Al_2O_3/(LaSr)CoO_3 50/50 in the outlet region to (LaSr)CoO3 in the inlet region. The grading was achieved by spraying from multiple containers as outlined above for Example 1. Figure 10 illustrates the obtained structure.

CLAIMS:

1. An electrode for a solid oxide cell or membrane, the electrode having a graded multilayer structure, comprising a support layer and at least 10 layers, wherein each of the at least 10 layers is at least partially in contact with the support layer,

wherein the at least 10 layers differ from each other in at least one property selected from layer composition, porosity and conductivity, and

wherein the at least 10 layers are arranged such that the layer composition, porosity and/or conductivity horizontally to the support layer forms a gradient over the total layer area.

2. The electrode of claim 1, wherein each of the at least 10 layers is at least partially in contact with the support layer and in contact with at least one other layer.

3. The electrode of claim 1 or 2, wherein the surface of the at least 10 layers which is in contact with the support layer also contacts the surface of at least one of the at least 10 layers.

4. The electrode of any one of claims 1 to 3, wherein at least one of the at least 10 layers comprises LSCM $(La_{1-x}Sr_x)_s(Cr_{1-y}Mn_y)O_{3-\delta}$, yttria stabilized zirconia (YSZ), scandia yttria stabilized zirconia (SYSZ), STN $Sr_s(Ti_{1-y}Nb_y)O_{3-\delta}$, or CGO $Ce_{1-x}Gd_xO_{2-\delta}$, with $0 < x/y \leq 1$ and $0 < \delta \leq 1$.

5. The electrode of any one of claims 1 to 3, wherein at least one of the at least 10 layers comprises LSC $(La_{1-x}Sr_x)CoO_{3-\delta}$, LSM $(La_{1-x}Sr_x)MnO_{3-\delta}$, yttria stabilized zirconia (YSZ), scandia yttria stabilized zirconia (SYSZ), CGO $Ce_{1-x}Gd_xO_{2-\delta}$, or LSCF $(La_{1-x}Sr_x)_s(Co_{1-y}Fe_y)O_{3-\delta}$, with $0 < x/y \leq 1$ and $0 < \delta \leq 1$.

6. The electrode of any one of claims 1 to 3, wherein at least one of the at least 10 layers comprises MgO, CGO $Ce_{1-x}Gd_xO_{2-\delta}$, Ru, LSCr $(La_{1-x}Sr_x)CrO_{3-\delta}$, LSCrF $(La_{1-x}Sr_x)_s(Cr_{1-y}Fe_y)O_{3-\delta}$, yttria stabilized zirconia (YSZ), scandia yttria

stabilized zirconia (SYSZ), or LSC $(La_{1-x}Sr_x)CoO_{3-\delta}$, with $0 < x/y \leq 1$ and $0 < \delta \leq 1$.

7. The electrode of any one of claims 1 to 3, wherein at least one of the at least 10 layers comprises doped manganite/cobaltites or metal oxides.

8. The electrode of any one of claims 1 to 7, further comprising an additional layer on top of the at least 10 layers, wherein the additional layer contacts all of the at least 10 layers.

9. The electrode of claim 6, wherein at least one of the at least 10 layers is a lanthanum strontium chromium oxide layer.

10. The electrode of any one of claims 1 to 9, comprising at least 20 layers.

11. The electrode of any one of claims 1 to 10, wherein the at least 10 layers are porous layers.

12. A solid oxide fuel cell, comprising the electrode of any one of claims 1 to 11.

13. A method for producing the electrode of claim 1, comprising the steps of:

providing a support layer;

applying a first layer on top of said support layer;

applying a second layer such that the second layer is at least partially in contact with the support layer;

applying a third to tenth layer such that the each of said layers is at least partially in contact with the support layer;

optionally applying at least one further layer such that the further layer is at least partially in contact with the support layer; and

laminating the multilayer structure,

wherein the application of each of the layers is carried out by tape-casting or screen printing.

14. The method of claim 13, wherein the second layer is applied such that the second layer is at least partially in contact with the support layer and in contact with the first layer; and wherein the optional at least one further layer is applied such that the further layer is at least partially in contact with the support layer and in contact with at least one layer.

15. The method of claim 13, wherein the second layer is applied such that the second layer is at least partially in contact with the support layer and in contact with the first layer, and wherein the at least two layers and the optional layer being in contact with the support layer also contact the surface of at least one of the at least two layers.

16. The method of claim 14, wherein the application of the layers is carried out by tape-casting.

17. The method of claim 13, wherein the step of laminating is carried out at a temperature of at least 100°C.

18. The method of claim 13, wherein the second layer is a porous layer.

19. Use of the electrode of any one of claims 1 to 11 in a solid oxide cell.

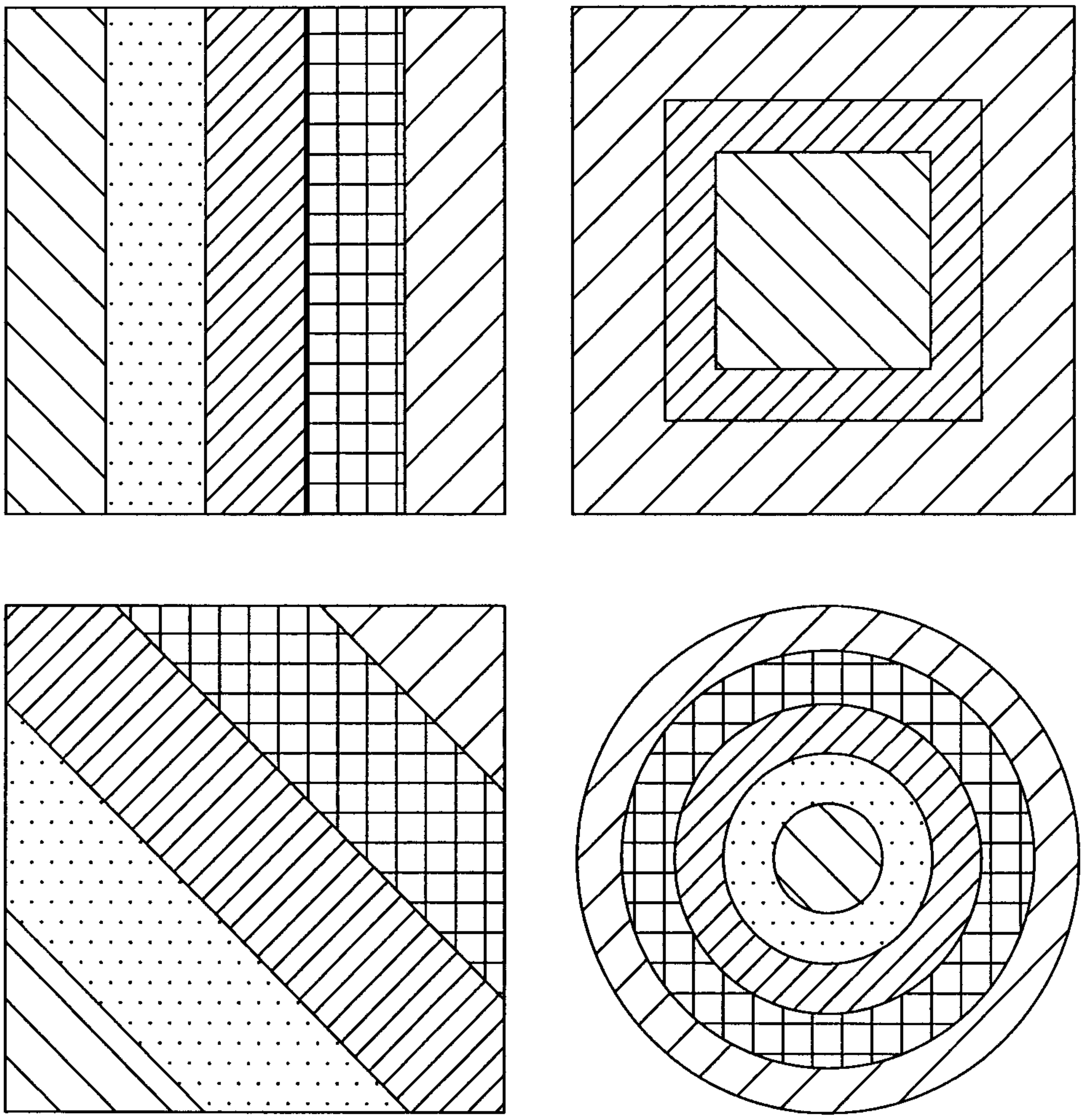


Figure 1

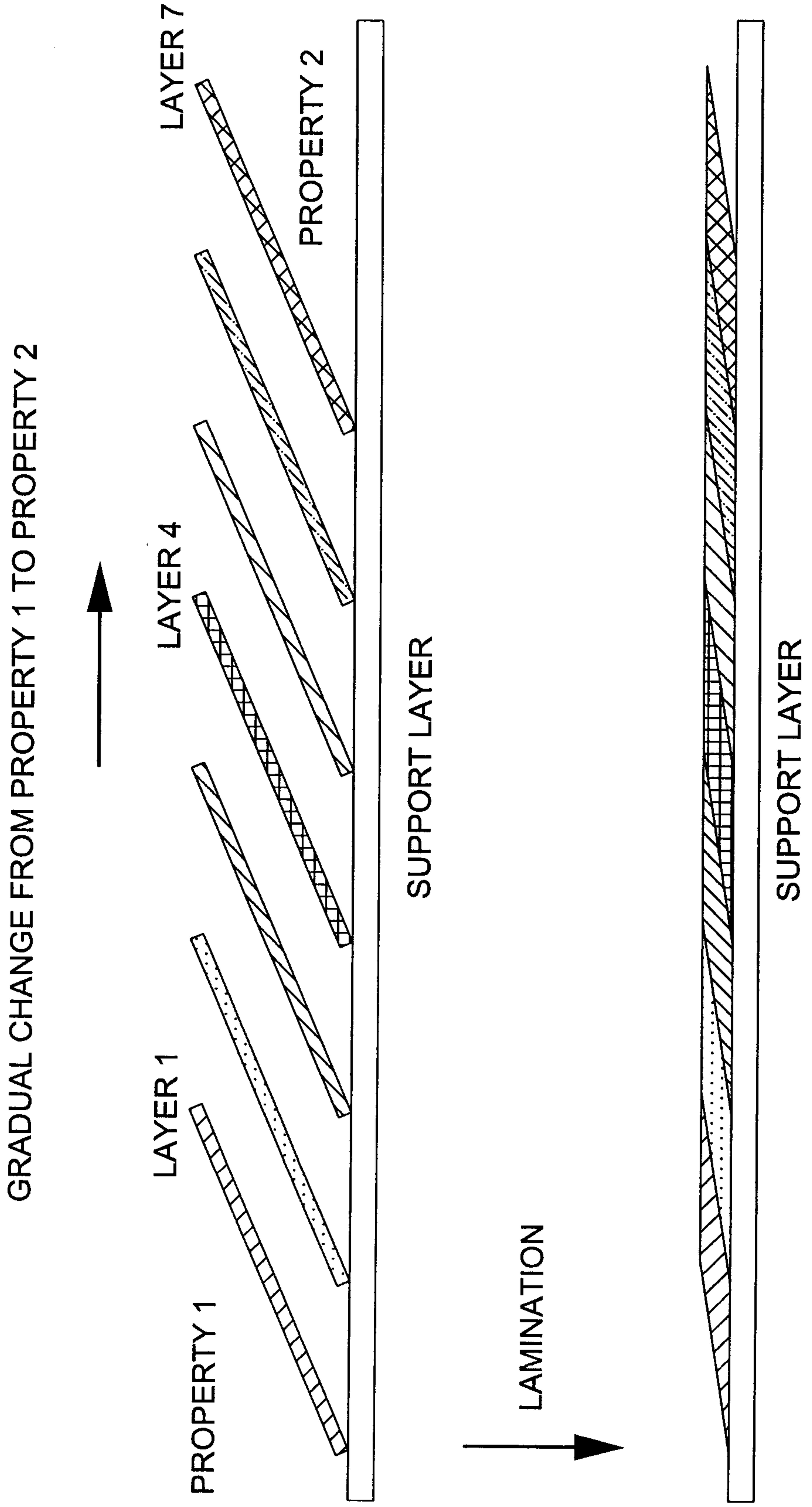
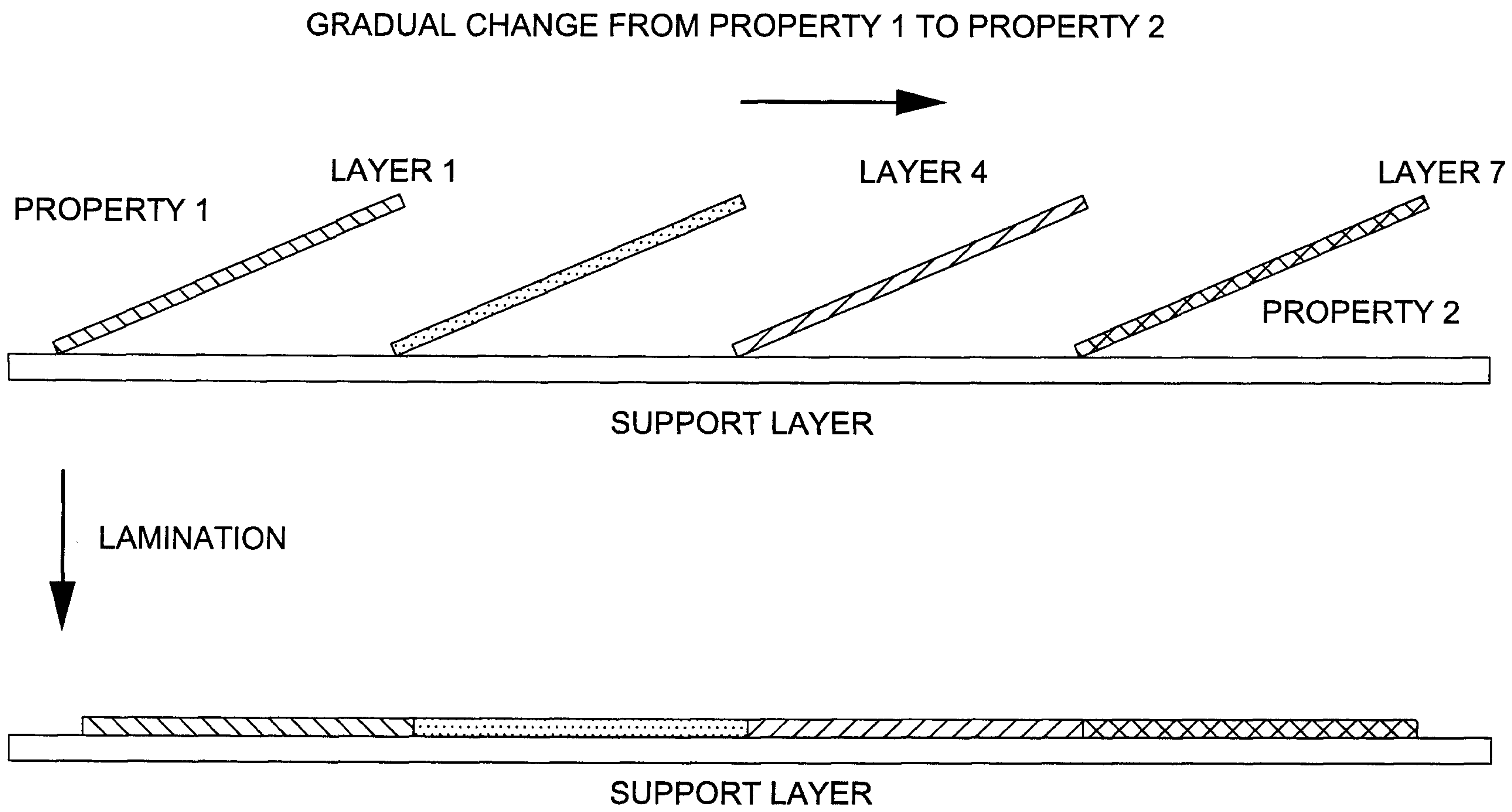

GRADUAL CHANGE FROM PROPERTY 1 TO PROPERTY 2
PROPERTY 1
LAYER 1
LAYER 4
LAYER 7
PROPERTY 2
SUPPORT LAYER
LAMINATION
SUPPORT LAYER

Figure 2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LAYER 1
LAYER 4
LAYER 7
PROPERTY 1
PROPERTY 2
SUPPORT LAYER
LAMINATION
SUPPORT LAYER

Figure 3

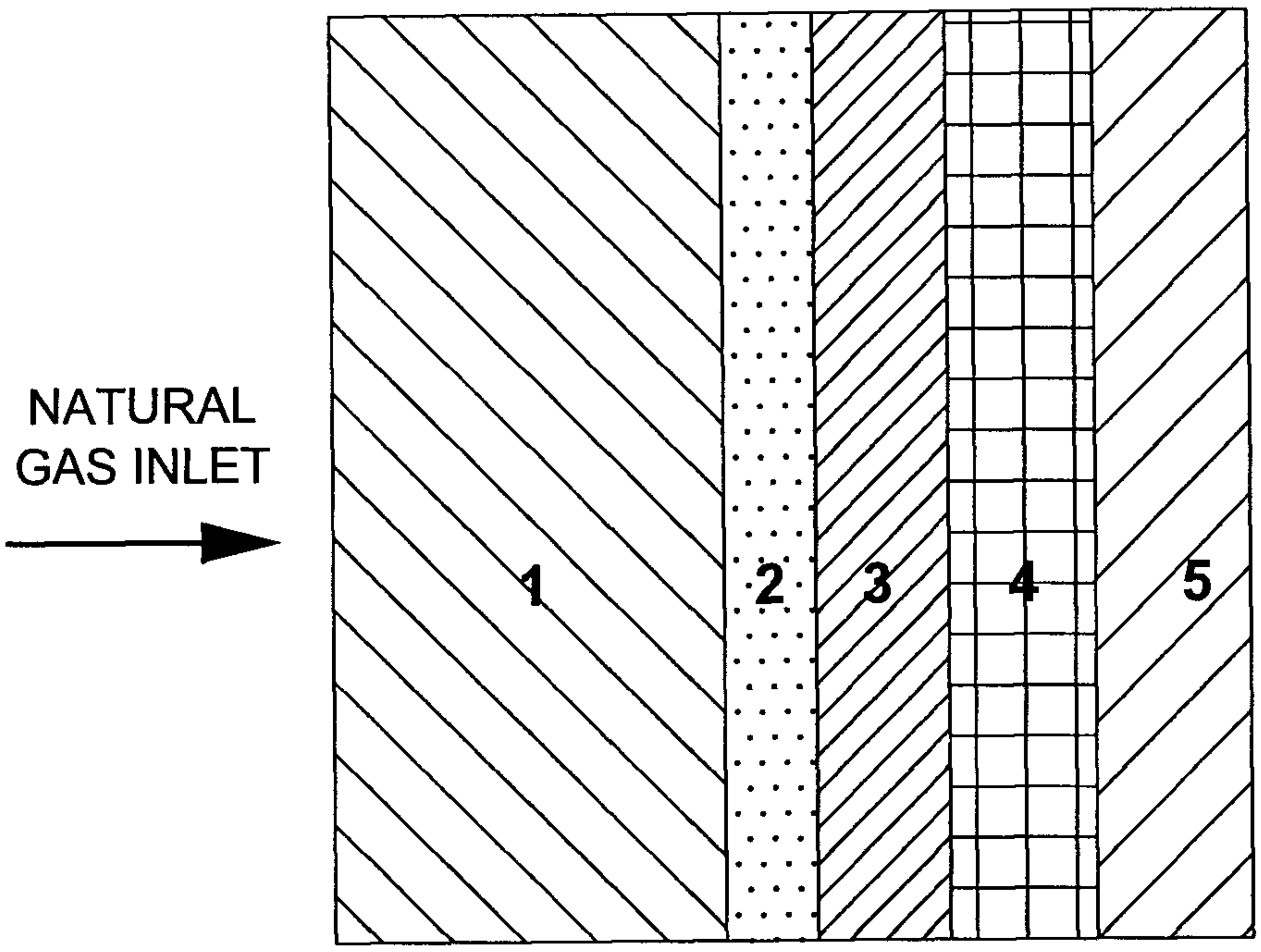


Figure 4

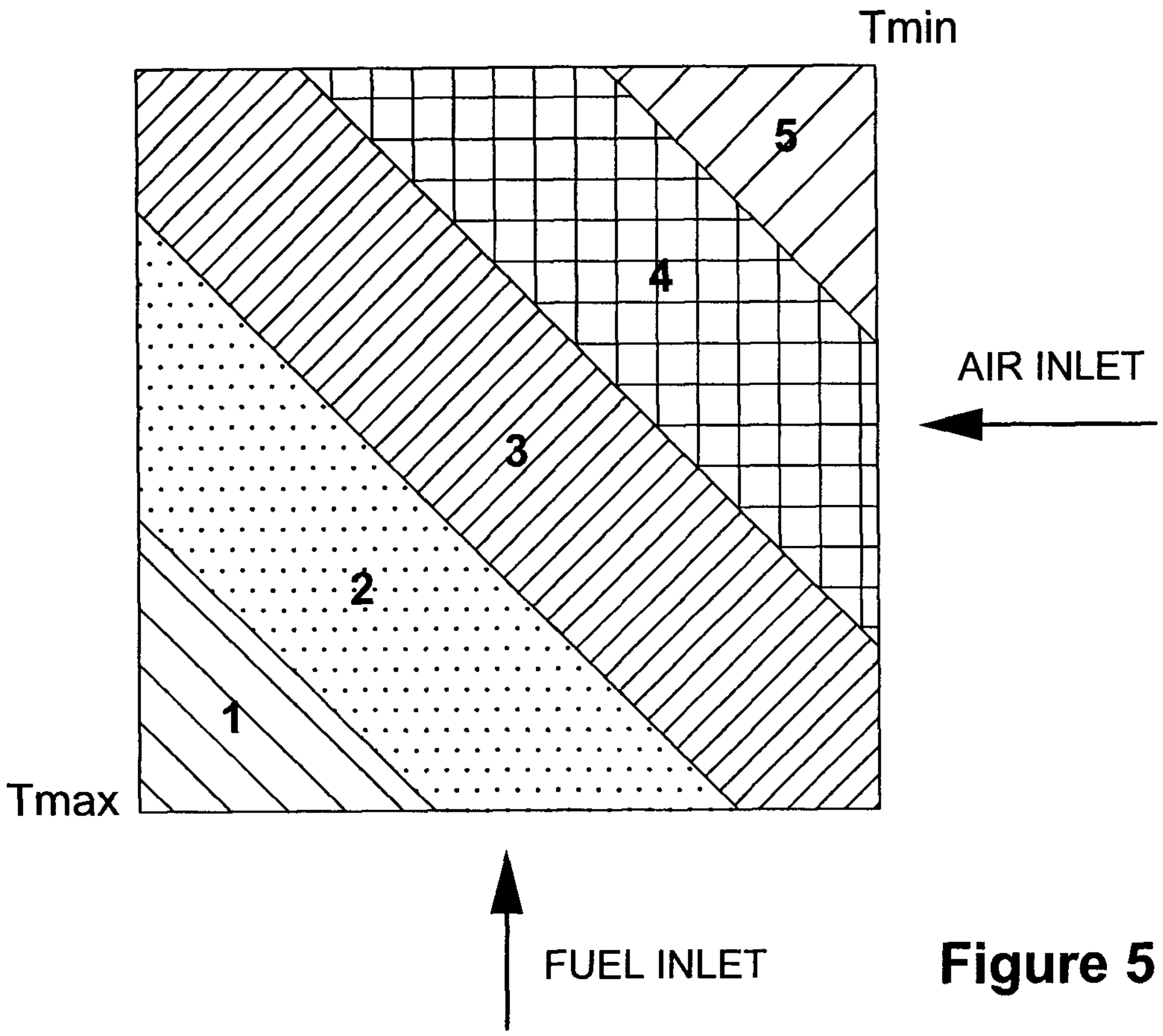


Figure 5

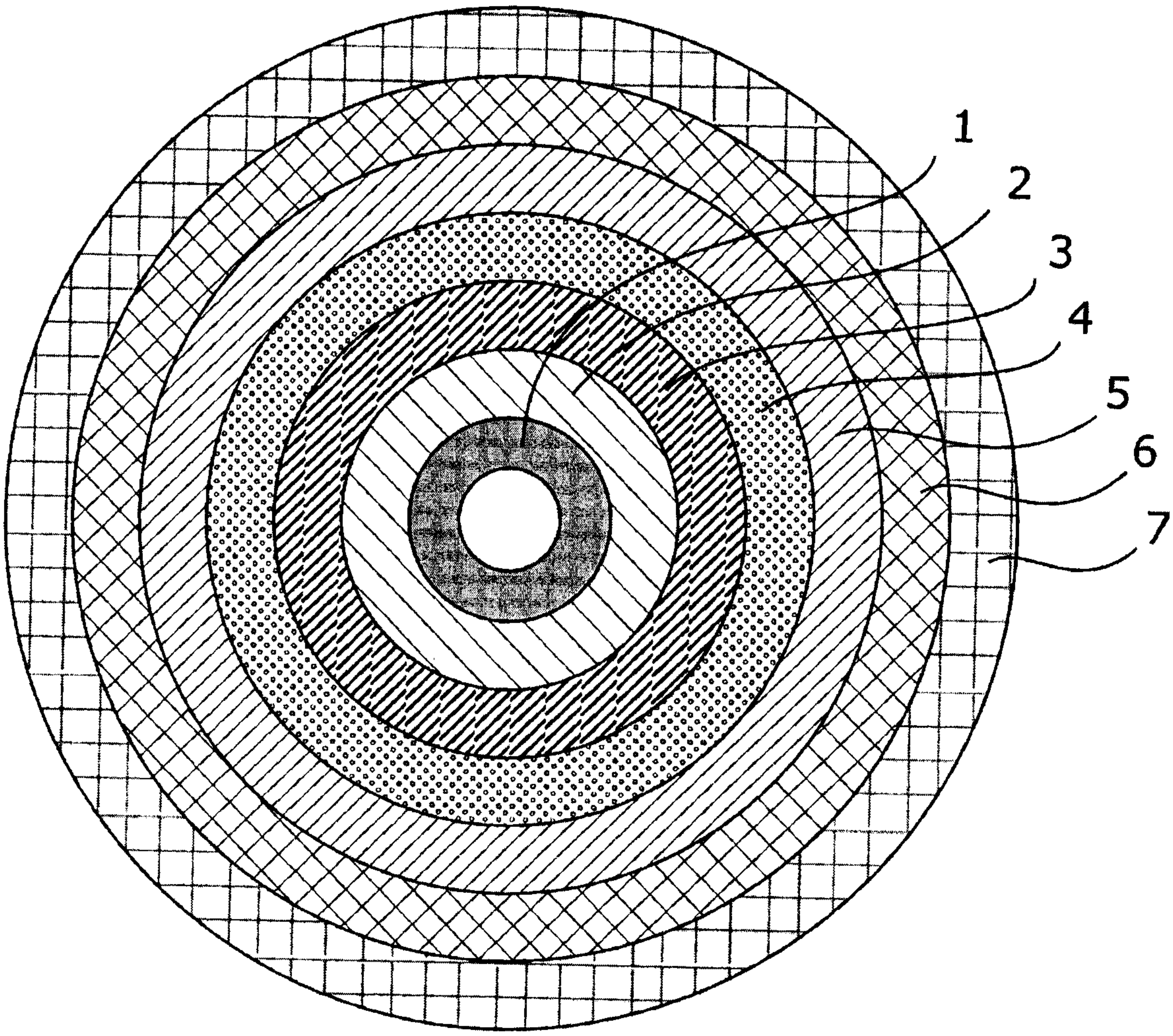


Figure 6.

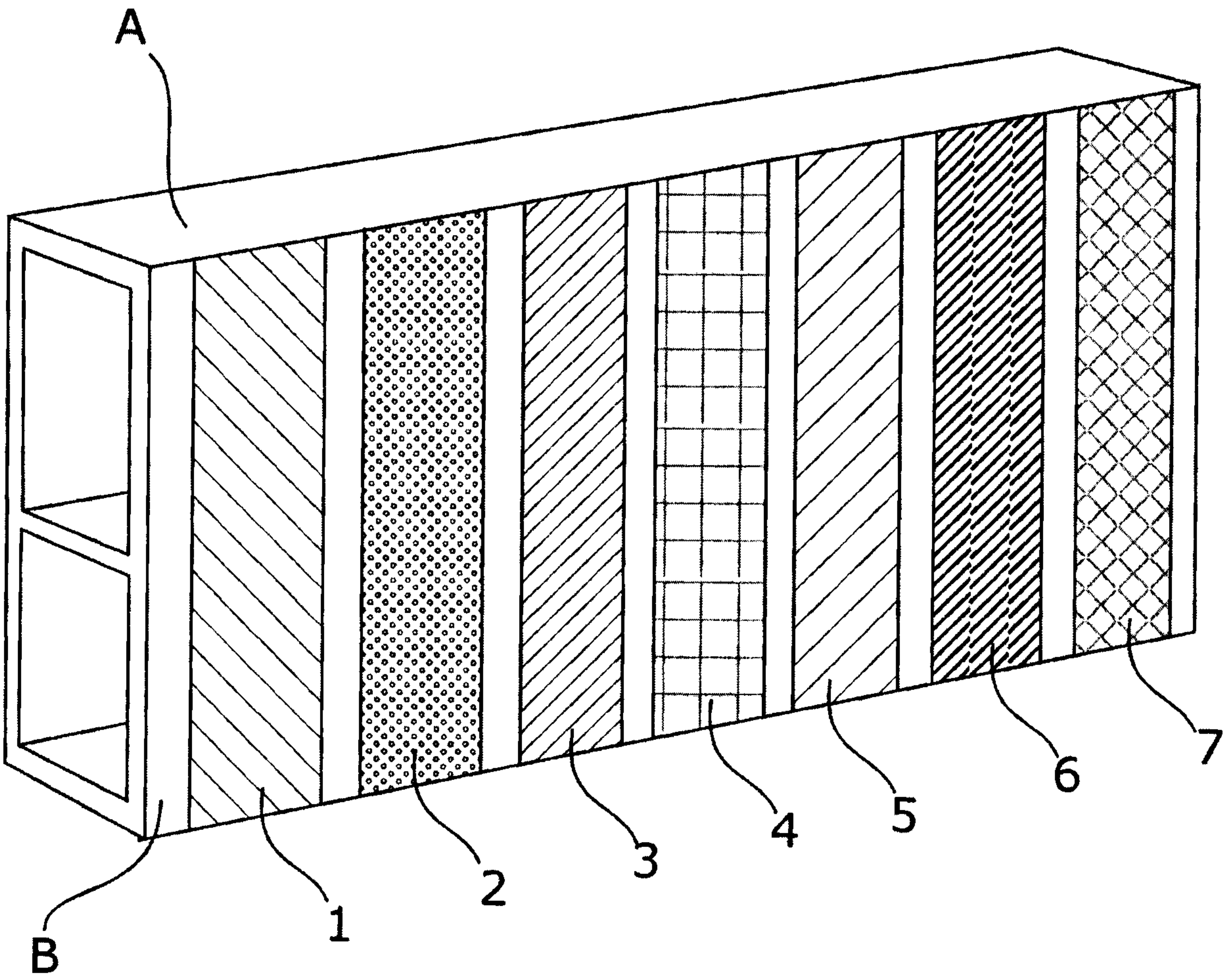


Figure 7

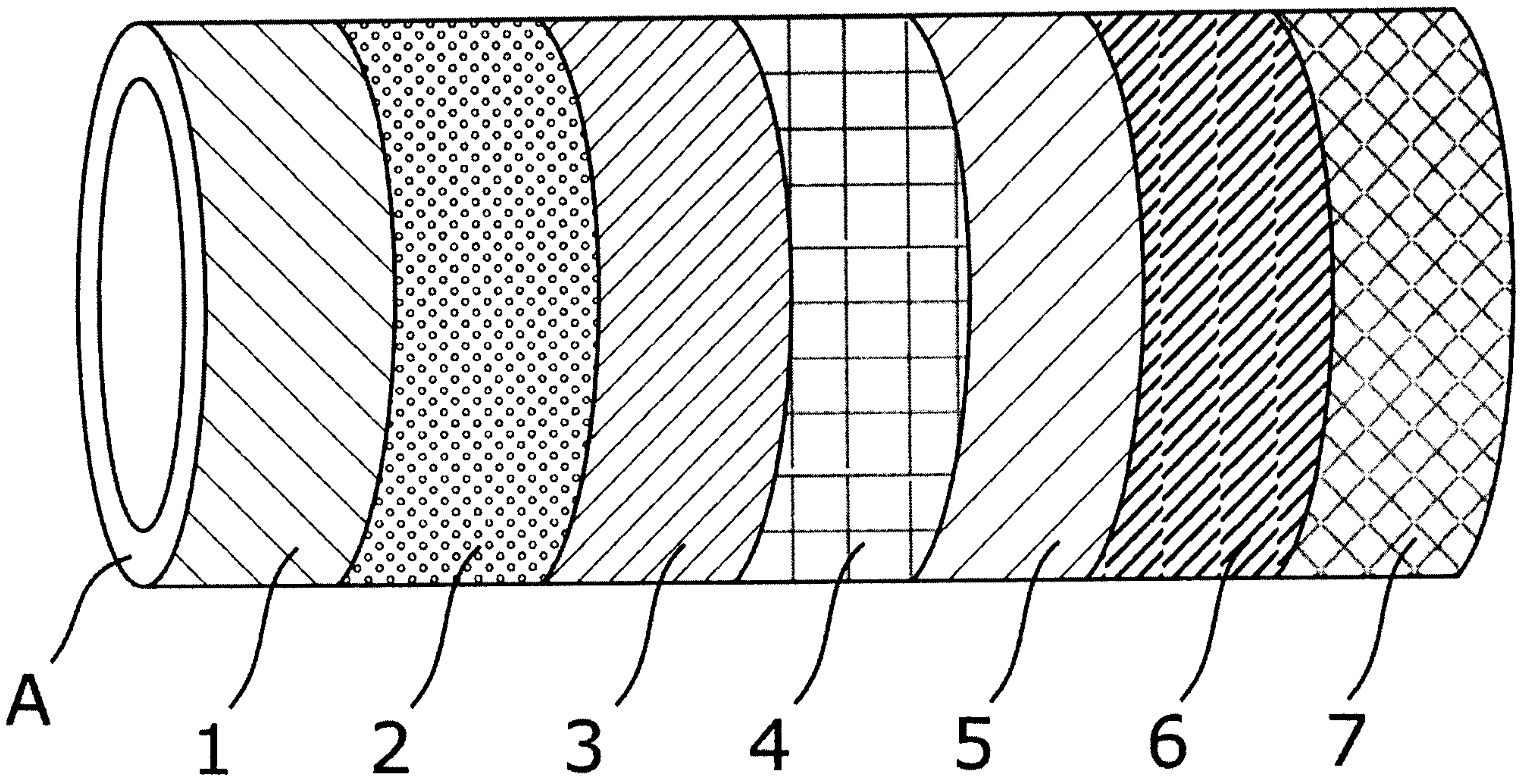


Figure 8.

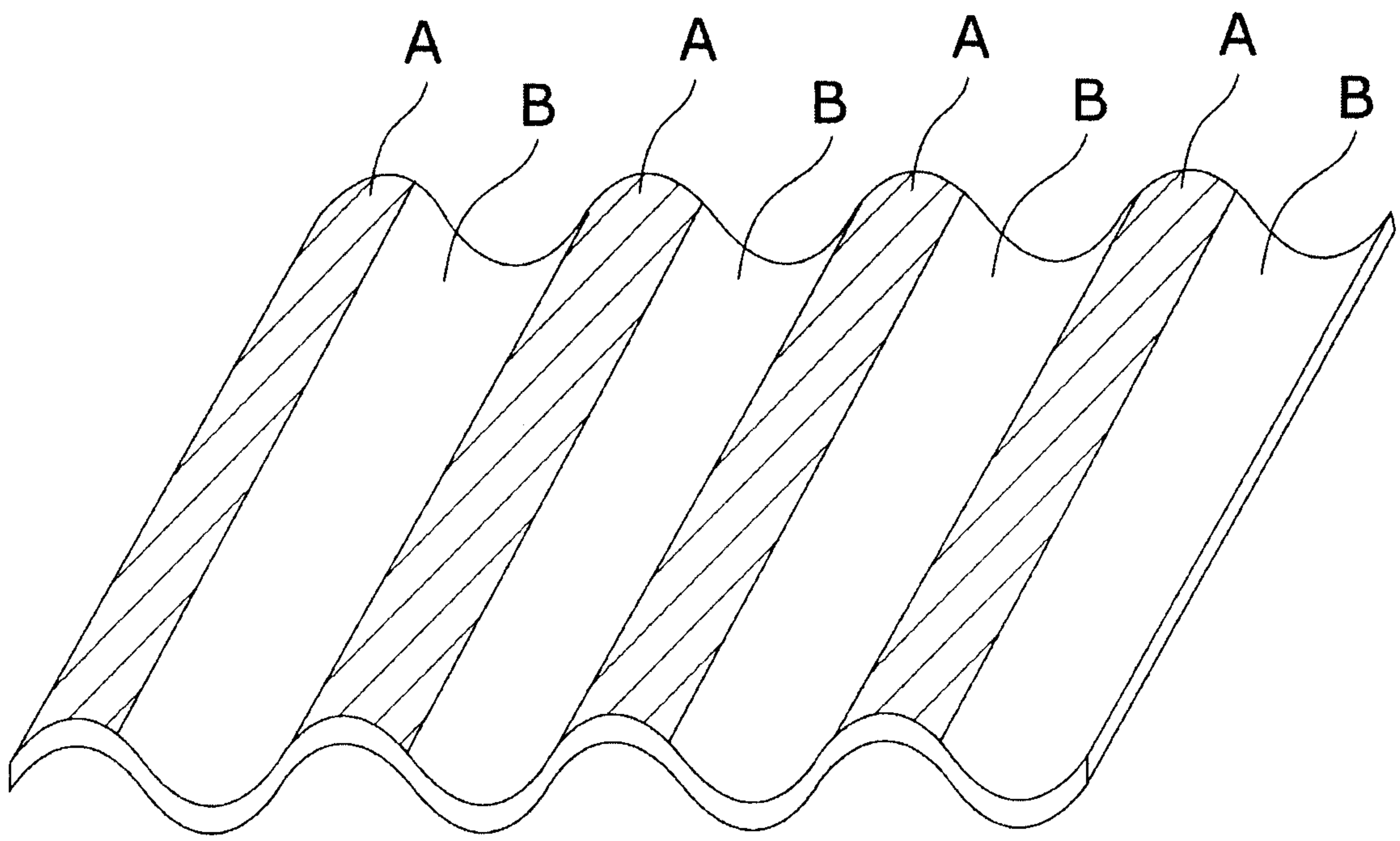


Figure 9

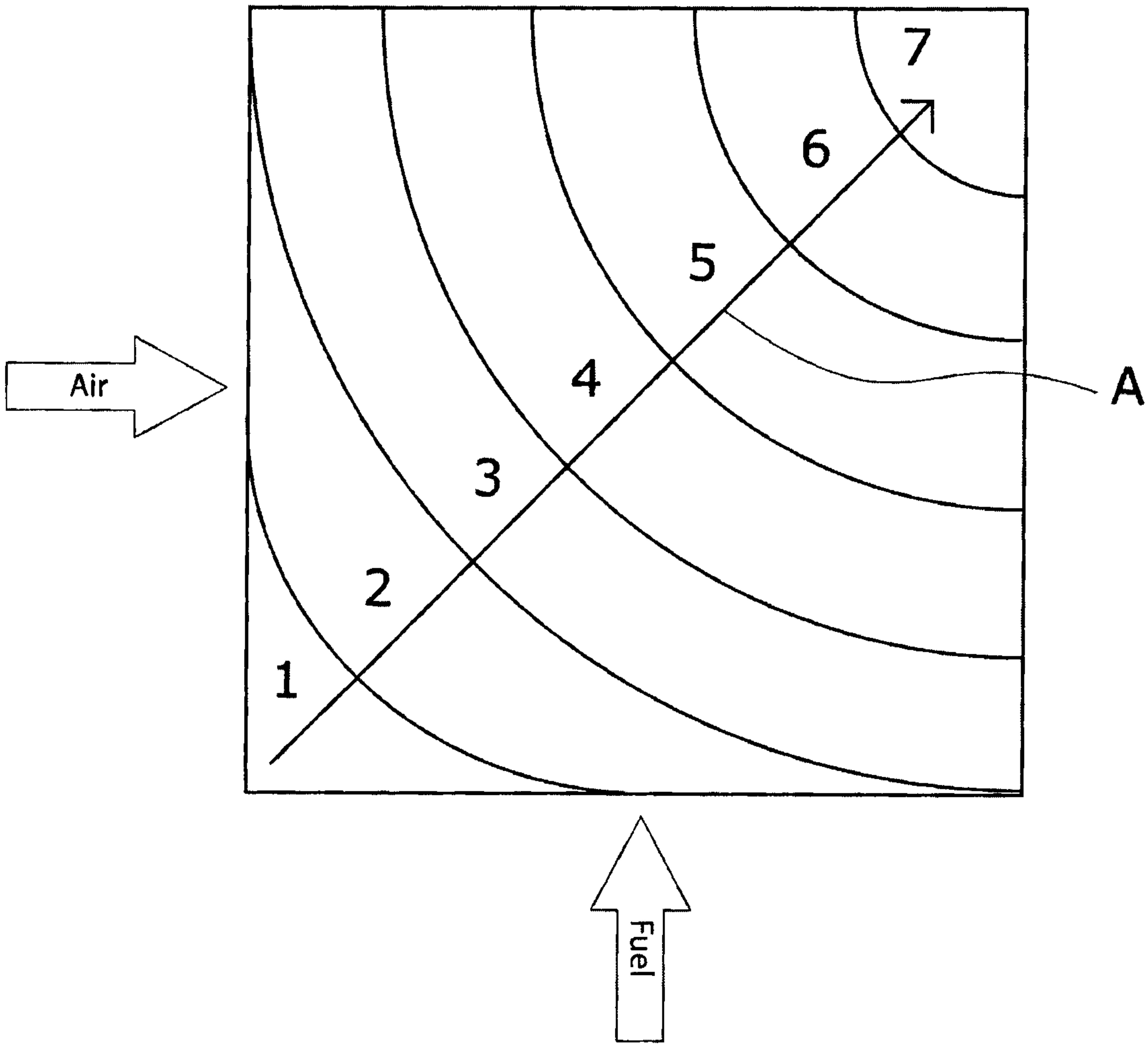
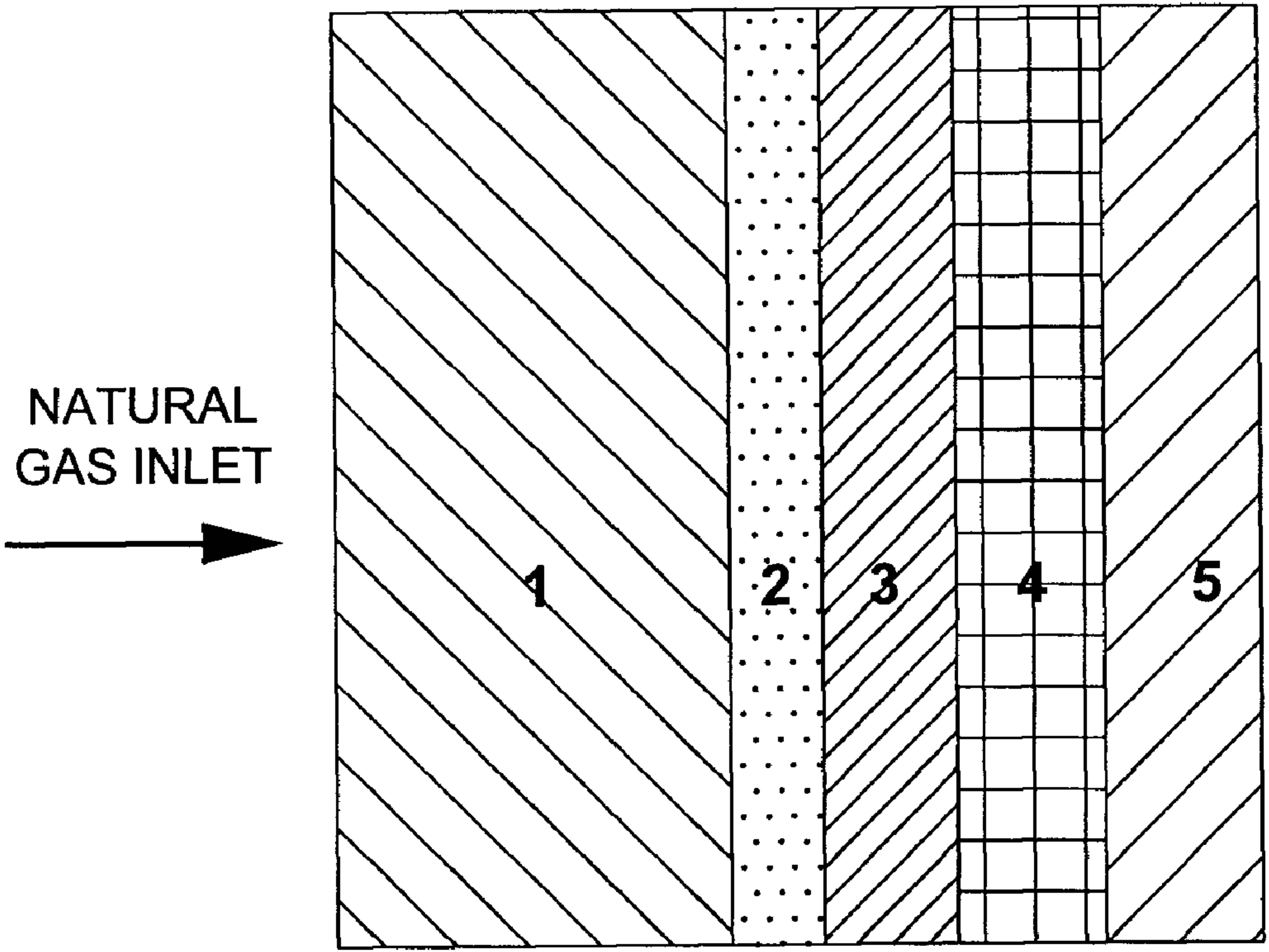


Figure 10



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