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(57) Abstract: The present invention concerns membranes and a process of realizing membranes that comprises the following steps: - preparing a substrate by sintering of metal powders, ceramics or their composites, with dimensions between 1 and 50 microns; - covering said substrate by thermal deposition of a layer of the same or different ceramic material, metal or alloys and composites; - cooling said layer during and/or after its thermal deposition; and possibly - a further step of covering said layer realized by thermal deposition through physical vapor deposition (PVD) or chemical vapor deposition (CVD) of a layer of a same or different material.



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MEMBRANES AND PROCESS FOR THE REALIZATION THEREOF

The present invention relates to membranes and a process for realisation thereof.

5 More particularly, the invention relates to ceramic and non-ceramic membranes, consisting of a plurality of superimposed layers with decreasing porosity, these layers being possibly made of different materials.

10 As is well known, ceramic membranes are often used in processes of separation by filtration, which consist of an active part, which allows the selective permeability of materials and, optionally, auxiliary parts, for example as mechanical support or drainage. Compared to the common filtration, membrane filtration allows for retaining much smaller particles and in particular ceramic membranes allow for retaining particles
15 of nanometer or micrometer size. A ceramic membrane, therefore, can be thought of as a selective permeability barrier or as a sieve to separate, depending on its porosity distribution, large particles, dispersions, colloids down to molecules and ions.

20 At present, therefore, the ceramic membranes are used in industrial processes of microfiltration, ultrafiltration, nanofiltration, reverse osmosis, separation of vapors and gaseous phases, pervaporation, dialysis, biochemical reactions, catalysis and contactors.

25 The two most important parameters that describe the performance of a membrane are its permeability and separation factor. For porous membranes, these parameters are governed by the thickness of the membrane and its porosity distribution, while for the dense membranes the variables involved are much more difficult to determine, since atomic phenomena are also involved that are not always quantifiable.

30 From a structural point of view, ceramic membranes are composed of one or more layers, which can also be made of different materials. The structural element is composed of a macroporous support or substrate, on which one or more mesoporous intermediate layers (or inter-layers) rest. The outer layer (or top layer) is the really filtering element and often it is characterized by having a finely dispersed porosity
35 of micrometer or nanometer size.

The macroporous support is designed to mechanically support the top layer while the inter-layers have the function to bind and to give structural continuity between the substrate and the top-layer. In general, all

structural continuity between the substrate and the top-layer. In general, all the constituent elements of the membrane are metal oxides such as Al_2O_3 , TiO_2 , ZrO_2 , SiO_2 .

5 The porosity characteristics of a membrane are a function of the thickness of the different layers of which it is made; in fact, the dimensions of the pores range from a few nanometers (top layer) to a few microns (support) and this is only possible by inserting one or more inter-layers with pores of intermediate size.

10 At present, most commercially available membrane are sold as cartridges having the shape of a disk, plate or tube. The number of cartridges are assembled together to form a module, several modules can be installed in platform (skid) and the union of more skids leads to the construction of modular systems of any size.

15 In order to increase the ratio between exchange surface area and volume of the membrane, tubular monolithic elements of various sizes and shape have been developed; in the case of tubular systems this ratio is about 30 to 250 m^2/m^3 , while for monolithic multi-channel systems can be up to 400 m^2/m^3 .

20 Similarly, plate or disk-shaped cartridge can be assembled in a stacked configuration (stack), achieving high packing density.

Potentially, ceramic membranes have the same filtering characteristics of polymeric membranes, but differ in a number of peculiarities that make them indispensable in the case of special applications. First, they have a greater mechanical strength, with the result
25 that they can also operate at pressures above 200 bar. In addition, the high surface hardness limits the phenomena of wear due to the use of fluids rich in abrasive dispersions. The metal oxides such as zirconia, alumina and silica have also high refractory properties (ability to work at very high temperatures) and a remarkable resistance to attacks of strong
30 acids and bases (operating environments with a pH between 0 and 14).

According to the prior art, ceramic membranes are realized through a process that involves a series of steps. The support is produced by the well-known technology of sintering, starting from a powder compact (green) which is obtained by molding or extrusion. The green, which has a
35 very plastic consistency, is sintered according to ramps of temperature and time that can provide a component structurally acceptable but with an adjoining open porosity as high as possible. The following step is the

deposition of the inter-layers and the top layer, which are typically applied with subsequent steps using sol-gel or dip-casting technologies.

5 Ceramic membranes of a known type, however, also have several disadvantages that are the direct result of the production technology. First, the lack of process automation, due to the presence of several steps rather critical and difficult to automate. In addition, ceramic membranes produced according to the prior art are very expensive, primarily due to the fact that this type of process has rather long production time and investments related to economies of scale, so the profitability is reached only in case of high production, and secondly because of the number of rejects and non-compliant pieces due to the complexity of the chain process/product.

10 A further limit is the high fragility. In fact, any single ceramic cartridge produced is a mechanical element with a remarkable hardness but with a inherent fragility and very low resistance to dynamic loads, shock or vibration.

Still, the prior art is applicable to a small number of materials, usually traditional ceramic oxides, since the sintering process is based on the thermodynamics of the stable equilibria. By sintering, for example, it would be impossible to produce a composite article of γ alumina and barium titanate, since the sintering time and temperature would lead to the formation of unwanted sub-phases, according to those laws that are described by the quaternary state diagram O, Ti, Ba, Al.

20 Finally, a further limit of the solutions according to the prior art consists of the operative critical aspects. Ceramic cartridges obtained by sintering must work in critical mechanical conditions, that is placed with their walls in traction, because of the need to maximize the exchange surface. By contrast, the optimal mechanical configuration would be that according to which the cartridge that operates under compression conditions.

30 In light of the above, it is clear the need to have membranes with a greater resistance to fracture and that can be realized from materials chosen from a wide range, as well as procedures to get them allowing for high automation and low costs.

35 In this context, it is integrated the solution according to the present invention, which proposes the use of ceramic, metal or composite

coverings deposited on porous ceramic, metal or composite supports by means of thermal deposition and/or vapor deposition.

The aim of the present invention is therefore to create membranes that allow to overcome the limitations of the membranes according to the prior art and to obtain the technical results discussed above and a procedure to obtain them.

A further aim of the invention is that these membranes can be produced with reduced production time and costs substantially low, both in terms of production costs with respect to operating costs.

Not last purpose of the invention is to propose a procedure for the production of membranes that is repeatable, essentially simple, safe and reliable.

It is therefore a first specific object of the present invention a process of realizing a membrane that comprises the following steps:

- preparing a substrate by sintering of metal powders, ceramics or their composites, with dimensions between 1 and 50 microns;
- covering said substrate by thermal deposition of a layer of the same or different ceramic material, metal or alloys and composites;
- cooling said layer during and/or after its thermal deposition;
- and possibly
- a further step of covering said layer realized by thermal deposition through physical vapor deposition (PVD) or chemical vapor deposition (CVD) of a layer of a same or different material.

Further, it is a second specific object of the present invention a membrane made of a substrate of sintered material coated with a layer of material obtained by thermal deposition, the microstructure of which is lamellar with interconnected nanometer-sized fractures, and optionally of a further layer of material, covering said layer obtained for thermal deposition, obtained by physical vapor deposition (PVD) or chemical vapor deposition (CVD), the microstructure of said additional layer comprising columnar monocrystals with strong packing.

It is a third specific object of the present invention a cartridge for filtration with a membrane as defined above that has cylindrical or hexagonal prism shape, with a minimum diameter of 6 mm and length between 300 and 1000 mm. By virtue of the process by which it is realized, the membrane can adapt to any shape of substrate.

The advantages of the membranes of the present invention and the process for obtaining them, compared to the prior art solutions are varied and are presented below.

5 First, the high automation. It is well known that the cycles of production of ceramic components by sintering are discontinuous and rather long, with temperature ramps of tens of hours that involve the use of machines and ovens of considerable size and power. Differently, the use of thermal deposition and vapor phase deposition drastically reduces the energy, time and plant usage. A single cartridge, in fact, can be covered in
10 less than 2 minutes and the production process can be fully automated.

Another advantage of the solution according to the present invention is to reduce costs. The energy required to produce a single cartridge with thermal deposition is in fact significantly less than that required for the same cartridge using sintering technology. In addition, the
15 drastic reduction of production times, the high automation, the reduction of fixed costs due to smaller plants and fewer waste and non-compliant pieces due to the critical aspects of the process/product chain remarkably reduce the cost of individual component increasing the standard of quality and production rate.

20 The membranes of the invention also have a higher fracture resistance compared to those according to the prior art. The ceramic cartridges currently produced are elements with a high mechanical hardness but with an intrinsic fragility and very low resistance to dynamic loads, shock or vibration. According to the present invention it is possible
25 to produce membranes and ceramic membranes in particular, with a lifetime definitely superior to any polymer membrane and ceramic units currently marketed. It must be considered, in fact, that ceramic membranes at present commercially available are bulk ceramic components with very high probability of failure in production and service
30 (if only for the cyclic stress of back-flush that are submitted). A small chip of the module leads inexorably to his replacement. Membranes designed in the form of coverings rather have as a minimum unit of construction the cartridge; multiple cartridges lead to the construction of the module. The breakage of a cartridge leads to the replacement of the single cartridge
35 and not the whole module (modular cartridge system). In addition, while the classical ceramic membranes are entirely made up of extremely fragile ceramic elements, cartridges produced by thermal deposition have an

internal metal structure (extremely resistant) on which a membrane is deposited artificially cracked and with a finely distributed interconnected porosity. Such a microstructure, unloading any opening tension of possible unstable cracks, strongly limits the mean walk by increasing the average K_{IC} of the device. The component then has a significantly higher resistance to fracture and mechanical reliability.

In addition, the process according to the present invention leads to the formation of coatings that typically have compressive residual stress, which further increases the resistance to fracture of the component.

The solution according to the present invention allows the use of membranes with a wide range of ceramic materials, metal alloys and their composites. The classical forming processes are based on the thermodynamics of stable equilibria according to which the materials that can be processed are usually traditional ceramic oxides, while the thermal deposition (cooling rate of the order of a million kelvin per second) allows to obtain a range of crystal structures, nanocrystals, amorphous structures and dispersions and alloys that are incompatible with the normal laws of thermodynamics. The same can be extended to the contrast between sol-gel coating process and vapor phase deposition.

A further advantage relates to the critical operational conditions. All the ceramic cartridges produced by sintering work with the external walls working in traction. This operative choice is dictated by the need to maximize the exchange surface. The cartridges produced according to the present invention rather work with the outer surface under conditions of strong turbulence and especially under compression, resulting in increased operating pressures and operating life.

The process of realization of membranes of the present invention makes it possible to create membranes with a composite structure obtained by the superimposition of several layers. It must be considered for example the deposition of a layer of 600 μm zirconia on which a layer of 200 nm of gold is deposited by PVD for the separation of gaseous mixtures at high temperature.

According to the present invention is then possible to obtain membranes with any shape (the shape is given by the substrate). In a particularly preferred embodiment of the invention, the single cartridge is made of a hexagonal prism-shape, as the hexagonal structure with

honeycomb order maximizes the surface/volume ratio maximizing the exchange and flow of permeate.

Still, the fact that it is possible to use an unlimited amount of materials (including semiconductors and variously doped composites) allows to create catalytic membranes or membranes with reactive surfaces. As an example, it is possible to imagine the construction of a module of micro/ultrafiltration of oxidized wastewater in which, during filtration, it is also possible to explicate the disinfection step, thus making the use of specific lines of disinfection by NaOCl, UV or ozone unnecessary.

Finally, the possibility to choose the materials the modules, cartridges and membranes are made of allows to operate at very high temperatures (even 1000 °C), with pH ranges between 0 and 14, pressures above 200 bar, and with high flow rate with liquid in which abrasive particles are present (high resistance to erosion).

The invention will be described below for illustrative, not limitative purposes, with particular reference to some illustrative examples and to the enclosed figures, in which:

- Figure 1 shows a perspective view of the substrate of a filter cartridge according to the present invention,

- Figure 2 shows the filter cartridge of Figure 1, covered with a layer of material deposited by thermal deposition,

- Figure 3 shows the filter cartridge of Figure 2, covered with a layer of material deposited by vapor deposition,

- Figure 4 shows a plurality of filtration cartridges with hexagonal cross section packed according to a honeycomb configuration,

- Figure 5 shows a SEM micrograph of a membrane $\text{Al}_2\text{O}_3 + \text{TiO}_2$ 30% by weight, prepared according to example 1, obtained using APS (Air Plasma Spray) technology, magnification 650x BSE (Back Scattering Electron),

- Figure 6 shows a SEM micrograph of a membrane $\text{Al}_2\text{O}_3 + \text{TiO}_2$ 30% by weight, prepared according to example 1, obtained using APS technology, magnification 5000x BSE,

- Figure 7 shows the trend of the permeability (expressed in L/hm^2) of a membrane $\text{Al}_2\text{O}_3 + \text{TiO}_2$ 30% by weight, prepared according to example 1, and two additional membranes, respectively, a membrane

based on Al_2O_3 and a membrane made of $\text{ZrO}_2 + \text{Y}_2\text{O}_3$, varying the pressure (in bar),

5 - Figure 8 shows a SEM micrograph of a membrane $\text{Cr}_2\text{O}_3 + \text{Al}$ 20% by weight + $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ 20% by weight, prepared according to example 2, magnification 2000x BSE,

 - Figure 9 shows a SEM micrograph of a membrane $\text{Cr}_2\text{O}_3 + \text{Al}$ to 20% by weight + $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ 20% by weight, prepared according to example 2, magnification 6500x BSE,

10 - Figure 10 shows a SEM micrograph of a TiO_2 membrane deposited in Ar atmosphere (1200 mbar), prepared according to example 3, magnification 2500x BSE,

 - Figure 11 shows a SEM micrograph of a TiO_2 membrane deposited in Ar atmosphere (1200 mbar), prepared according to example 3, magnification 6500x BSE,

15 - Figure 12 shows a SEM micrograph of a membrane WC-Co 17% by weight, prepared according to example 4, obtained using APS technology, magnification 1850x BSE,

 - Figure 13 shows a SEM micrograph of a membrane WC-Co 17% by weight, prepared according to example 4, obtained using APS technology, magnification 7500x BSE,

20 - Figure 14 shows a SEM micrograph of a membrane $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ 9% + SrTiO_3 20% by weight, prepared according to example 5, obtained using APS technology, magnification 2500x BSE,

 - Figure 15 shows a SEM micrograph of a membrane $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ 9% + SrTiO_3 20% by weight, prepared according to example 5, obtained using APS technology, magnification 8000x BSE,

25 - Figure 16 shows a SEM micrograph of sintered SiAlON, magnification 20000X SE,

 - Figure 17 shows a SEM micrograph of $\text{Cr}_2\text{O}_3 + \text{BaTiO}_3$ 60% by weight, magnification 2500x BSE,

30 - Figure 18 shows a micrograph of a Solgel silica film produced on a alumina interlayer,

 - Figure 19 shows a coating of YSZ grown on a substrate of CeO_2 by PVD,

35 - Figure 20 shows a SEM micrograph of a membrane $\text{Cr}_2\text{O}_3 + \text{ITO}$ 5% by weight, prepared using APS technology, magnification 2500x BSE,

- Figure 21 shows a SEM micrograph of a membrane Cr_2O_3 + ITO 5% by weight, prepared using APS technology, magnification 15000x BSE, and

5 - Figure 22 shows a SEM micrograph of a membrane Al_2O_3 + Cr_2O_3 13% by weight, obtained using APS technology, magnification 3500x BSE.

10 According to the present invention it is proposed the realization of ceramic membranes and of filtration and separation cartridges based on ceramic membranes made of composite structures using composite materials.

The mechanical substrate (support) consists of a sintered coarse-grained (1 to 50 μm particles, the optimal value being 10 μm) material of metal powders (such as steel, brass, and alloys based on nickel, cobalt, aluminum, or magnesium), ceramic powders (low melting
15 glass, aluminosilicates, carbides, nitrides) or their composites. From a technical/commercial point of view, the simplest case is the use of pressed powders of AISI 420 or brass, as they are readily available on the market at low costs.

20 The substrate can be any shape (discs, plates, tubes), although, to maximize the exchange surface, cylindrical geometries or hexagonal tubes are preferred, as shown with reference to Figure 1. In addition, the substrate can be any size compatible with the mechanical stress to which it must be submitted. It can typically have a minimum diameter of 6 mm with lengths ranging from 300 to 1000 mm.

25 After the sintering of the substrate, its surface is modified by sandblasting of silicon carbide powder with a particle size bimodal (100 and 2000 μm) to increase the mechanical bond between the coating and substrate and clean the surface from fats, oils and impurities. Particle size, porosity, roughness parameters and surface preparation of the substrate
30 are essential factors for the realization of a ceramic membrane with controlled permeability and selectivity. After the substrate is properly prepared the deposition of a ceramic coating on the substrate is performed. This coating is made by means of one of a variety of thermal deposition techniques and their properly applied variants, using ceramic,
35 metal materials or their alloys and composites. These technologies produce thick films, i.e. coverings with thicknesses that can range from 50 microns up to several centimeters.

The coating technologies by thermal deposition allow obtaining specific surface properties (in particular resistance to wear, corrosion and thermal stress, electrical and magnetic conductivity, optical properties) without altering the characteristics of the substrate (toughness and structural characteristics). The covering must have a good chemical compatibility with the support and high adhesion properties.

Thermal deposition processes consist in the realization of a coating from metallic powders, ceramic or cermet (ceramic phase dispersion in metal matrixes). The material to be deposited is melted inside an energy source and accelerated toward the substrate where it solidifies quickly, resulting in superimposed lamellar structures. When the molten particle reaches the surface to be coated it has a high kinetic energy and, at the time of impact, it flattens forming a blade called splat. The structure of the coating is then given by the superimposition of solidified plates and anchored to each other; as well as overlapping plates, pores, non melted particles and oxide inclusions, typical defects of such coatings, are present. The oxide inclusions are derived both from the interaction between the particles and the environment in which the spraying takes place, and from the heating of the surface of the coating being formed. Upon impact, the oxide film covering the particle breaks down and becomes trapped between the slats. In general, the coatings deposited with the parameters and the standard techniques do not present interconnected open porosity and can not be used as membranes.

To promote and develop a network of interconnecting cracks nano it is necessary to promote a cooling rate such as to induce violent thermal shocks during the phase of solidification of the splat. Such shocks produce, depending on the rate of cooling, a series of interconnected nanometer-sized cracks (nanocracks).

The promotion of this phenomenon depends on the deposition parameters used and some variants of the process, including the following:

- Distance of deposition: compared to the standard must be increased (for plasma deposition: from a standard distance of 80 to 110 mm up to a distance according to the present invention of 130 to 160 mm. For HVOF: from standard 340 to 420 mm up to a distance of 460 to 520

mm.). In this way, the deposition efficiency decreases but the particles reach the substrate having lost some of their latent heat of solidification;

- Scan Speed: To minimize the amount of thermal energy transferred from the material in the air and the torch to a point of the substrate scanning speed must be increased significantly. Typical linear velocities of these processes are about 50-200 mm/s while in the present case, to limit the point heat input scanning speed equal to or greater than 1000 mm/s are used;

- Mobile cooling nozzles: cooling nozzles are keyed on the torch that move in synchronism with the scanning of the torch. These nozzles blowing argon or nitrogen gas at high pressure (over 20 bar) to cool instantly each pass of deposition. If particularly violent cooling is needed it is possible to spray on the newly formed coating liquid argon or nitrogen;

- Fixed cooling nozzles: the substrate is a hollow profile with cylindrical geometry with circular or prismatic cross section. A further contribution to the instant cooling of the coating is given by fixed nozzles that blow argon and nitrogen gas on the substrate during its rotation during deposition. A further injection of cooling gas is applied directly on the head hole of the substrate. This provides an additional source of cooling of the article during its production. Again the process can be to the extreme by using argon and nitrogen in liquid rather than gaseous form.

The instant and continuous cooling throughout the coating process step does not provide a percentage increase of porosity of the coating, but increases the formation of interconnected cracks of nanosized dimension and purely thermal origin.

It was noted that, while the coatings produced according to the prior art, i.e. without using the parameters described above (porosity and surface characteristics of the substrate and deposition and cooling parameters) have little or no permeability $\text{cL/m}^2 \cdot \text{h} \cdot \text{bar}$ (cL), by contrast, the proposed procedure according to the present invention leads to membranes with permeability higher than $300 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$ (cl), almost comparable to the commercial polymer membranes for ultrafiltration.

II The coating formed on the substrate can have a thickness ranging from $50\mu\text{m}$ to several millimeters, and, for reasons of economic losses, preferably between 100 and $400 \mu\text{m}$.

The coating process of a single support is totally automated and takes no more than a few minutes. The coating thus obtained generally has a porosity dependent on the materials deposited and the process parameters used and the characteristics of the substrate, the average size of pores ranging from 50 to 300 nm.

The cartridge thus produced (Figure 2) can be directly used in all the industrial processes of micro/ultrafiltration.

In case it is necessary to push the levels of porosity to a few tens of nanometers and up to a few Angstroms (nanofiltration, reverse osmosis, separation of gaseous phases), the coating is used as thermo deposited inter-layer for a subsequent thin coating (only a few microns to tens of nanometers thick) produced by physical deposition (PVD) or chemical (CVD) vapor (Figure 3).

The top layer produced by vapor deposition have remarkable mechanical strength and adhesion. They can also be lithographed in order to increase their surface physical properties and superhydrophobicity and ebullioscopicity (significant increase of activation sites for the production phase vapor/gas to liquid phases).

The cartridges thus produced in order to be used must be housed inside a metal or polymer housing, forming a filtration module. The configuration that best maximizes the value of exchange surface is a beam of cartridges (similar to the heat exchanger tube bundles) arranged in a honeycomb.. With an average width of the cartridge of the order of 7 mm and a distance between cartridge of 0.2 mm it is possible to achieve a packing more than $500 \text{ m}^2 / \text{m}^3$.

Figure 4 shows that 191 cartridges with hexagonal cross section can be packed in a honeycomb configuration within a cylindrical module of 50 mm radius. Ducts on the surface of the cylindrical form are the inlet (at high pressure) of the fluid to be filtered and the outlet of the concentrate. The permeate passes through the membrane, through the cartridge and is collected and extracted from the bottom and head of the module.

As previously noted, the coatings of the cartridges work under compression and not under tension as the classic elements.

Here are five examples that describe the construction of cartridges using materials and technologies according to different embodiments of the present invention.

Example 1. Production of a microfiltration cartridge by thermal deposition of $\text{Al}_2\text{O}_3 + \text{TiO}_{2-x}$ 30% by weight with plasma spray technology

The alumina-based composite coating was deposited using plasma spray technology in configuration APS (Air Plasma Spray). The deposition substrate was a sintered AISI 316 with particle size of 10 μm . The substrate has a hexagonal cross section with dimensions of the side of the hexagon of 5 mm and a length of 300 mm.

The deposition parameters used are summarized in Table 1.

Table 1

Ar flow rate (SLPM)	H ₂ flow rate (SLPM)	Plasma current (A)	Plasma Voltage (V)	Deposition distance (mm)	Yield ($\mu\text{m}/\text{pass.}$) ($\mu\text{m} / \text{pass.}$)
50	14.9	580	72	130	2.5

(SLPM = standard liters per minute)

The torch used is a Sulzer Metco-model F4MB with anode diameter of 6 mm.

The powders used (Al_2O_3 and TiO_{2-x} 30% by weight) were mixed by mechanical stirring for 1 hour and kept in an oven at 115 ° C for 24 hours before the deposition.

The gas used for the transport of dust supply to the head of the torch is As with a flow rate of 3.5 SLPM.

The torch is run through a 5-axis anthropomorphic manipulator, while the substrate is mounted vertically on a turntable with a tangential speed of deposition of 1200 mm/sec.

Two nozzles are mounted on the torch blowing argon gas to 20 bar immediately before (to cool the substrate) and immediately after (to cool the coating just deposited) spraying. Four fixed nozzles blow argon over the entire length of the article and throughout the deposition. A further contribution to cooling is given by a nozzle mounted on the cartridge head blowing argon gas at high pressure inside and along the section of the cartridge. Alternatively, cooling can be produced with gaseous nitrogen or argon and nitrogen in liquid form.

The micrographs shown in Figures 5 and 6 show, with different levels of magnification, a section of the membrane where the different phases are clearly highlighted in the form of strips of different colors. The open porosity, which can give the characteristics of ultrafiltration, is due to

the multitude of nanocracks that are generated between the blades due to the fast cooling and subsequent solidification.

The percentage of porosity and interconnecting nano cracks and their size distribution was derived empirically using two types of tests:
5 a test of permeability of water thermostatically controlled at 20°C and a filtration test with oil and nano sized graphite.

Permeability test with a thermostatically controlled water at 20 °C. The membranes were deposited on a porous bronze substrate with a thickness of 5 mm and diameter 50 mm. The sample was then placed
10 inside a purpose-built filtration module which has been subjected to a cross flow at various pressures with a thermostatically controlled water at 20 °C. In this way, it was possible to easily determine the value of specific permeability of the membrane ($\text{L/m}^2 \cdot \text{h} \cdot \text{bar}$). Figure 7 shows the trend of the permeability (expressed in L/hm^2) of the membrane, varying the
15 pressure (in bar). Figure 7 also shows the evolution of permeability for various membranes, i.e. a membrane based of Al_2O_3 and a membrane made of $\text{ZrO}_2 + \text{Y}_2\text{O}_3$.

These tests have allowed to calculate a permeability of $5.5 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$.

20 Test with oil and graphite nano-filtration. The membranes with promising value of permeability (20 to $300 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$) were subjected, using the same set-up test, to a test of purification of water contaminated by engine oil and graphite. The test allows to assess the maximum size of nano-cracks and the ability of membranes to separate organic liquids such
25 as oils and oils from water.

Example 2. Production of an ultrafiltration cartridge with catalytic properties by thermal deposition of $\text{Cr}_2\text{O}_3 + \text{Al}$ 20% weight $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ 20% by weight with plasma spray technology

The chromium-based composite coating was deposited using
30 plasma spray technology in configuration APS (Air Plasma Spray). The deposition substrate is a sintered AISI 316 with particle size of 10 microns. The substrate has a hexagonal cross section with a size of 5 mm hex side and a length of 300 mm.

The deposition parameters used are summarized in Table 2.

Table 2

Ar flow rate (SLPM)	H ₂ flow rate (SLPM)	Plasma current (A)	Plasma Voltage (V)	Deposition distance (mm)	Yield (μm/pass)
45	14	580	71	130	8.6

(SLPM = standard liters per minute)

The torch used is a Sulzer Metco-model F4MB anode diameter of 6 mm.

5 The powders used (Cr_2O_3 + Al 20% by weight + $\text{La}_{0.5}\text{Sr}_{0.5}\text{MnO}_3$ 20% by weight) were mixed by mechanical stirring for 1 hour and kept in an oven at 115 ° C for 24 hours before the deposition.

The gas used for the transport of dust supply to the head of the torch is Ar with a flow rate of 3.5 SLPM.

10 The torch is run through a 5-axis anthropomorphic manipulator, while the substrate is mounted vertically on a turntable with a tangential speed of deposition equal to 1200 mm / sec.

Two copper nozzles are mounted on the torch blowing argon gas at 20 bar immediately before (to cool the substrate) and immediately after (to cool the coating just deposited) spraying. Four fixed nozzles blowing argon over the entire length of the article and throughout the deposition. A further contribution to cooling is given by a nozzle mounted on the cartridge head blowing argon gas high pressure inside and along the section of the cartridge. Alternatively, cooling can be obtained with
20 gaseous nitrogen or argon and nitrogen in liquid form.

The micrographs shown in Figures 8 and 9 show, with different levels of magnification, a section of the membrane in which the different phases are clearly highlighted in the form of strips of different colors. The open porosity, which can give the characteristics of ultrafiltration is due to
25 the multitude of nanocracks that are generated between the blades due to the fast cooling and subsequent solidification.

The permeability measured using the methodology previously exposed is equal to 25.0 L/m² * h bar).

30 The substoichiometric array of colors and dispersion semiconductor LSM give the cartridge catalytic characteristics.

Example 3. Production of a self-disinfectant ultrafiltration cartridge for MBR water treatment systems using thermal deposition of

TiO₂ by plasma spray technology in a controlled atmosphere of Ar at 1200 mbar pressure in the deposition chamber

The titania coating of TiO_{2-x} was deposited using plasma spray technology in configuration APS (Air Plasma Spray). The deposition substrate is a sintered AISI 316 with particle size of 10 µm. The substrate has a hexagonal section of the side of the hexagon with a size of 5 mm and a length of 300 mm.

The deposition parameters used are summarized in Table 3.

Table 3

Ar flow rate (SLPM)	H ₂ flow rate (SLPM)	Plasma current (A)	Plasma Voltage (V)	Deposition distance (mm)	Yield (µm/pass.)
52	15	600	67	130	10.8

(SLPM = standard liters per minute)

The torch used is a Sulzer Metco-model F4MB anode diameter of 6 mm.

The powders used were kept in an oven at 115 ° C for 24 hours before the deposition.

The gas used for the transport of dust supply to the head of the torch is As with a flow rate of 3.5 SLPM.

The torch is run through an anthropomorphic 5-axis manipulator while the substrate is mounted vertically on a turntable with a tangential speed of deposition of 1200 mm / sec.

Two copper nozzles are mounted on the torch blowing argon gas at 20 bar immediately before (to cool the substrate) and immediately after (to cool the coating just deposited) spraying. Four fixed nozzles blow argon over the entire length of the article and throughout the deposition. A further contribution to cooling is given by a nozzle mounted on the cartridge head blowing argon gas at high pressure inside and along the section of the cartridge. Alternatively, cooling can be produced with gaseous nitrogen or argon and nitrogen in liquid form.

The micrographs shown in Figures 10 and 11 show, with different levels of magnification, a section of the membrane where it is easy to identify the intricate and well-distributed network of interconnected micropores able to confer the characteristics of ultrafiltration to the material. The network is generated by the multitude of nanocracks that are

generated between the blades because of fast cooling and subsequent solidification.

The permeability measured using the methodology previously exposed is equal to $46.5 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$.

5 The oxidizing power of the composite material that makes up the membrane gives the characteristics of self disinfection. In fact, the substoichiometric titania TiO_{2-x} is a semiconductor with high resistivity able to give up electrons. Obviously, in order to work properly, all should be closed on a circuit powered by DC voltage.

10 Example 4. Production of a microfiltration cartridge by thermal deposition of WC-Co 17% by weight with high velocity oxy-fuel technology (HVOF)

15 The cobalt matrix composite coating was deposited using HVOF technology. The deposition substrate is a sintered AISI 316 with particle size of $10 \mu\text{m}$. The substrate has a hexagonal section with a size of 5 mm hex side and a length of 300 mm.

The deposition parameters used are shown in Table 4.

Table 4

O ₂ Flow (SCFH)	Kerosene Flow (GPH)	O ₂ Pressure (psi)	Kerosene Pressure (psi)	Deposition distance (mm)	Yield ($\mu\text{m/pass.}$)
2000	6	129	123	380	12,3

(SCFH = standard cubic feet per hour; GPH = gallons per hour)

20 The torch used is a Tafa JP-5000 model with 8-inch barrel.

The powders used (WC-Co 17% by weight) were kept in an oven at 115°C for 24 hours before the deposition.

The gas used for the transport of dust supply to the head of the torch is Ar with rotation speed of the dosing cochlea of 330 rpm.

25 The torch is run through a 5-axis anthropomorphic manipulator, while the substrate is mounted vertically on a turntable with a tangential speed of deposition equal to 1200 mm / sec .

30 Two copper nozzles are mounted on the torch blowing argon gas at 20 bar immediately before (to cool the substrate) and immediately after (to cool the coating just deposited) spraying. Four fixed nozzles blow argon over the entire length of the article and throughout the deposition. A further contribution to cooling is given by a nozzle mounted on the cartridge head blowing argon gas at high pressure inside and along the

section of the cartridge. Alternatively, cooling can be produced with gaseous nitrogen or argon and nitrogen in liquid form.

The micrographs shown in Figures 12 and 13 show, with different levels of magnification, a section of the cermet membrane, where different phases are clearly highlighted. The blades, in this particular case, consist of a matrix of cobalt enriched in different points of tungsten and carbon (different shades of gray) while the tungsten carbide is easily identifiable in the bright reinforcement evenly dispersed. The open porosity, giving the characteristics of ultrafiltration, is due to the multitude of nanocracks that are generated between the blades because of the fast cooling and subsequent solidification.

The permeability measured using the methodology previously exposed is equal to $0.7 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$.

Example 5. Production of a cartridge microfiltration using thermal deposition of $\text{ZrO}_2 + \text{Y}_2\text{O}_3$ 9% + SrTiO_3 20% by weight with plasma spray technology

An alumina based composite coating was deposited using plasma spray technology in configuration APS (Air Plasma spray). The deposition substrate is a sintered AISI 316 with particle size of $10 \mu\text{m}$. The substrate has a hexagonal section with the side of the hexagon having a size of 5 mm and a length of 300 mm and was pre-sanded with silicon carbide powders of bimodal particle size (100 and 2000 m).

The deposition parameters used are summarized in Table 5.

Table 5

Ar flow rate (SLPM)	H ₂ flow rate (SLPM)	Plasma current (A)	Plasma Voltage (V)	Deposition distance (mm)	Yield ($\mu\text{m/pass.}$)
45	13	520	69	130	1.5

(SLPM = standard liters per minute)

The torch used is a Sulzer Metco-model F4MB with anode diameter of 6 mm.

The powders used ($\text{ZrO}_2 + \text{Y}_2\text{O}_3$ 9% + SrTiO_3 20% by weight) were mixed by mechanical stirring for 1 hour and kept in an oven at 115°C for 24 hours before the deposition.

Il gas impiegato per il trasporto delle polveri dall'alimentatore alla testa della torcia è Ar con una portata di 3,5 SLPM. The gas used for

the transport of dust supply to the head of the torch is Ar with a flow rate of 3.5 SLPM.

5 The torch is run by a 5-axis anthropomorphic manipulator, while the substrate is mounted vertically on a turntable with a tangential speed of deposition equal to 1200 mm/sec.

Two copper nozzles are mounted on the torch spraying liquid argon immediately before (to cool the substrate) and immediately after (to cool the coating just deposited) deposition. Four fixed nozzles blow argon gas over the entire length of the article and throughout the deposition. A
10 further contribution to cooling is given by a nozzle mounted on the cartridge head that pumps liquid argon within and along the section of the cartridge.

The micrographs shown in Figures 14 and 15 show, with different levels of magnification, a section of the membrane where the
15 different phases are clearly highlighted in the form of blades of different colors. The open porosity, giving the characteristics of ultrafiltration, is due to the multitude of nanocracks that are generated between the blades due to the fast cooling and subsequent solidification.

The permeability measured using the methodology previously
20 exposed is equal to $190 \text{ L/m}^2 \cdot \text{h} \cdot \text{bar}$.

The data given here will allow to highlight a series of structural and microstructural differences between the membranes according to the present invention and those according to the prior art; differences are substantial, easily identifiable by laboratory investigations and directly
25 related to process technology.

In particular, according to the present invention, for the operation of microfiltration, ultrafiltration and nanofiltration membranes are proposed that, compared to the sintered ones commonly used for such purposes, are covered with a layer of material obtained by thermal
30 deposition with deposition parameters and cooling rates optimized for the purpose of the invention.

The different microstructure is detectable by a simple observation with an optic or electronic microscopy. With reference to Figures 16 and 17, in the case of a sintered ceramic (Figure 16) it is
35 possible to easily identify the starting particles and how, after a more or less prolonged residence at high temperature, as a result of diffusion phenomena the particles are fused together to form a porous structure.

The size of the open porosity is directly dependent on the particle size of departure, and on the combination time/temperature of the process. The process follows the laws of thermodynamics equilibria and the phases that can be obtained are limited and easily identified by consulting the reference phase diagram.

On the contrary, with reference to Figure 17, the technology of thermal deposition provides for a rapid heating with deposition and subsequent instantaneous cooling (million Kelvin per second) of the particles that form the coating. The whole process is governed by kinetics, so it is possible to get an infinite series of phases and composites that are not compatible with the normal laws of thermodynamics. The microstructure of any coating deposited by thermal deposition (Figure 17) is of the lamellar type and is directly dependent on process parameters used. The fact that such coatings show a connecting open porosity due to nano cracks can not be achieved according to the process of the prior art and, as far as it is known, can be obtained according to the process of the present invention by virtue of the inter-relationships that are promoted among the interlamellar crevices, defects such as inclusions and porosity produced during deposition and violent thermal shock during the solidification and cooling step. In the particular case illustrated in Figure 17 of a coating of $\text{Cr}_2\text{O}_3 + \text{BaTiO}_3$ 60% by weight, the very fact that such a coating exist is an evidence that it was deposited by thermal deposition, because no other process is able to create microstructures of such a genre with two phases like cromia and barium titanate packed in insulated slats. In the case of a sintering process, in fact, the result would be a mixture of compounds described with the quaternary diagram Cr, Ba, Ti and O.

The two technologies will lead to the formation of two products totally different and in no way interchangeable.

Similar considerations can be made for the top layer produced by vapor phase deposition, in accordance with the present invention, or by Solgel deposition, according to the prior art. Again, the two different top layers can be easily distinguished by a simple microscopic investigation.

In fact, in this case also, the vapor phase deposition allows for obtaining multiplayer alloys and composites not otherwise possible to obtain with the technologies of the prior art, involving high temperature processes and therefore dependent on the conditions of thermodynamic

equilibrium. It follows that the microstructure is considerably different. The sol-gel and dip-coating processes lead, after heat treatment, the formation of a compact, dense layer with a porosity that can be compared to the size of the interstices left by the nano particles forming the layer (Figure 18, taken by Ceramic Membranes for Separation and Reaction - Kang Li, John Wiley & Sons Ltd (2007) ISBN 978-0-470-01440-0 Great Britain). For densifications close to the theoretical one, the porosity coincides with the same lattice distances.

The vapor phase growth on the other hand, leads to the formation of columnar crystals with strong packing (Figure 19, taken from Handbook of Superconducting Materials: Superconductivity, Materials and Processes , David S. Ginley , ISBN 0750308982, 9780750308984). In this case, the porosity has a bimodal distribution, mainly due to the lattice distances within individual columns and intergranular defects that bind together the various columns.

Finally, for comprehensive purposes, figures 20-22 show micrographs of additional membranes obtained through the process of the present invention and show the nano cracks produced during the deposition conditions of forced cooling.

The present invention has been described for illustrative, not limitative purposes, according to its preferred embodiments, but it is to be understood that variations and/or modifications may be made by the experts in the field without escaping the relative protection scope, as defined by the enclosed claims.

CLAIMS

1) Process of realization of a membrane that includes the following steps:

- preparing of a substrate by sintering of metal powders, ceramics or their composites, with dimensions between 1 and 50 microns;
- covering said substrate by thermal deposition of a layer of the same or different ceramic material, metal or alloys and composites;
- cooling said layer during and/or after its thermal deposition.

2) Process of realization of a membrane according to claim 1, characterized in that it comprises a further step of covering said layer realized by thermal deposition through physical vapor deposition (PVD) or chemical vapor deposition (CVD) of a layer of a same or different material.

3) Process of realization of a membrane according to claim 1 or 2, characterized by the fact that said powders have a size of 10 μm .

4) Process of realization of a membrane according to any of the preceding claims, characterized by the fact that, following said step of preparation of the substrate and before said step of covering the substrate it is provided the following step:

- blasting the substrate.

5) Process of realization of a membrane according to claim 4, characterized in that said step of sanding is made with dusts of silicon carbide-grained bimodal.

6) Process of realization of a membrane according to any of the preceding claims, characterized in that said cooling of the layer obtained by thermal deposition is achieved by setting the deposition distances between 130 and 160 mm for the plasma thermal deposition and between 460 and 520 mm for the HVOF thermal deposition.

7) Process of realization of a membrane according to any of the preceding claims, characterized in that said cooling of the layer obtained by thermal deposition is achieved by setting the scanning speed of the thermal deposition torch equal to or greater than 1000 mm/s.

8) Process of realization of a membrane according to any of the preceding claims, characterized in that said cooling of the layer obtained by thermal deposition is made by using jets of inert gases at low temperature and high pressure, or by spraying liquefied inert gas.

9) Membrane characterized by being composed of a substrate of sintered material, with particle size between 1 and 50 μm , coated with a

layer of material obtained by thermal deposition and cooling, the microstructure of which is of the lamellar type with interconnected cracks of nanometric size.

5 10) Membrane according to claim 9, characterized in that the particle size of sintered material is 10 μm .

10 11) Membrane according to claim 9 or 10, characterized in that it comprises an additional layer of material, covering said layer obtained for thermal deposition, obtained by physical vapor deposition (PVD) or chemical vapor deposition (CVD), the microstructure of said additional layer comprising columnar crystals with strong packing.

12) Membrane according to claim 11, characterized in that said layer obtained by physical vapor deposition (PVD) or chemical vapor deposition (CVD) has a thickness between 10 and 1000 nm.

15 13) Membrane according to any of claims 9 to 12, characterized in that said layer obtained by thermal deposition has a thickness comprised between 50 and 600 μm .

14) Membrane according to claim 13, characterized in that said layer obtained by thermal deposition has a thickness comprised between 100 and 400 μm .

20 15) Membrane according to any of claims 9 to 14, characterized in that said layer obtained by thermal deposition has average size of pores and of the nanocracks ranging from 10 to 1000 nm.

25 16) Membrane according to claim 15, characterized in that said layer obtained by thermal deposition has average size of pores and nanocracks ranging from 50 to 300 nm.

17) Filtration cartridge with a membrane as defined in claims 9 to 16, characterized by having cylindrical shape or prismatic shape with hexagonal cross section.

30 18) Filtration cartridge according to claim 17, characterized by having a minimum diameter of 6 mm and length between 300 and 1000 mm.

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2011/000262

A. CLASSIFICATION OF SUBJECT MATTER INV. B01D71/02 B01D69/12 B01D67/00 B01D61/14 ADD.		
According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) B01D C04B		
Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched		
Electronic data base consulted during the international search (name of data base and, where practical, search terms used) EPO-Internal, WPI Data		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X Y Y	US 6 309 546 B1 (HERRMANN ROBERT C [US] ET AL) 30 October 2001 (2001-10-30) column 4; claim 1; figures 1, 4 column 6, line 63 - line 9 the whole document ----- US 2009/241496 A1 (PINTAULT BRUNO [FR] ET AL) 1 October 2009 (2009-10-01) paragraphs [0013], [0021], [0049] - [0053], [0120] - [0121], [0132], [0188] - [0189], [0192], [0228]; claims 38,59-60, 67-69 the whole document ----- -/-	1-3,9, 10,15-18 4-8, 11-14 1-18
☒ Further documents are listed in the continuation of Box C. ☒ See patent family annex.		
* Special categories of cited documents : "A" document defining the general state of the art which is not considered to be of particular relevance "E" earlier document but published on or after the international filing date "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) "O" document referring to an oral disclosure, use, exhibition or other means "P" document published prior to the international filing date but later than the priority date claimed "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 "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone "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. "&" document member of the same patent family		
Date of the actual completion of the international search 4 November 2011		Date of mailing of the international search report 21/11/2011
Name and mailing address of the ISA/ European Patent Office, P.B. 5818 Patentlaan 2 NL - 2280 HV Rijswijk Tel. (+31-70) 340-2040, Fax: (+31-70) 340-3016		Authorized officer Veríssimo, Sónia

INTERNATIONAL SEARCH REPORT

International application No
PCT/IT2011/000262

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
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