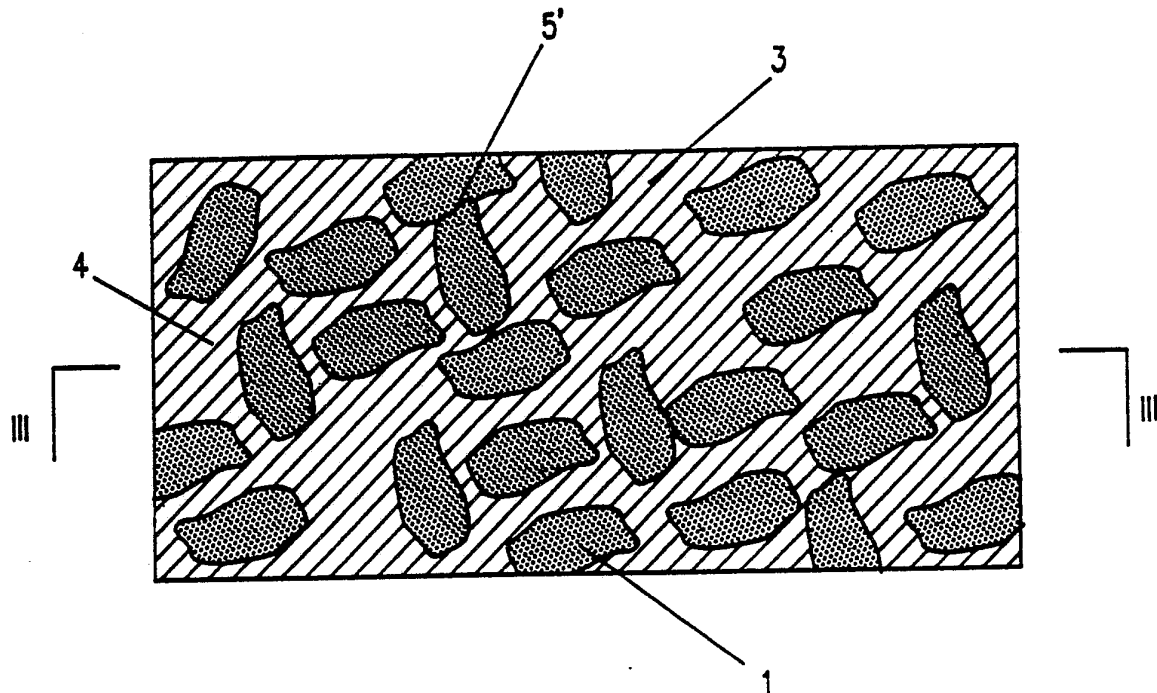




## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

<p>(51) International Patent Classification<sup>4</sup> : <b>C25C 3/08, C04B 35/62, 35/58</b></p>	<p><b>A1</b></p>	<p>(11) International Publication Number: <b>WO 89/ 02488</b> (43) International Publication Date: 23 March 1989 (23.03.89)</p>
<p>(21) International Application Number: PCT/US87/02355 (22) International Filing Date: 16 September 1987 (16.09.87) (71) Applicant (for all designated States except US): ELTECH SYSTEMS CORPORATION [US/US]; Town Executive Center, 6100 Glades Road, Suite 305, Boca Raton, FL 33434 (US). (72) Inventor; and (75) Inventor/Applicant (for US only) : DURUZ, Jean-Jacques [CH/CH]; 4, rue de Hesse, CH-1204 Geneva (CH). (74) Agent: FREER, John, J.; Eltech Systems Corporation, 625 East Street, Fairport Harbor, OH 44077 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CH (European patent), DE (European patent), FR (European patent), GB (European patent), IT (European patent), JP, LU (European patent), NL (European patent), NO,</p>		<p>SE (European patent), US.  <b>Published</b> <i>With international search report.</i></p>

(54) Title: REFRACTORY OXYCOMPOUND/REFRACTORY HARD METAL COMPOSITE



## (57) Abstract

A composite material comprises a body, e.g., a slab, of a fused or sintered refractory oxycompound (3) having a multiplicity of discrete inclusions such as lumps (1) of an aluminum-wettable RHM in its surface. These bodies are especially useful as aluminum-wettable but non-current carrying components of aluminum reduction cells.

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REFRACTORY OXYCOMPOUND/REFRACTORY  
HARD METAL COMPOSITE

TECHNICAL FIELD

The invention relates to composite materials formed of alumina or other refractory oxycompounds and refractory hard metal (RHM), which are wettable by molten aluminum but which do not need to be electrically non-conductive in  
5 applications in which they do not serve for the supply of electric current. The invention also relates to methods of making these composite materials as well as their use as components of aluminum production cells.

BACKGROUND ART

In the production of aluminum, there have been  
10 numerous proposals for composite materials based on alumina or other refractory oxycompounds and the so-called Refractory Hard Metals.

In this specification, the term "Refractory Hard Metals" or "RHM" designates the borides and carbides of

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Groups IVA and IVB of the periodic table of the elements. The RHMs contemplated for this invention are aluminum-wettable. Also, "RHM" as used herein includes composites based on RHM and which include sufficient RHM  
5 at least at their surface to provide permanent wettability to molten aluminum as well as other materials stable in the presence of molten aluminum and wettable by the molten aluminum.

10 Conventional Hall-Heroult cells for the electrolytic production of aluminum employ a carbon cell bottom which serves to supply current to a deep pool of molten aluminum forming the cathode. The cathodic aluminum is necessarily  
15 thick (at least 80-100 mm) because carbon is non-wettable by molten aluminum. Problems arise because of wave motion in the thick aluminum pool caused by the considerable forces generated by the magnetic fields. The use of RHM to alleviate these problems has been contemplated, but so far has not met with success.

20 U.S. Patents 4,650,552 and 4,600,481 described families of composite materials including conductive alumina-aluminum composites having RHM additives to enhance wettability and electrical conductivity. These  
25 materials were mainly intended for use as components such as cathodes and cathode current feeders which serve to supply electrical current to the cell. Considerable development work did not however lead to a material which combined electrical conductivity, wettability, resistance  
30 to molten aluminum and cryolite and other desirable properties.

U.S. Patent 4,560,448 describes a structural component of an aluminum production cell which is in

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contact with molten aluminum, made of a non-wettable material such as alumina which is rendered wettable by a thin coating of  $TiB_2$ . However, to prevent dissolution of this thin (up to 100 micron) coating the molten  
5 aluminum had to be maintained saturated with titanium and boron.

A dense essentially non-porous titanium diboride-alumina composite material of specific  
10 microstructure is described in U.S. Patent 4,647,405. In this microstructure, submicronic boride is distributed in intimate wetting contact with the surfaces of alumina agglomerates. This material shows promise for use in the environment of an aluminum production cell but the  
15 manufacture of large components is expensive.

A hard, dense refractory vitrified composition consisting of alumina with aluminum nitride is known from U.S. Patent 2,480,475. Such material is non-wettable by  
20 molten aluminum, and its use is therefore limited.

Various electrically-conductive composites composed of an electrically conductive matrix (such as graphite with pitch and other binders) including particles of RHM  
25 are also known, e.g., from U.S. Patents 3,661,736, 4,376,029, 4,465,581, 4,466,996, as well as from WO 83/04271 and WO 84/02930. These materials are intended mainly as a replacement of the conventional current-carrying carbon lining of aluminum production  
30 cells, but so far have not found acceptance.

It has also been proposed to cover the carbon bottom of Hall-Heroult cells with tiles or slabs of RHM such as  $TiB_2$ . For example, U.S. Patent 4,231,853 discloses

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fixing  $TiB_2$  files loosely on pins. However, the cost of  $TiB_2$  tiles is high and attaching the tiles to the bottom involves difficulties.

5           The aluminum production cell described in U.S. Patent 4,383,910 employs a carbon cell bottom from which  $TiB_2$  tiles project upwardly to form the cathode surface. On the cell bottom, surrounding the tiles, is a layer of solid cryolite/alumina which protects the carbon bottom  
10 from attack by molten aluminum. Again, this cell has not proven to be practical.

#### DISCLOSURE OF INVENTION

15           This invention is based on the insight that if alumina (or other suitable ceramic oxycompounds) could adequately be rendered wettable by molten aluminum, without simultaneously seeking to make them serve as  
20 current feeders, and if such wettability could be maintained permanently and at moderate cost, the material would be ideal as a non-current carrying component of an aluminum production cell in particular as a non-conductive cell bottom. Such a wettable, non-conductive cell bottom  
25 could be covered by a relatively shallow pool of aluminum forming the cathode, thereby alleviating the undesirable wave motion effect described above.

30           As set out in the claims, the invention provides an aluminum-wettable composite material characterized in that it comprises a body of fused or sintered alumina or other refractory oxycompound and a multiplicity of discrete inclusions of aluminum-wettable RHM in the surface of the body, there being fused or sintered alumina separating the

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RHM inclusions.

The material according to the invention can be conveniently manufactured in the form of slabs, bricks or pieces of other shapes by casting or sintering techniques as set out below. For most applications, the RHM inclusions need only be present on one face of the slab, brick or other shape of material. Thus, in preferred embodiments the RHM inclusions are located solely at the surface of the material whereas the inside and the rest of the material can be made of solid fused or sintered alumina or other refractory oxycompounds. Other less preferred embodiments incorporate some inclusions also in the body of the material, preferably in low concentration since they add to the cost of the material without improving its surface wettability.

The amount and general distribution of the RHM inclusions over the surface will depend on the intended application and the required degree of wettability. For most applications, 20-90% and more preferably 30-80% of the projected area of the surface of the material may be taken up by the discrete RHM inclusions.

For cost reasons, it is advantageous to use RHM inclusions of random shapes and dimensions, because these can be manufactured much more inexpensively. Thus, the inclusions can be pieces of RHM in the form of irregular lumps or flakes. However, it is equally possible to use regular shapes such as balls, cones, small cylinders, or plates of various shapes such as hexagons, rings or star shapes. As a general rule the diameter or maximum transverse dimension of the inclusions will be in the range of 1-25 mm, mostly in the range 2-15 mm. However,

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it is also possible to produce fused bodies containing inclusions of RHM powder with an average particle size as low as 50 micron. When irregular shapes and sizes are used, the average transverse dimension of the inclusions will usually be in the same ranges. As various shapes, sizes and mixtures of RHM materials of different shapes and sizes can be used, the given dimension ranges should be regarded as a general guidance only.

10           The inclusions may be flush with the surface or the body, e.g., when the surface is machined. This is particularly suitable for applications where the material is used as a drained cathode covered only by a very thin film of molten aluminum. For applications where the material is in contact with a shallow pool of aluminum, say 5-30 mm thick, some or all of the RHM inclusions can protrude slightly from the alumina at the surface of the material.

20           The spacing and distribution of the inclusions can be non-uniform/random or in a pattern. Generally, all of the inclusions will be separated from one another but, depending on the manufacturing process, some pieces of the RHM may touch or cluster together. When the material is designed for applications where surface conductivity of the material is not required or may be detrimental, obviously the RHM inclusions should not touch in lined-up formation to form a current-carrying path. In such cases essentially all or preferably at least 50% of the inclusions are electrically insulated from one another by the refractory oxycompound.

As stated above, for most applications it is not necessary to have the RHM inclusions on the surface in



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touching contact with one another. However, where limited surface conductivity of the material is not a disadvantage, the inclusions can touch one another. This can be achieved by casting or sintering with pieces of

5 TiB<sub>2</sub> packed in a monolayer or in a packed multilayer. This is also suitable when fine RHM powders are cast into the surface of a fused ceramic body. It is also possible by lining up the inclusions to provide surface

10 conductivity along a given direction. These fused or sintered bodies incorporating a packed surface layer of RHM inclusions can of course be used to advantage in applications where both surface wettability by aluminum and surface conductivity are required. In other

15 embodiments, it is possible to arrange for conductivity through the body via the RHM inclusions, with or without surface conductivity as well. Nevertheless, the presently preferred embodiments are bodies surface wettable by molten aluminum but non-conductors (on the surface and through the body). Such bodies can be used to great

20 advantage in aluminum production cells as non-current carrying but aluminum wettable components.

TiB<sub>2</sub> is the preferred RHM on account of its excellent wettability and corrosion resistance to molten

25 aluminum and molten cryolite. However, composite materials including TiB<sub>2</sub> are also contemplated, e.g., the Al<sub>2</sub>O<sub>3</sub>.TiB<sub>2</sub> composite described in U.S. Patent 4,647,405. For example, pieces of this material can be made by reaction sintering. This material can then be

30 machined or broken into smaller pieces of desired shapes, which are included in the fused or sintered alumina composite materials of this invention.

When alumina is chosen as the ceramic oxycompound

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phase of the composite material, use will preferably be made of the usual grades of highly-purified calcined alumina powder as currently used in aluminum electrowinning where this powder is added directly to the molten bath. Use can also be made of highly pure white fused alumina with an  $\text{Al}_2\text{O}_3$  content of 98.5 to 99.5%, and in some cases the less pure grades of regular fused alumina (94 to 96 %  $\text{Al}_2\text{O}_3$ ) and semi-friable fused alumina (96 to 98 %  $\text{Al}_2\text{O}_3$ ).

Other ceramic aluminum oxycompounds useful in the practice of the invention are the aluminates of lithium, sodium, potassium, beryllium, magnesium, calcium, strontium, barium, scandium, yttrium, lanthanum, hafnium, cerium, neodymium, samarium, ytterbium, thorium and other rare earths. Specific examples are the perovskite  $\text{Y}_2\text{O}_3 \cdot \text{Al}_2\text{O}_3$  and the garnet  $3\text{Y}_2\text{O}_3 \cdot 5\text{Al}_2\text{O}_3$ . Another useful aluminum oxycompound for cathode applications is alumina oxynitride.

Other useful ceramic oxycompound materials include the  $\text{MgO} \cdot \text{MgAl}_2\text{O}_4$  refractories which have an optimum composition of 30-40 w% alumina and 60-70 % MgO. Generally, MgO, CaO and  $\text{Ca}_2\text{F}$  are desirable components of the oxycompounds. Oxyfluorides are also particularly suitable for applications of the material in aluminum production cells. As a general requirement, the refractory oxycompound material must fuse or sinter below the fusion point of the selected RHM.

The composite materials according to the invention can be easily manufactured by casting, e.g., (in the case of fused alumina or fused alumina-magnesia) or by sintering.

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The casting method involves distributing pieces or a coarse or fine powder of RHM in a mould, casting molten refractory oxycompound into the mould and allowing the molten oxycompound to solidify into a body containing discrete RHM inclusions which extend to the surface of the body.

Typically, in the production by fusion casting, the pieces or powders of RHM are distributed on the bottom of a suitable mould, e.g., of graphite. Then molten alumina or another suitable refractory oxycompound is poured in. The temperature of the melt is well below the fusion point of the RHM. After cooling, the inclusions of RHM are present at one surface of the resulting body. If necessary or desired, this surface can be machined to provide an optimum exposure of the RHM.

The RHM pieces can be a monolayer on the bottom of the mould, spaced apart from one another or in touching relationship, or may occupy a greater depth, for instance packed layers. Powders can be arranged in a layer of any suitable depth.

In the sintering production method, the RHM pieces or coarse powder are distributed in a fine powder of the alumina or other sinterable refractory oxycompound. The RHM pieces, whether of random shapes and sizes or regular, will be somewhat larger than the grain size of the sinterable refractory oxycompound, typically at least 100 times bigger. The RHM pieces may be arranged to occupy only the surface of the resulting body, in non-touching or touching relationship, or they may be located throughout the body although for most applications this will not be preferred. Sintering can take place in a conventional

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way. If desired, the body can be compacted into a self-sustaining green prior to final sintering.

Another aspect of the invention is an aluminum  
5 reduction cell comprising a component having an  
aluminum-wettable surface in contact with molten aluminum  
in operation of the cell, characterized in that the  
component comprises a body of fused or sintered refractory  
oxycompound the surface of which is rendered wettable by  
10 molten aluminum by inclusions of RHM in the surface  
separated by the fused or sintered oxycompound.

Advantageously, these materials are used as  
aluminum-wettable but non-current carrying components.  
15 Such components include cell floors, walls, baffles,  
weirs, divider walls or packing elements, e.g., for use in  
the packed cathode bed described in European Patent  
EP-B-0 033 630. Previous attempts to use RHM materials as  
components of aluminum-production cells have been mainly  
20 as current-carrying components such as cathode current  
feeders or conductive cell base linings. Aside from cost  
which has been a major obstacle to their use, the  
materials have often failed to meet up to multiple  
stringent requirements including conductivity,  
25 wettability, resistance to the cell environment and fixing  
in place. By eliminating the current-carrying requirement  
and by securely fixing the RHM inclusions in the cast or  
sintered matrix, the materials according to the invention  
are able to provide excellent wettability at reduced cost  
30 by making effective use of the wettable surfaces of the  
inclusions.

BRIEF DESCRIPTION OF DRAWINGS

The invention will be further described with reference to the accompanying schematic drawings, in which:

5

Fig. 1 is a schematic illustration showing the manufacture of a fused alumina/TiB<sub>2</sub> composite by casting;

Fig. 2 is a top plan view of this fused alumina TiB<sub>2</sub> composite after machining its surface along line II-II of Fig. 1;

Fig. 3 is a cross-section along line III-III of Fig. 2;

15

Figs. 4, 5, 6, 7 and 8 are views similar to Fig. 3 of different composite materials according to the invention.

20

DESCRIPTION OF PREFERRED EMBODIMENTS

Fig. 1 illustrates the production of a block of TiB<sub>2</sub>/alumina by casting.

Lumps 1 of TiB<sub>2</sub> are scattered on the bottom of a mould 2, conveniently made of graphite. The mould 2 is surrounded by an annealing powder, not shown. The TiB<sub>2</sub> lumps 1 are of irregular shapes. Their average transverse dimension is conveniently in the range 3-30 mm with no lumps bigger than 50 mm or smaller than 1 mm. The lumps 1 are arranged so that they form a monolayer on the bottom of the mold, and for the most part are not in touching relationship with one another.

30

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Alumina is melted in an electric arc furnace and poured into the graphite mold 2 to fill it to the required level with alumina 3.

5           After cooling and removal from the mould 2, the surface of the block of fused alumina containing the lumps 1 is machined flat along line II-II. The exposed, flat surface 4 shown in Figs. 2 and 3 contains inclusions 5 formed by the lumps 1 whose surfaces are machined flat  
10 with surface 4. These  $TiB_2$  inclusions 5 are randomly distributed over the flat fused alumina surface. Most inclusions 5 are entirely separate from one another, but a small number may touch, as at 5'.

15           Figs. 4 and 5 show alternative forms of the composite material.

          In Fig. 4, the  $TiB_2$  inclusions 5 protrude from the surface 4. This can be achieved by pressing the  $TiB_2$   
20 lumps into the surface of the mould 2 before casting the molten alumina.

          In Fig. 5 the fused or sintered alumina is made into a thinner sheet so that the inclusions 5 extend to both  
25 surfaces. There are no paths for electrical current in the plane of the sheet, but the  $TiB_2$  inclusions provide for conductivity through the sheet, generally perpendicular to the plane of the sheet.

30           The material illustrated in Fig. 6 has inclusions 5 of regular truncated conical shape in side-by-side touching relationship on one face of the body. The larger faces of the truncated cones face outwards. These pieces are laid flat on the bottom of the mould, so that the Fig.

6 form may be obtained without further machining.

Fig. 7 shows a material in which irregular pieces 5 of RHM are packed into the mould. After casting the alumina and cooling, one face 4 is machined to maximize the accessible  $TiB_2$  surfaces. This body is electrically conductive in all directions.

Fig. 8 shows a material in which several layers of powder inclusions, e.g., a powder of average diameter from 50 micron to 1mm is packed to a depth of 200 micron to 2.5mm, are embodied in the surface of a body of fused alumina 3 by the technique described in connection with Fig. 1. After casting, the body can be machined to provide a surface maximizing the wettable RHM area by machining along line IV-IV.

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CLAIMS

1. An aluminum-wettable refractory oxycompound/RHM composite material characterized in that it comprises a  
5 body of fused or sintered refractory oxycompound and a multiplicity of discrete inclusions of aluminum-wettable RHM in the surface of the body, the RHM inclusions being separated by fused or sintered alumina.
- 10 2. The composite material of claim 1, in the form of a slab having inclusions in only one face thereof.
3. The composite material of claim 1 or 2, in which  
15 20-90% of the projected area of the surface of the material is occupied by the inclusions.
4. The composite material of claim 1, 2 or 3, in which the inclusions are irregular lumps or flakes.
- 20 5. The composite material of any preceding claim, in which the maximum transverse dimension of the inclusions is in the range 50 micrometer to 50mm.
- 25 6. The composite material of any preceding claim, in which the inclusions are flush with the surface of the material.
7. The composite material of any one of claims 1-5, in which at least some of the inclusions protrude from the  
30 surface of the material.
8. The composite material of any preceding claim, in which at least 50% of the inclusions are electrically insulated from one another by the refractory oxycompound.



9. The composite material of any one of claims 1-7, comprising at least one layer of inclusions in touching relationship with one another.

5 10. The composite material of any preceding claim, in which the ceramic oxycompound is alumina.

10 11. The composite material of any preceding claim, in which the RHM is  $TiB_2$ .

12. A method of producing an aluminum-wettable composite material of a refractory oxycompound and a RHM comprising:

15 - distributing pieces or a powder of RHM in a mould,

- casting molten refractory oxycompound into the mould, and

20 - allowing the molten oxycompound to solidify into a body containing discrete RHM inclusions which extend to the surface of the body.

25 13. The method of claim 12, in which a monolayer of pieces of RHM is distributed in the mould with the RHM pieces spaced apart from one another.

30 14. The method of claim 12, in which at least one packed layer of pieces or powder of RHM is distributed in the mould.

15. The method of claim 12, 13 or 14, comprising machining the solidified body to expose machined surfaces of the inclusions.

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16. The method of any one of claims 12-15, in which the refractory oxycompound is alumina.

17. The method of any one of claims 12-16, in which  
5 the RHM is  $TiB_2$ .

18. An aluminum reduction cell comprising a component having an aluminum-wettable surface in contact with molten aluminum during operation of the cell and  
10 which does not serve to conduct electric current, characterized in that the component comprises a body of fused or sintered refractory oxycompound the surface of which is rendered wettable by molten aluminum by  
15 inclusions of RHM in the surface separated by the fused or sintered oxycompound.

19. Use of the aluminum-wettable composite material of any one of claims 1-11 as component of an aluminum production cell in contact with molten aluminum.

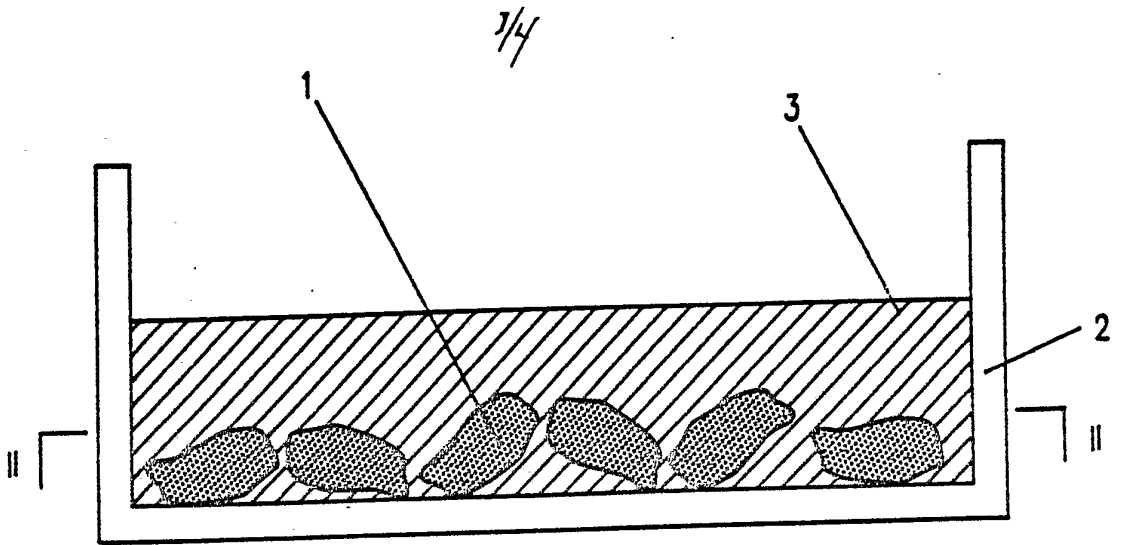


FIG. 1

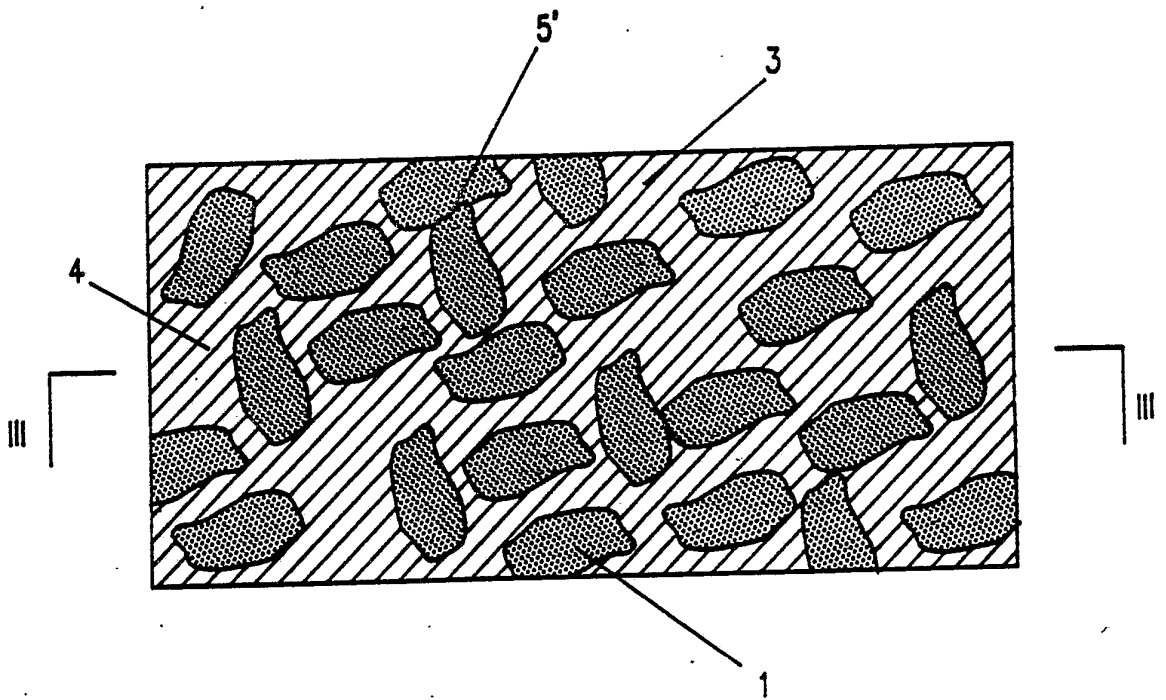


FIG. 2

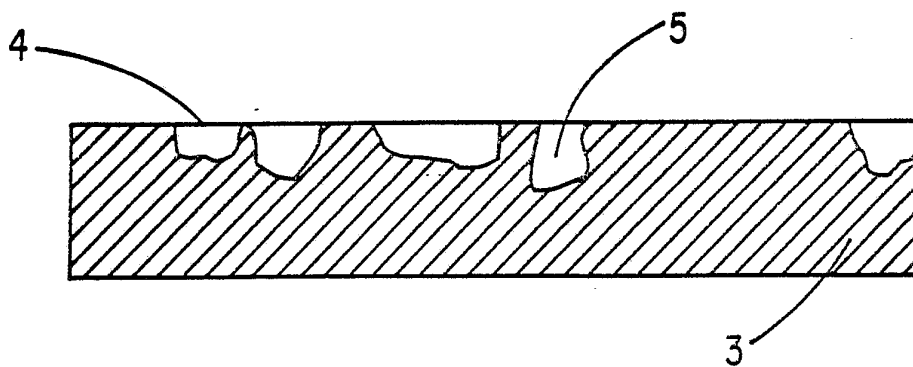


FIG. 3

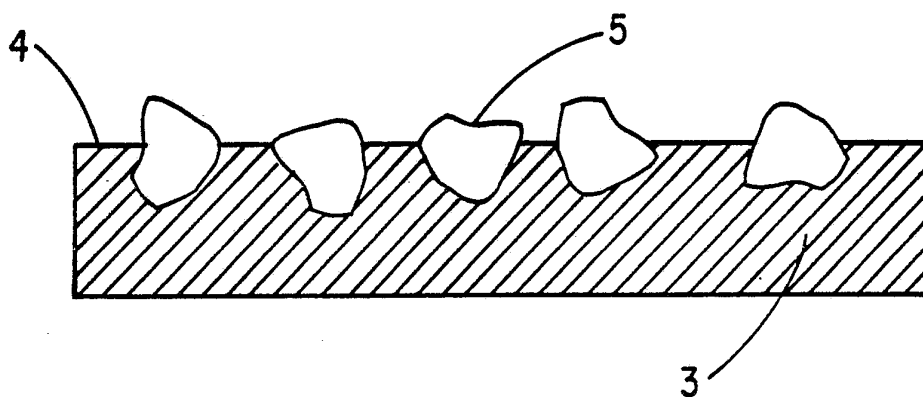


FIG. 4

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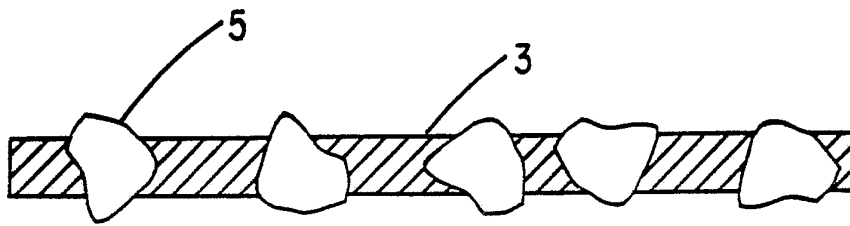


FIG. 5

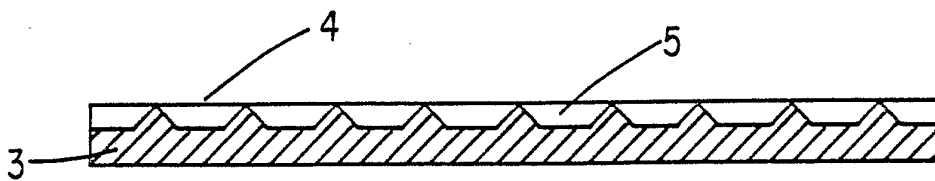


FIG. 6

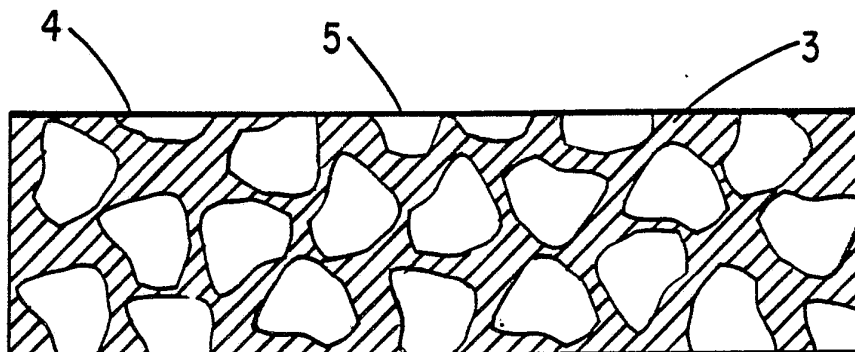


FIG. 7

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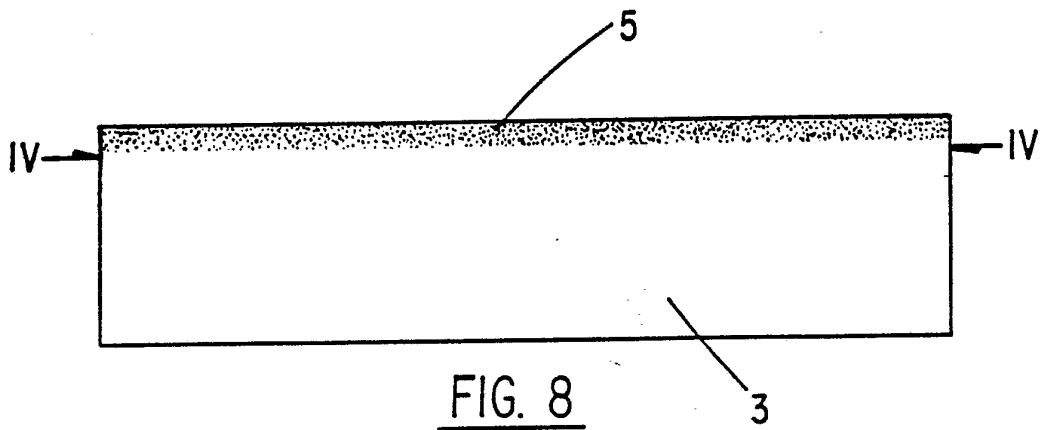
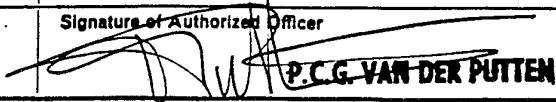


FIG. 8

# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 87/02355

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (if several classification symbols apply, indicate all) <sup>6</sup>		
According to International Patent Classification (IPC) or to both National Classification and IPC		
IPC <sup>4</sup> : C 25 C 3/08; C 04 B 35/62; C 04 B 35/58		
<b>II. FIELDS SEARCHED</b>		
Minimum Documentation Searched <sup>7</sup>		
Classification System	Classification Symbols	
IPC <sup>4</sup>	C 25 C; C 04 B	
Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched <sup>8</sup>		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT <sup>9</sup></b>		
Category <sup>9</sup>	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
X	EP, A, 0117366 (ALCAN INTERNATIONAL LTD) 5 September 1984 see claims 1,2,5,6,11,12; page 2, lines 17-26; page 5, lines 6-10	1-3,8-11, 18,19
Y	--	4-7,12-17
X	FR, A, 2349633 (SOFREM) 25 November 1977 see claims 1,2,4-6; page 4, lines 15-24	1
Y	--	4-7,12-17
A	EP, A, 0095854 (ALCAN INTERNATIONAL TD) 7 December 1983 see claims 1-7; page 7, lines 17-21	1-3,18,19
-----		
<p><sup>10</sup> Special categories of cited documents:</p> <p>"A" document defining the general state of the art which is not considered to be of particular relevance</p> <p>"E" earlier document but published on or after the international filing date</p> <p>"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)</p> <p>"O" document referring to an oral disclosure, use, exhibition or other means</p> <p>"P" document published prior to the international filing date but later than the priority date claimed</p> <p>"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention</p> <p>"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step</p> <p>"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.</p> <p>"&amp;" document member of the same patent family</p>		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search	Date of Mailing of this International Search Report	
13th May 1988	17 JUN 1988	
International Searching Authority	Signature of Authorized Officer	
EUROPEAN PATENT OFFICE	 <b>P.C.G. VAN DER PUTTEN</b>	

**ANNEX TO THE INTERNATIONAL SEARCH REPORT  
ON INTERNATIONAL PATENT APPLICATION NO.**

US 8702355  
SA 18809

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 06/06/88. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

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		US-A- 4599320	08-07-86
		AU-B- 562967	25-06-87
FR-A- 2349633	25-11-77	None	
EP-A- 0095854	07-12-83	JP-A- 58213888	12-12-83
		AU-A- 1509983	01-12-83
		US-A- 4592820	03-06-86
		CA-A- 1216254	06-01-87
		AU-B- 561730	14-05-87