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High-Temperature Fuel Cell and High-Temperature Fuel Cell Stack

ABSTRACT

5 In the high-temperature fuel cell (2) having two components (4, 6) which are
joined together in a joining region (12) by a layer (10, 10a, 10b, 10c), the layer
(10, 10a, 10b, 10c) includes at least one ply (14, 22, 24, 26, 30, 32, 34) of a glass
solder and at least one ply (16, 18, 20, 28, 36, 38) of a glass ceramic. Because of this
provision, the components (4, 6) are joined together mechanically and chemically stably
10 and yet economically.



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COMPLETE SPECIFICATION

FOR A STANDARD PATENT

ORIGINAL

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Invention Title: High-Temperature Fuel Cell and High-Temperature Fuel
Cell Stack

The following statement is a full description of this invention, including the best method of performing it known to me/us:-

Description

High-Temperature Fuel Cell and High-Temperature Fuel Cell Stack

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The invention relates to a high-temperature fuel cell and to a stack of high-temperature fuel cells.

10 It is known that in the electrolysis of water the water molecules are decomposed by electric current into hydrogen (H_2) and oxygen (O_2). In a fuel cell, this process proceeds in reverse order. An electrochemical combination of hydrogen (H_2) and oxygen (O_2) into water produces electric current with high efficiency and, if pure hydrogen (H_2) is used as the gaseous
15 fuel, without emitting pollutants and carbon dioxide (CO_2). Even with an industrial fuel gas, such as natural gas or coal gas, and air (which may additionally be enriched with oxygen (O_2)) instead of pure oxygen (O_2), a fuel cell generates markedly less pollution and less carbon dioxide (CO_2) than
20 other energy producers that use fossil fuels. The industrial application of the principal of the fuel cell has led to various embodiments using different kinds of electrolytes and with operating temperatures between 80 C and 1000 C.

25 Depending on their operating temperature, the fuel cells can be classified as low-temperature, medium-temperature, and high- temperature fuel cells, which in turn are distinguished by different technical embodiments.

30 In the high-temperature fuel cell stack composed of many high-temperature fuel cells (in the professional literature, a fuel cell stack is also called a "stack"), below an upper composite printing circuit board that covers the high-temperature fuel cell stack, there are in order at least one guard layer, a

contact layer, an electrolyte electrode unit, a further contact layer, a further composite printing circuit board, and so forth.

- 5 The electrolyte electrode unit includes two electrodes and a solid electrolyte, embodied as a membrane, disposed between the two electrodes. Each electrolyte electrode unit located between adjacent composite printing circuit boards, together with the contact layers immediately adjacent the electrolyte electrode unit, form one high-temperature fuel cell, which also includes the sides of each of the two composite printing circuit boards adjoining the contact layers. This type of fuel cell and other types are known for instance from the "Fuel Cell Handbook" by A.J. Appleby and F.R. Foulkes, 1989, pp. 440-454.

- The components (such as the two metal composite printing circuit boards) of the high-temperature fuel cell are joined together for operation in subregions (the so-called joining regions; in the case of the composite printing circuit boards, for instance in the edge region). The term "joining" is understood to mean placement together in a fitting way or combining of work pieces or materials by various methods (such as screwing, riveting, welding, and so forth).
- 25 Correspondingly, the parting opening between two work pieces (in this case components) to be joined is called a seam.

- Various demands are made of the layer that in the joining region closes the seam between the components: The layer must have adequate gas-tightness. By means of a joining region disposed for instance in the peripheral region of the fuel cell (also called an outer joining region), it is thus assured that the fuel media, which in the fuel cell are in the gaseous state, cannot escape from the fuel cell to the environment.

If the joining region is disposed in the interior of the fuel cell (internal joining region), then mixing of various fuel media (such as hydrogen (H_2) and oxygen (O_2)), is for instance prevented.

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The layer must furthermore be invulnerable to an elevated pressure. The fuel media in the fuel cell in fact have an elevated pressure relative to the ambient atmosphere.

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The layer must furthermore have adequate mechanical stability in the face of mechanical stresses that occur in the fuel cell. Temperature changes, for instance when a high-temperature fuel cell stack, which as a rule is composed of at least 40 fuel cells, is turned on and off, or changes in operating temperature (which depending on requirements can be between 600 and 1000 C) exert considerable mechanical forces on the joining region. When the high-temperature fuel cell stack is assembled as well (or more precisely when the stack mechanically subsides), mechanical stresses cannot be avoided.

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The material comprising the layer in the outer joining regions should furthermore have added electrical insulation. An electrical short circuit between the components that are joined together by the layer must be avoided, because that would reduce the efficiency of the fuel cell. Electrochemical stability must exist, so that the slight electric current loss that nevertheless flows out via the layer will not destroy the material comprising the layer and cause the layer to leak and allow gas to flow through.

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The material comprising the layer must furthermore be stable in the face of a chemical reaction with the fuel media inside the fuel cell. The fuel media in the fuel cell are in the form of reducing humid gasses, which can act chemically

aggressively on the material of the layer. This can again cause leaks in the joining region of the fuel cell. Chemical compatibility with the material comprising the components to be joined must be assured as well.

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From international patent application WO 96/17394, layers for joining components of a high-temperature fuel cell are known that contain plies of a glass and plies of a ceramic. The plies of glass or ceramic are available in the form of prefabricated frames. Manufacturing these frames involves high cost, because the frames must be manufactured to high precision (in the μm range). In addition, assembling the various plies, because of the large number of fuel cells in a stack, requires considerable effort for adjustment and measurement. To obtain sufficiently stable glass frames, the glass is provided with additives (such as arsenic oxide (As_2O_3)). The additives can impair the quality of the joining region with regard to the properties required.

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The ceramic frames are preferably produced by atmospheric plasma spraying or by vacuum plasma spraying. The frames produced in this way do not have adequate gas-tightness when used for relatively long times in the fuel cell. It is now the object of the invention to disclose a high-temperature fuel cell in which the fuel cell components are joined together in a mechanically and chemically stable yet economical way.

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In a high-temperature fuel cell with two components that are joined together in a joining region by a layer, the layer according to the invention includes at least one ply of a glass solder and at least one ply of a glass ceramic. The term "glass ceramic" (also known as vitro ceramic) designates polycrystalline solid bodies which are made by ceramicizing glasses, that is, by controlled devitrification

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(crystallization) of glass. A glass ceramic is created by heat treatment of a suitable glass in which crystals are thereby generated. These glass ceramic materials, like ceramic materials, still contain a certain proportion of glass phase along with these crystals. "Glass solder" (also known as solder glass) means a low melting glass with low viscosity and low surface tension, with a melting temperature between 400 and 700 C. A distinction is made between glass solders that can be thermally devitrified (crystallized) and glass solders that are relatively resistant to devitrification.

The layer that contains at least one glass solder and one glass ceramic is gas-tight. If the layer is used to join two components inside the fuel cell, that is, not in the peripheral region of the fuel cell, then by means of the at least two-layer, two gas chambers with different gaseous fuel media are insulated from one another in gas-tight fashion. If the layer is disposed in the outer region of the fuel cell, no fuel media from the fuel cell then reaches the atmosphere.

The layer has a high electrical insulation performance of several hundred kilohms per cm^2 . After more than 1000 hours in operation it is still chemically unchanged; that is, the material comprising the layer has not undergone any chemical decomposition.

After a heat treatment of more than 1000 hours, the layer has substantially crystallized out. The glass ceramic ply has crystallized out completely, while the glass solder ply has crystallized out at least partially. Because of the high degree of crystallization of the layer, there is little interaction with the components to be joined, which for instance comprise a chromium-iron-based alloy, or zirconium oxide (ZrO_2). With respect to a chemical reaction with a fuel

medium of the fuel cell (for instance with hydrogen (H_2) or oxygen (O_2)), as well, the plies of substantially crystallized-out materials are substantially more resistant than plies of non-crystallizing solders.

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The substantially crystallized-out layer has higher viscosity than pure glasses and is accordingly also substantially more press-resistant. In operation of the fuel cell, there is a pressure drop between the interior of the fuel cell and the ambient atmosphere. The fuel media of the fuel cell have an

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elevated pressure relative to the ambient atmosphere. The two-ply layer, because of the high degree of crystallization of the glass ceramic ply and the thin glass solder ply, is capable of withstanding this pressure exerted from the inside

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outward. In the layers known from the prior art for joining components of a fuel cell, the layer can be forced partway out of the fuel cell (in other words, blown out) by the resultant pressure. This causes the fuel cell to leak.

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The glass solder does not crystallize until toward the end of the joining process (that is, upon curing at elevated

temperature. During the joining process, the mechanical subsidence of a fuel cell stack can thus be adjusted in a defined way. By means of the residual viscosity (dictated by the residual glass phase, since the ply has not crystallized

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out completely), compensation of mechanical stresses and/or a reduction in stress within the stack is possible. In addition, the intermeshing of the crystallized-out plies of a glass solder and a glass ceramic produces high mechanical

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stability. By means of a suitable composition of the materials (that is, of the glass solder and the glass ceramic), the coefficient of thermal longitudinal expansion can be adjusted in a defined way.

The layer may comprise one ply of a glass solder and one ply of a glass ceramic. This two-ply layer is the simplest to produce at the least financial expense, while still achieving all the aforementioned advantages.

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In particular, the layer comprises two plies of a glass solder and one ply of a glass ceramic, and the ply of glass ceramic may be disposed between the two plies of glass solder. Since here two layers of glass solder are used, better performance with regard to the occurrence of mechanical stresses is obtained. The mechanical stresses are compensated for here or reduced by the two plies of glass solder.

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In a further feature, the glass solder contains from 11 to 13 weight percent aluminum oxide (Al_2O_3), 10 to 14 weight percent boric oxide (BO_2), approximately 5 weight percent calcium oxide (CaO), 23 to 26 weight percent barium oxide (BaO), and approximately 50 weight percent silicone oxide (SiO_2).

15

Preferably, the glass ceramic contains from 9 to 11 weight percent aluminum oxide (Al_2O_3), 11 to 13 weight percent boric oxide (BO_2), 22 to 23 weight percent barium oxide (BaO), approximately 45 weight percent silicone oxide (SiO_2), approximately 10 weight percent magnesium oxide (MgO) and approximately 1 weight percent titanium oxide (TiO_2). These

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compositions of material for the glass solder and the glass ceramic have proven themselves especially well in practice for joining together metal components that for instance comprise a chromium- or iron-based alloy. The glass solder and the glass ceramic are also suitable for joining ceramic components. The coefficient of longitudinal expansion can be easily adapted by varying the proportions by weight to the materials of the components to be joined together. It may be advantageous to vary the chemical composition for different plies of glass solder, in order to achieve a graduated transition from one

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component to the next. The same is true for a plurality of layers of glass ceramic.

5 In particular, the components may be metal composite printing circuit boards or a composite printing circuit board and the electrolyte of the electrolyte electrode unit of the fuel cell.

10 According to the invention, a tb stack comprises a number of such high-temperature fuel cells.

Further advantageous features are defined by the dependent claims.

15 For better comprehension of the invention and its refinements, several exemplary embodiments will now be described in conjunction with four drawing figures. The figures each show a schematic detail of a high-temperature fuel cell.

20 In Fig. 1, a high-temperature fuel cell 2 (fuel cell 2) with two components 4, 6 can be seen. The components 4, 6 are either two metal composite printing circuit boards or one metal composite printing circuit board and the electrolyte of the electrolyte electrode unit of the fuel cell 2. The
25 composite printing circuit boards of the fuel cell 2 as a rule contain a chromium- based alloy (that is, the material contains at least 50 weight % chromium (Cr)). The ceramic electrolyte of the fuel cell 2 contains zirconium oxide (ZrO_2), for instance.

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In the seam 8 formed between the two components 4, 6, which defines the spacing between the two components 4, 6, there is a layer 10 that fills up the seam 8 (that is, the two components 4, 6 are joined to one another by the layer 10).

The layer 10 extends across a joining region 12; the joining region 12, in the case of two composite printing circuit boards to be joined together, is disposed in the peripheral region of the composite printing circuit boards and thus of the fuel cell 2. The layer 10 seals off the interior of the fuel cell 2 from the outside atmosphere. If the two components 4, 6 are one composite printing circuit board and the electrolyte, then the joining region 12 is disposed in the interior of the fuel cell 2. In this embodiment, the layer 10 seals off two gas chambers, which contain two different fuel media of the fuel cell 2, from one another.

The layer 10 comprises one ply 14 of a glass solder and one ply 16 of a glass ceramic. The glass solder ply 14 is disposed directly on the component 4. The remaining free space of the seam 8 between the two components 4, 6 is filled by the ply 16 of glass ceramic; that is, the glass ceramic ply 16 is disposed between the glass solder ply 12 and the component 6. The order of the two plies 14, 16 between the two components 4, 6 can equally well be reversed. The seam 8 as a rule has a width between 100 and 800 μm . If the joining region 12 is disposed in the interior of the fuel cell 2, the width of the seam 8 is as a rule less than when the joining region 12 is disposed in the peripheral region of the fuel cell 2. The glass solder ply 14 has a thickness between 50 and 200 μm , while conversely the glass ceramic ply 16 has a thickness between 50 and 600 μm . Thicknesses below 400 μm , however, are more advantageous for the glass ceramic ply 16.

The glass solder of the ply 14 contains from 11 to 13 weight percent aluminum oxide (Al_2O_3), 10 to 14 weight percent boric oxide (BO_2), approximately 5 weight percent calcium oxide (CaO), 23 to 26 weight percent barium oxide (BaO), and approximately 50 weight percent silicone oxide (SiO_2). The

glass ceramic of the ply 16 conversely contains from 9 to 11 weight percent aluminum oxide (Al_2O_3), 11 to 13 weight percent boric oxide (BO_2), 22 to 23 weight percent barium oxide (BaO), approximately 45 weight percent silicone oxide (SiO_2), approximately 10 weight percent magnesium oxide (MgO) and approximately 1 weight percent titanium oxide (TiO_2). By the end of the joining process, these materials for the plies 14, 16 have largely crystallized out; the glass solder of the ply 14, however, still has a residual glass component, or in other words a viscous component. In principle, glass solders and glass ceramics that have largely crystallized out after the joining process are suitable as materials for the plies 14, 16.

15 The layer 14 of a glass solder is applied for instance by wet powder spraying or screenprinting and is then annealed at elevated temperature. Optionally, the ply 14 can be mechanically machined (reground or lapped) in addition. The mechanical treatment can be done before or after the
20 annealing.

The glass ceramic ply 16 is applied by laying on a sheet, or by wet powder spraying or screenprinting, and is then sintered at elevated temperature. The ply 16 can likewise optionally
25 be mechanically treated in addition.

The fuel cell 2 is especially well suited for installation in a stack of high-temperature fuel cells.

30 As shown in Fig. 2, the layer 10a, which closes the seam 8 between the components 4, 6, includes two plies 18, 20 of a glass ceramic and one ply 22 of a glass solder; the ply 22 of glass solder is disposed between the two plies 18, 20 of glass ceramic. In this exemplary embodiment, the seam 8 is closed

by a soldering process (that is, by soldering the ply 22 of a glass solder). The glass solder and the glass ceramic in this exemplary embodiment, as in the exemplary embodiments of Figs. 3 and 4, each have a composition that has already been named in conjunction with the exemplary embodiments of Fig. 1.

10 In Fig. 3, the layer 10b includes two plies 24, 26 of a glass solder and one ply 28 of a glass ceramic, the latter being disposed between the two glass solder plies 24, 26. This embodiment has the advantage that two glass solder plies 24, 26 spatially separate from one another are available in order to meet the mechanical demands made of the fuel cell 2. For example, the weight of a stack itself is compensated for considerably better by means of two plies than by one ply.

15 In particular (when at least two plies of glass solder and/or glass ceramic are used), different materials can be provided for the glass solder plies and/or for the glass ceramic plies. This makes it possible to meet different demands (mechanical or chemical) by means of different plies.

20 In Fig. 4, the layer 10 includes three plies 30-34 of a glass solder and two plies 36, 38 of a glass ceramic. The glass solder ply 30 is disposed over the component 4, and the glass solder ply 34 is disposed over the component 6. The glass ceramic ply 36 is disposed over the glass solder ply 30, and the glass ceramic ply 38 is disposed over the glass solder ply 34. The two glass ceramic plies 36, 38 are joined together by the glass solder ply 32. By using a plurality of glass solder plies 30-34 and a plurality of glass ceramic plies 36 and 38, the mechanical disposition of the fuel cell 2 (as well as of the stack of fuel cells) is more extensively stabilized.

A layer that includes plies of a glass solder and plies of a glass ceramic is fundamentally suitable for joining metal and ceramic components. That is, even outside a fuel cell, it can be used for other technical purposes.



~~Patent claims~~

The claims defining the invention are as follows:

1. A high-temperature fuel cell (2) having two components (4, 6) which are joined together in a joining region (12) by a layer (10; 10a; 10b; 10c),

characterized in that

- the layer (10; 10a; 10b; 10c) includes at least one ply (14; 22; 24, 26; 30, 32, 34) of a glass solder and at least one ply (16; 18, 20; 28; 36, 38) of a glass ceramic.

2. The fuel cell (2) of claim 1,

- characterized in that the layer (10) comprises one ply (14) of a glass solder and one ply (16) of a glass ceramic.

3. The fuel cell (2) of claim 1,

- characterized in that the layer (10) comprises two plies (18, 20) of a glass ceramic and one ply (22) of a glass solder, and the ply (22) of glass solder is disposed between the two plies (18, 22) of glass ceramic.

4. The fuel cell (2) of claim 1,

- characterized in that the layer (10) comprises two plies (24, 26) of a glass solder and one ply (28) of a glass ceramic, and the ply (28) of glass ceramic is disposed between the two plies (24, 26) of glass solder.

5. The fuel cell (2) of claim 1, characterized in that the layer (10) comprises three plies (30, 32, 34) of a glass solder and two plies (36, 38) of a glass ceramic, and one ply

(36, 38) of glass ceramic is disposed between each two plies (30, 32, 34) of glass solder.

6. The fuel cell of one of the foregoing claims,
5 characterized in that the glass solder of the plies (14; 22; 24, 26; 30, 32, 34) contains from 11 to 13 weight percent aluminum oxide (Al_2O_3), 10 to 14 weight percent boric oxide (BO_2), approximately 5 weight percent calcium oxide (CaO), 23
10 to 26 weight percent barium oxide (BaO), and approximately 50 weight percent silicone oxide (SiO_2).

7. The fuel cell of one of the foregoing claims,
characterized in that the glass ceramic of the plies (16; 18, 20; 28; 36, 38) contains from 9 to 11 weight percent aluminum
15 oxide (Al_2O_3), 11 to 13 weight percent boric oxide (BO_2), 22 to 23 weight percent barium oxide (BaO), approximately 45 weight percent silicone oxide (SiO_2), approximately 10 weight
percent magnesium oxide (MgO) and approximately 1 weight
percent titanium oxide (TiO_2).

20 8. The fuel cell (2) of claim 4,

characterized in that the plies (24, 26; 30, 32, 34) of the glass solder have different compositions.

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9. The fuel cell (2) of claim 5,
characterized in that the ply (32) of the glass solder,
disposed between the plies (36, 38) of the glass ceramic, has
30 a different composition from the two outer plies (30, 34) of the glass solder.

10. The fuel cell (2) of one of the foregoing claims,

characterized in that

the components (4, 6) are metallic composite printed circuit
5 boards.

11. The fuel cell (2) of one of claims 1 through 9,
characterized in that one of the components (4, 6) is a metal
composite printing circuit board, and the other of the two
10 components (4, 6) is the electrolyte of the electrolyte-
electrode unit.

12. The fuel cell (2) of one of the foregoing claims,
15 characterized in that between the two components (4, 6), a
seam (8) with a width between 100 and 800 μm is formed, which
is practically filled by the layer (10; 10a; 10b; 10c).

13. The fuel cell (2) of one of the foregoing claims,
20 characterized in that the ply (14; 22; 24, 26; 30, 32, 34) of
the glass solder has a thickness between 50 and 200 μm .

14. The fuel cell (2) of one of the foregoing claims,
25 characterized in that no ply (16; 18, 20; 28; 36, 38) of glass
ceramic is thicker than 400 μm .

15. A high-temperature fuel cell stack with high-temperature
30 fuel cells (2) of one of claims 1 through 14.

16. A high temperature fuel cell, substantially as described herein in relation to any one of the embodiments with reference to the accompanying drawings.

DATED this First Day of October 1998

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Siemens Aktiengesellschaft

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SPRUSON & FERGUSON

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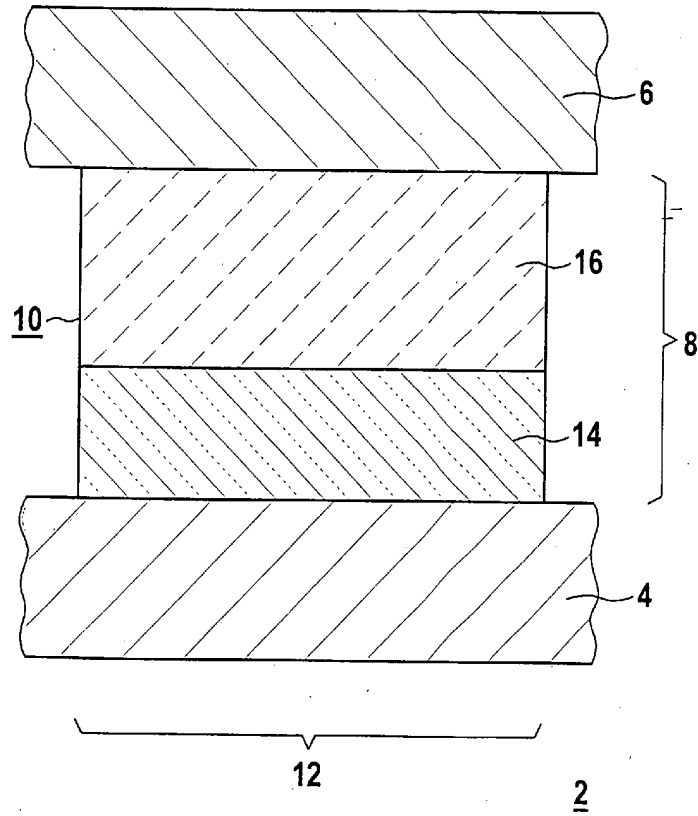


FIG 1

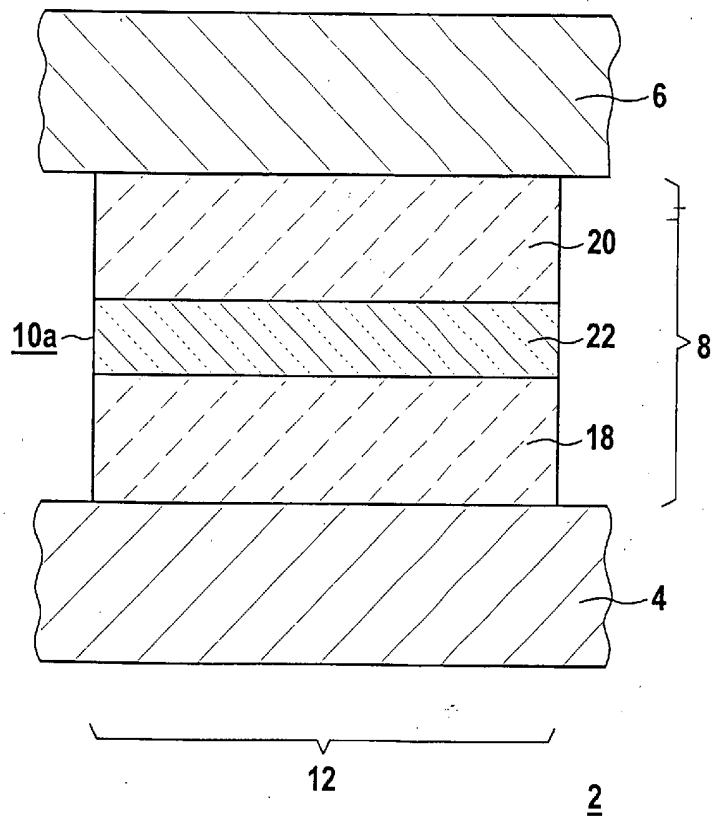


FIG 2

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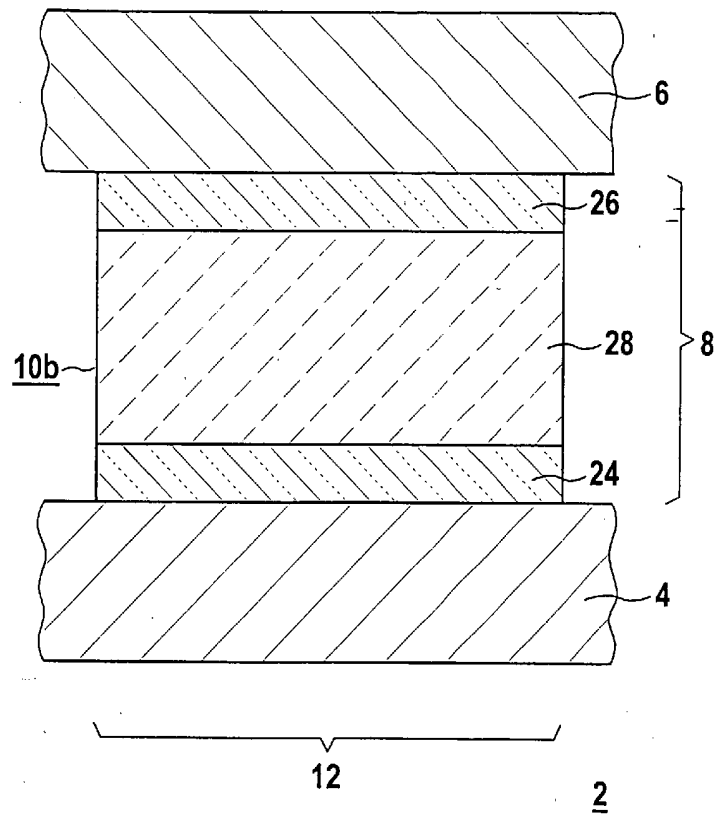


FIG 3

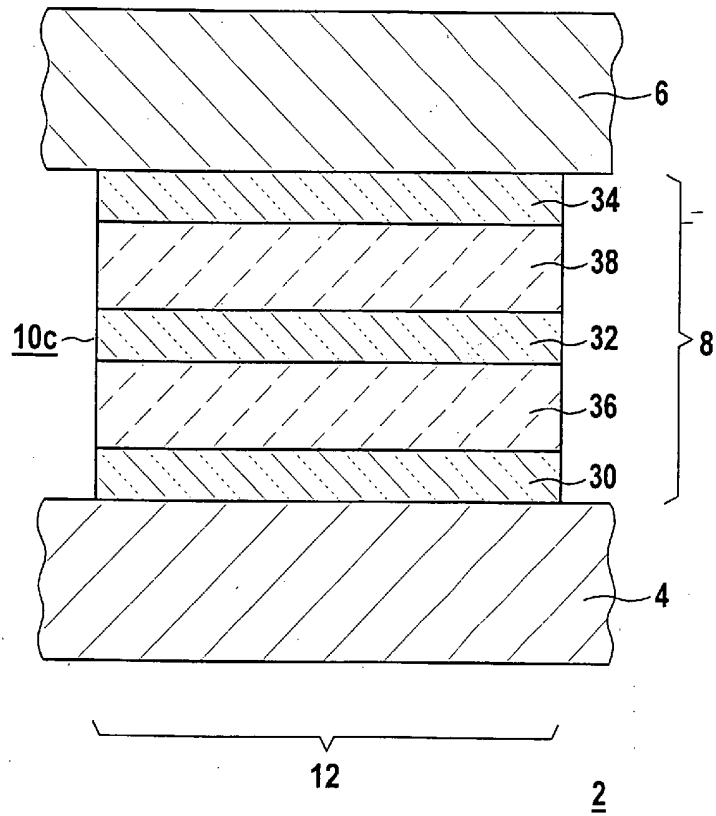


FIG 4