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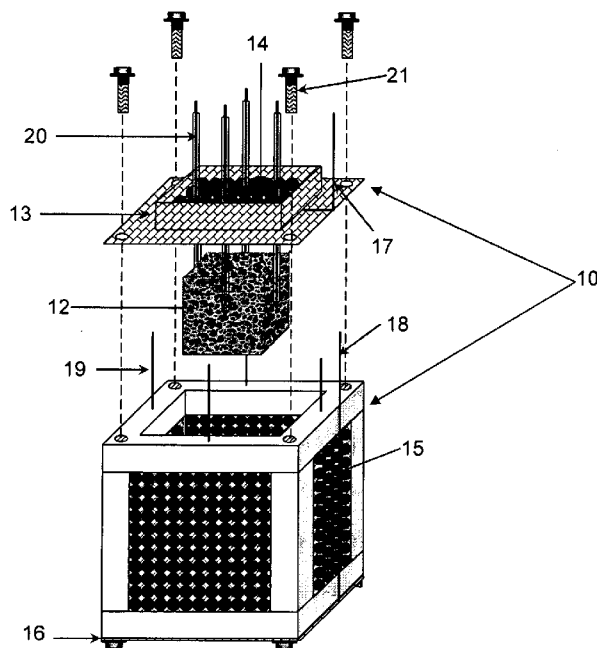
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(54) Title: METAL FOAMS

Fig. 1



(57) Abstract: There is described an open cell porous structure the cells of which are optionally filled with an elastomeric or thermosetting plastic comprising a nanocrystalline metallic or nanocrystalline metal matrix composite coating wherein the nanocrystals have a crystallite size of from about 5 nm to about 150 nm. A process for preparing the coated open cell porous structures is also disclosed.



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## METAL FOAMS

### FIELD OF THE INVENTION

5 The present invention relates to open cell porous structures comprising a nanocrystalline metallic or a nanocrystalline metal matrix composite coating and to a process for producing the structures.

### BACKGROUND OF THE INVENTION

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Metal foams are known materials and are e.g. described in EP 0 151 064 A1. They are open cell porous structures with an outer surface that conventionally consists of a more or less dense metallic coating deposited by electroplating. The coated metal foams disclosed in EP 0 558 142 A1 have particularly large surfaces with metal crystallites having a high aspect

15 ration and are obtained by adding a chemical compound having the properties of a second class brightener to an electrolytic nickel bath.

Metals foams have many desirable properties. They possess a large surface, are light-weighted and still have good mechanical properties. This makes them suitable for many

20 applications, among others in electrochemical applications, as construction materials and as a support for catalytic materials.

It has now been found that in particular the mechanical properties of conventional metal foams can be greatly improved by modifying the metallic coating thereof such that the

25 coating comprises nanocrystals.

### SUMMARY OF THE INVENTION

Thus, the present invention relates to an open cell porous structure the cells of which are

30 optionally filled with an elastomeric or thermosetting plastics, the open cell porous structure comprising a nanocrystalline metallic or nanocrystalline metal matrix composite coating wherein the nanocrystals have a crystallite size of from about 5 nm to about 150 nm.

The invention further relates to a process for the production of these open cell porous structures, comprising: coating the uncoated porous structure, if not made from an electrically conducting material; with an electrically conducting layer to form an electrically conducting intermediate open cell porous structure, and coating the electrically conducting uncoated or intermediate open cell porous structure with a metal, metal alloy or nanocrystalline metal matrix composite by electroplating using a pulsed or a direct current or, in the case of a metal matrix composite, a pulse reverse current electroplating process, the cathode being the electrically conducting uncoated or intermediate open cell porous structure and the anode or anodes which is/are positioned opposite to each outer surface of the cathode is/are (a) sacrificial anode(s) comprising an inert conducting material and a sacrificial metal or metal alloy to be coated onto the uncoated or intermediate open cell porous structure to form the open cell porous structure coated with a nanocrystalline metallic or nanocrystalline metal matrix composite coating; and optionally filling the pores of the open cell porous structure with an elastomeric or thermosetting plastics material.

## SHORT DESCRIPTION OF THE DRAWINGS

Fig. 1 is a schematic exploded view of a cathode (raw or intermediate metal foam) and an anode according to the invention.

Fig. 2 shows a schematic front sectional view of a cathode (raw or intermediate metal foam) and an anode according to the invention submersed in an outer electrolyte bath for coating the cathode with a metal matrix composite.

Fig. 3 shows the energy absorption capability of various foams according to the invention compared to non-coated foams.

## DESCRIPTION OF THE EMBODIMENTS

The open cell porous structure of the invention comprises a nanocrystalline metallic or nanocrystalline metal matrix composite coating wherein the nanocrystals have a crystallite size of from about 5 nm to about 150 nm. Such a structure will sometimes hereinafter be referred to as metal foam or metal foam of the invention.

The cells may optionally be filled with an elastomeric or thermosetting plastics.

In one embodiment the crystallite size of the nanocrystals is from about 10 nm to about 100 nm. The specific crystallite size depends on the intended application. If a foam having a high strength is desired, the crystallite size will be in the lower range, if the foam is intended to be more deformable and absorb energy, the crystallites will be larger so that the coating is ductile enough for the foam structure to deform and not to break because of brittleness. In the latter case, e.g. a crystallite size of 40 to 50 nm for a nickel coating is preferred.

The metal, metal alloy or nanocrystalline metal matrix composite forming the nanocrystalline coating of the open cell porous structures of the invention may be selected from any metal, metal alloy and metal matrix composite stable in aqueous surroundings, depending on the intended use of the inventive structures. As examples of metals useful in the present invention nickel, zinc, tin, chromium, iron, copper, titanium, silver, gold, platinum and the other elements of the platinum group, such as Ru, Os, Rh, Ir and Pd, are given. Metal alloys may e.g. be selected from brass, bronze, monel metal, iron-chromium alloys, and combinations thereof. For certain applications, nickel and nickel alloys are particularly preferred.

The metal matrix composite comprises a matrix of a metal or metal alloy, as mentioned above, wherein co-deposited metal oxide, carbide, sulfide or nitride nanoparticles, nano-diamond particles, PTFE (polytetrafluoroethylene) nanoparticles or CNT (carbon nanotubes) (hereinafter collectively called "non-metal component") are included. The metallic component in the co-deposited metal oxide, carbide, sulphide or nitride nanoparticles may be any suitable metal, e.g. the ones mentioned above. Particularly preferred metals are: Al, Ti, Zr, Hf, W, Y, Nb, V, Ta and Mo. The size of the co-deposited, included particles is in the range of 10-200 nm, preferably 10 to 150 nm, more preferably 10 to 100 nm.

The thickness of the nanocrystalline metallic coating may be substantially uniform, which means that the deviation from the mean thickness is not greater than about 20%, and may vary to a great degree. Generally the thicknesses are within a range of from 1 to 1000  $\mu\text{m}$ .

More usual thicknesses are from 20 to 500  $\mu\text{m}$ . For certain applications thicknesses of from 50 to 250  $\mu\text{m}$  are preferred.

On the other hand, there may be a substantially linear or also exponential gradient in the thickness of the coating, i.e. decrease from the outside of the metal foam to the interior of the metal foam or from one side of the metal foam to the other. The gradient may e.g. be such that the outer (or upper) region of the porous structure is covered with a (if desired, thick) coating while the interior (or lower region) of the structure is substantially uncoated.

The uncoated or raw open cell porous structure (the substrate) can be made of a great variety of materials e.g. selected from one or more of a metal or metal alloys; a metal (e.g. aluminium) or metal alloy (e.g. AlSi7Mg0.3) foam; The material of the substrate foam could also consist of a metal oxide, carbide and/or nitride, carbon, an organic polymeric material, silicone and a material derived from natural polymers and fibers and combinations thereof. In the case of non-conductive materials the foam substrates have to be coated with a conductive material.

"Uncoated" in this context means "not coated by the inventive nanocrystalline metallic coating".

The raw open cell porous structure may be a felt, a woven fabric, a knitted fabric and the like, made from fibers of the above materials.

Often the raw open cell porous structure is a reticulated foam made from an organic polymeric material, a silicone, a ceramic or a metal. Metal foams are available from a number of suppliers, e.g, ERG Materials and Aerospace Corporation, Oakland, California, USA, Norsk Hydro a.s., Sunndalsøra, Norway, Georgia Institute of Technology, Materials Science and Engineering, Atlanta, Georgia, USA, INCO Limited, Mississauga, Ontario, Canada, and M-Pore GmbH, Dresden, Germany. For certain applications, an aluminium foam (e.g. "Duocel" from ERG, Oakland, California, USA) or a AlSi7Mg0.3 foam (e.g. available from M-Pore GmbH, Dresden, Germany) is particularly preferred.

If the raw open cell porous structure is electrically non-conductive, it is coated with a thin conductive layer underneath the nanocrystalline metallic coating.

This layer may e.g. be selected from metals and metal alloys, conducting ceramic and oxide materials, carbon and conducting polymers. If a metal is used, it may be the same metal as used for the nanocrystalline coating, or a different metal.

5

The size of the pores of the open cell porous structure of the invention may vary within a broad range from micrometers to centimeters and depends on the intended use of the material. A common measure for the pore size is ppi (pores per inch).

- 10 The porosity of the open cell porous structure of the invention usually is high, e.g. greater than 80%, even greater than 90%, and in certain cases as high as 95 to 98 %.

The dimensions of the metal foam may vary from extremely thin in the millimeter or, for special applications, even in the micrometer range (such as about 100  $\mu\text{m}$ ) to very thick

- 15 structures in the range of several centimeters e.g. in the case of construction materials. Such large electroplated porous structures are available by the specific process of the invention described below and are nowhere described in the prior art. Thus, structures having a thickness of more than about 1 cm, about 2 cm, about 3 cm and particularly about 4 cm or even about 5 cm may easily be prepared by the inventive process.

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The mechanical properties of the metal foams of the invention, such as compression strength, energy absorption capability, flexibility and tensile strength, vary with the material of the raw open cell structure, the thickness, the pore size, the coating thickness and the size of the nanocrystallites of the open cell porous structure of the invention. In any case they are superior to the corresponding mechanical properties of similar open cell porous structures that have a conventional non-nanocrystalline metal coating. Without wishing to be bound by theory, it is believed that one of the reasons for the improved mechanical properties is the fact that the nanocrystallites inhibit the propagation of fissures and cracks.

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- 30 The metal foams of the invention may have a further outer coating. Such coating may e.g. be selected from a protective coating such as a silicone coating, or a coating comprising an inorganic, organic or biochemical catalyst, such as an enzyme.

The uses of the open cell porous structure of the invention are numerous. They can e.g. serve as electrodes, as sieves, as supports for catalysts, as light-weighted construction materials e.g. for military or space applications, as antimicrobial materials (e.g. when plated with silver or copper) for the manufacture of a great variety of articles, and as shock-absorbing materials of all kinds, for example as bullet-proof vests. In the latter application, they are superior to Kevlar<sup>®</sup>, since Kevlar<sup>®</sup> is hygroscopic.

Metal foams filled with an elastomeric or thermosetting plastics show improved damping properties. This is important in vehicles or engines with a high vibration. Furthermore, the metal foam acts as a rigid grid structure which keeps the filling in its form under a load.

In the following, the process for preparing the open cell porous structures coated with a nanocrystalline metallic or metal matrix composite coating is described.

Generally speaking, a raw open cell porous structure, as describe above, and, if necessary, made conductive by an electrically conducting coating, is electroplated by using a pulsed, pulse reversed or a direct current and a specially designed anode.

The raw open cell porous structures, including their porosity, pore size and overall size, may be selected from the ones mentioned above. The manufacture of such structures, e.g. of metal foams, is broadly described in the prior art, and many of them are available commercially, as mentioned above.

A non-conducting raw open cell porous structure made e.g from an organic polymeric foam material can be made conductive by applying e.g. the above-mentioned materials through a great variety of methods known to the person skilled in the art. Therefore only a few selected methods are mentioned here. Organic foams can be metallized e.g. by cathode sputtering, chemical metallization or by deposition of gaseous metal carbonyl compounds. Another method to make organic foams conductive is by applying conductive carbon black e.g. from a colloidal suspension of carbon black in a volatile organic solvent. Coating of conductive ITO (indium tin oxide) films can be accomplished by means of a sol-gel process. The electrically conducting open cell porous structure so obtained is herein called "intermediate open cell porous structure".



The raw or intermediate open cell porous structure is then electroplated with a metal, a metal alloy or a nanocrystalline metal matrix composite. In order to obtain a nanocrystalline metallic coating by electrochemical deposition of the metal or alloy or a nanocrystalline metal matrix composite by additional deposition of the above-mentioned materials, specific conditions at least with respect to the anode have to be met.

In the electroplating process according to the invention, the conductive raw or intermediate porous structure (substrate) serves as the cathode. This cathode is surrounded from all sides by a sacrificial anode assembly. The anode or anodes are positioned opposite to each face of the raw or intermediate porous structure. In one embodiment the anode assembly forms a cubic or cuboidal cage around the cathode or substrate (see Fig. 1). This is preferred for the deposition of metals and metal alloys. In another embodiment the anode is made of six contiguous flat parts with interspaces between the side parts in order to circulate electrolyte through the anode assembly (see Fig. 2). This arrangement is preferred for the deposition of nanocrystalline metal matrix composites.

The anode, as depicted in Fig. 1 and Fig. 2, comprises a fluid-permeable, e.g. porous plate-shaped or grid-like metal structure inert under the electrolytic conditions, such as made of titanium expanded metal, the top and bottom part of which carries metal pieces, e.g. balls, of the metal to be plated (the actual sacrificial anode). The four side parts thereof have a double-walled structure, which is filled with further pieces of the metal to be plated (the remainder of the actual sacrificial anode). The metal anodally dissolves during the electrolysis.

These arrangements have the following effects. Because of the homogenous field due to the special arrangement of the anode, there is a homogenous electric double layer in the whole porous structure (substrate). This homogeneity prevents any inhomogenous crystal growth which is very important for the formation of nanocrystallites. Furthermore, the homogenous field allows a substantially homogenous growth of nanocrystals from the metal ions in the electrolytic bath throughout the porous structure without the necessity to circulate the bath through the structure when metals or metal alloys are deposited. In the case of a nanocrystalline metal matrix deposition where the circulation of the electrolyte is necessary, there is still a homogenous field. By this, much larger porous structures than hitherto possible can be uniformly coated also in the interior thereof.

The distance of the anodes from the outer surface of the porous structure to be coated is such that the electrical field between the cathodes and the anode remains homogenous. In special cases this distance may be about 2 cm.

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The electrolytic bath generally contains the same ingredients as used in conventional electroplating of metals, metal alloys or metal matrix composites. Exemplary electrolyte compositions are given in the Examples. The use of a surfactant or wetting agent, such as sodium dodecyl sulfate, is e.g. advantageous, when sulfate or halide salts of the metals to be coated are used.

10

A grain refiner may be added to the electrolyte. Grain refiners in this context are low molecular weight organic compounds that are easily adsorbed by and desorbed from the surface of the uncoated or intermediate porous structure. Examples thereof are the so-called first class brighteners that comprise a SO<sub>2</sub> containing group, such as saccharine, naphthalene sulfonic acids, alkyl sulfonic acids, benzene sulfonic acids, aryl sulfone sulfonates, sulphonamides, sulfonimides, low molecular weight compounds that comprise a phosphorus- or nitrogen-containing group), such as EDTA, butanediamine, ammonia, nicotinic acid and cyanides, as well as polycarboxylic acids, such as citric acid and tartaric acid. These grain refiners prevent the surface diffusion of atoms of island-like deposition of metal atoms and thus the formation of aggregations of the nanocrystallites. It must be emphasized that the so-called second class brighteners (for a definition see EP 0 558 142 B1) may not be used in the process of the invention, since they provide a smooth surface consisting of crystallites which are larger than nanocrystallites.

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The electric current applied to the electrolytic bath is a pulsed, pulse reverse or direct current. The pulsed, pulse reverse or direct current in combination with the above-mentioned anode arrangement allows the formation of nanocrystals.

30

Since not as common as the plating of metals or metal alloys with the aid direct current or pulsed current well-known to the person skilled in the art, the principles of pulse reverse plating and metal matrix composite plating will be briefly described in the following.

The in-situ formation of nano-structured or nano-sized oxides in a metal matrix can be achieved by pulsed reverse plating using metals which can be oxidized by electrochemically prepared oxygen (e.g. Cu, Ni, Co, Fe, Cr.). The procedure of the pulse reverse plating process works in two steps:

- 5 First step (cathodic pulse): During the negative polarisation of the working electrode nanostructured metal is deposited (e.g.  $\text{Ni}^{2+} + 2 \text{e}^- \rightarrow \text{Ni}$ ).

Second step (anodic pulse): During the positive polarisation of the working electrode highly reactive oxygen ( $\text{O}_2$ ) is generated from the aqueous electrolyte which oxidizes a part of the metal clusters prepared in step 1 ( $\text{O}^{2-} \rightarrow 0.5 \text{O}_2 + 2 \text{e}^-$ ).

10

In order to achieve only a partial oxidation of the deposited metal (from step 1) the charge (charge =  $t_{\text{on}} * I_{\text{pulse}}$ ; wherein  $t_{\text{on}}$  is the duration of the current of the pulse and  $I_{\text{pulse}}$  is the current of the pulse) of the anodic pulse must be less than the charge of the cathodic pulse.

- 15 Preferably the charge of the anodic pulse is between 30-90% of the charge of the cathodic pulse for a partial oxidation. The ratio metal : metal oxide can be controlled by the current density and the duration of the anodic pulse.

20 The anodic pulse follows the positive pulse with or without a time delay (0-80% of the  $t_{\text{off}}$  time;  $t_{\text{off}}$  is the duration with zero current).

A great advantage of this technique is a very homogeneous distribution of oxides in the metal matrix.

- 25 In the nanocrystalline metal matrix composite coatings of the present invention, the content of the non-metal component depends on the nature thereof and may comprise e.g. 3-30% by volume, more often 5-20% by volume, although higher proportions may be achieved.

30 The electrolyte in metal matrix composite plating is a dispersion electrolyte including one or more salts of the metal or metals to be deposited and a dispersion of nano-sized particles (e.g. from 20 to 100 nm) of one or more of the above-mentioned non-metal components. The particles must form a stable dispersion in the aqueous salt solution, .e.g. chemically by use of surface active agents or physically by agitating or blowing in of gases. The particle

content of the electrolyte depends on the nature of the particles and may be e.g. 10-200 g/l, more often 20 to 120 g/l.

The current used in the plating of nanocrystalline metal matrix composite may be a direct current, a pulsed current or a pulse reverse current. The particles usually carry a positive charge by having absorbed metal ions or a surface active agent on their surface and, thus, migrate in the electrical field to the cathode. They also migrate by convection and diffusion, which is important for their migration in the  $t_{\text{off}}$  time of a pulsed current and a reverse pulse current as well as in the time where the substrate is the anode in a reverse pulse plating.

The particle contents which may be achieved by a pulsed or reverse pulsed current are higher than in the case of a direct current. For very high contents of the non-metal component in the composite, low duty cycles in a reverse current process are preferable. The particles which may be deposited in a pulsed or reverse pulsed current are generally smaller than the particles in a direct current process.

The selection of the current parameters, i.e. current density, frequency and the pulse duration determine the size of the metal nanocrystallites and the properties of the coating, such as thickness, hardness, ductility and homogeneity. For direct current plating, exemplary parameters are an average current density  $j_m$  of from 0.2 to 40 mA/cm<sup>2</sup>, preferably from 0.4 to 20 mA/cm<sup>2</sup>. Exemplary parameters of a pulsed and pulse reverse current useful in the present invention are: an average current density  $j_m$  of from 0.2 to 40 mA/cm<sup>2</sup>, preferably from 0.4 to 20 mA/cm<sup>2</sup>, a frequency of from 10 Hz to 1 kHz, preferably from 50 Hz to 200 Hz, and a duty cycle, i.e. pulse length ( $t_{\text{on}}$ ) in percent of the period length ( $t_{\text{on}} + t_{\text{off}}$ ;  $t_{\text{off}}$  being the length of zero current) of from 5–70%, e.g. from 5-50%, preferably of from 15-40%, such as from 20-35% .

For pulse reverse plating the charge of the anodic pulse is in the range of from 0 to 50% of the charge of the cathodic pulse.

The average current of a pulse plating process is defined as:

$$I_m = I_p \cdot \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}}$$

wherein  $I_p$  is the current of the pulse.

The average current of a pulse reverse plating process is defined as:

$$I_m = \frac{I_{cathode} \cdot t_{cathode} - I_{anode} \cdot t_{anode}}{t_{cathode} + t_{anode}}$$

wherein  $I_{cathode}$ ,  $I_{anode}$  are the current of the cathodic/anodic pulse and  $t_{cathode}/t_{anode}$  are the length of the cathodic/anodic pulse.

If the thickness is homogenous, it is only controlled by the current density and the duration of the electroplating. By continuously reducing the electrolyte concentration during the electroplating, metal foams with a gradient in the thickness from the outside to the inside may be produced. A gradient from the top of the metal foam to the lower part thereof may be produced by either pumping off the electrolyte continuously or by continuously pulling the metal foam out of the electrolyte.

Usually, the bath temperature is from room temperature to about 60 °C. The temperature controls the crystallite size and the surface morphology. A higher temperature promotes a faster crystal growth and such a larger crystallite size.

The nano-coated open cell porous structure so obtained may be filled with an elastomeric or thermosetting plastics. This may be accomplished by pouring the molten or not yet hardened plastics into the metal foam or by dipping the metal foam into the molten or not yet hardened plastics, and cooling.

The nano-coated open cell porous structure of the invention may be further coated with an outer coating, e.g. a protective coating such as a silicone coating. It may also serve as a carrier for inorganic, organic or biochemical catalysts, such as enzymes. The processes for applying such further coatings or catalysts are not different from the ones used with conventional electroplated open cell porous structures and are known to the person skilled in the art.

There is, however, one compulsory restriction to any process conducted with the nano-coated open cell porous structures of the invention: the structure must not be heated to a temperature above about 60 °C for a significant time, since otherwise the nanocrystallites

will aggregate to larger units and the nano-coated porous structure will lose its favourable properties.

Fig. 1 is a schematic exploded view of a cubic cage-like anode assembly 10 and a cathode  
5 (raw or intermediate metal foam) 12 inserted therein. The fluid-permeable cage-like anode  
comprises a top part 13 made of expanded Ti metal and carrying balls of a sacrificial metal  
14 (part of the actual sacrificial anode), a bottom part 16 made of expanded Ti metal and  
inside covered with the sacrificial metal (another part the actual sacrificial anode) and four  
10 double-walled side parts 15 made of expanded Ti metal and filled with the sacrificial metal  
(the remainder of the actual sacrificial anode). There are separate electrical contacts (17, 18  
and 19, respectively) to each of the top 13, the bottom 16 and the four double-walled side  
parts 15 of the cage-like anode assembly 10. The cathode 12 has isolated electrical contacts  
20 which extend through balls of a sacrificial metal 14 in the top 13 of the anode assembly  
10. The anode assembly 10 is screwed together by screws 21 with isolation against the Ti  
15 expanded metal.

Fig. 2 shows a schematic front sectional view of a six-sided anode assembly 10' according  
to the invention and a cathode 12' (raw or intermediate metal foam) in the center thereof.  
The anode assembly 10' is submersed in an outer electrolyte bath 21' contained in a glass  
20 vessel 28' for coating the cathode 12' with a metal matrix composite. Non-metal component  
particles 22' are dispersed in the electrolyte bath 21'. A magnetic stirring bar 30' can be  
agitated by a magnetic stirrer 32'. The fluid-permeable six-sided anode 10' with interspaces  
23' between four double-walled side parts 15' comprises a top part 13' made of expanded Ti  
metal and carrying balls of a sacrificial metal 14' (part of the actual sacrificial anode), a  
25 bottom part 16' made of expanded Ti metal and also carrying sacrificial metal 14' (another  
part the actual sacrificial anode) and the four double-walled side parts 15' made of expanded  
Ti metal and filled with balls of sacrificial metal 14' (the remainder of the actual sacrificial  
anode). There is an electrical contact 19' to the top 13' of the six-sided anode assembly 10'.  
The cathode 12' has isolated electrical contacts 20' which extend through balls of a  
30 sacrificial metal 14' in the top 13' of the anode assembly 10'. The anode assembly 10' and  
the cathode 12' are suspended by luster terminals 26' in the electrolyte bath 21'.

The following non-limiting examples illustrate the invention further.

**EXAMPLES**

The following abbreviations are used in the Examples:

- 5           T = temperature  
          ppi = pores per inch  
           $t_{on}$  = duration of the current pulse  
           $t_{off}$  = duration of zero current  
           $j_p$  = current density of current pulse  
10           $j_m$  = average current density ( $j_m = j_p * t_{on} / (t_{on} + t_{off})$ )  
          t = duration of deposition

A raw metal foam cube having a side length of 4 cm was used in each example. A cage anode (see Fig. 1) was used in the production of metal foams having nanocrystalline a  
15          metallic coating of Examples 1 to 4, and an anode as shown in Fig. 2 ("six-sided anode")  
          was used for the production of metal foams having a metal matrix composite coating in  
          Example 5. The distance between the faces of the cage anode or the six-sided anode and the  
          faces of the cube was 2 cm in each example. The actual sacrificial anode consisted of the  
          metal to be deposited.

20

**Example 1**

Electrolyte:

- Nickelsulfamate concentrate (Enthone; 110 g/l Ni)  
25          5 g/l nickel chloride hexahydrate  
          35 g/l boric acid  
          pH = 3.8  
          T = 50°C

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Raw metal foam:

10 ppi aluminium foam (AlSi7Mg0.3, M-PORE, Dresden, Germany)

Parameters of deposition:

$t_{on}$ : 2.5 ms /  $t_{off}$ : 7.5 ms

$j_p$ : 1.8 mA/cm<sup>2</sup>

Frequency: 100 Hz

t: 3d 18h 25min

- 5 The product was an aluminium foam coated with a 50 µm thick layer of nano-Ni (average crystallite size: 28 nm)

### Example 2

10 Electrolyte

Nickelsulfamate concentrate (Enthone; 110 g/l Ni)

5 g/l nickel chloride hexahydrate

35 g/l boric acid

pH = 3.8

15 T = 50°C

Raw metal foam:

10 ppi aluminium foam (AlSi7Mg0.3, M-PORE, Dresden, Germany)

20 Parameters of deposition:

$j_m$ : 1.1 mA/cm<sup>2</sup>

t: 3d 1h 58min

- 25 The product was an aluminium foam coated with a 100 µm thick layer of nano-Ni (average crystallite size: 47 nm)

### Example 3

Electrolyte:

30 200 g/l copper sulfate pentahydrate

50 g/l conc. sulfuric acid

0.2 g/l sodium dodecyl sulfate

pH = 1,0

T = 40°C



Raw metal foam:

10 ppi aluminium foam (AlSi7Mg0.3, M-PORE, Dresden, Germany)

5 Parameters of deposition:

$j_m$ : 0.45 mA/cm<sup>2</sup>

t: 3d 1h 59min

10 The product was an aluminium foam coated with a 50 µm thick layer of nano-Cu (average crystallite size: 93nm)

#### Example 4

Electrolyte:

15 281 g/l nickel sulfate hexahydrate  
60 g/l nickel chloride hexahydrate  
30 g/l boric acid  
0.2 g/l sodium dodecyl sulfate

20 Raw metal foam:

10 ppi aluminium foam (AlSi7Mg0.3, M-PORE, Dresden, Germany)

Parameters of deposition:

$j_m$ : 1.1 mA/cm<sup>2</sup>

25 t: 3d 1h 58min

The product was an aluminium foam coated with a 100 µm thick layer of nano-Ni (average crystallite size: 43 nm)

#### 30 Example 5

Electrolyte:

281 g/l nickel sulfate hexahydrate  
60 g/l nickel chloride hexahydrate

30 g/l boric acid

0.2 g/l sodium dodecyl sulphate

7.5 g/l naphthalene-1,3,6-trisulfonic acid trisodium salt

120 g/l  $\alpha$ -Al<sub>2</sub>O<sub>3</sub>

5 pH = 4.1

T = 50°C

Raw metal foam:

10 ppi aluminium foam (AlSi7Mg0.3, M-PORE, Dresden, Germany)

10

Parameters of deposition:

$t_{on}$ : 3 ms /  $t_{off}$ : 7 ms

$j_p$ : 3.7 mA/cm<sup>2</sup>

Frequency: 100 Hz

15 t: 1d 13h 00min

The product was an aluminium foam coated with a 50  $\mu$ m thick layer of a nano-Ni/nano-Al<sub>2</sub>O<sub>3</sub> metal matrix composite coating (average crystallite size of the nickel matrix: 50 nm; Al<sub>2</sub>O<sub>3</sub> particle content: 14 vol.-%)

20

### **Example 6 - Mechanical behaviour of metal foams of the invention**

The mechanical behaviour of open cell aluminium foams with coatings of different metals was investigated under quasistatic compression loading in order to enhance the energy absorption capability of the foams. Investigated coating metals were nickel, copper and iron.

25

The best performance for the purpose of enhanced energy dissipation during compressive loading has been provided by a coating of nanocrystalline nickel having a crystallite size of 43 nm.

30

In a second step the effect of coating thickness and pore size was studied by slow and fast quasistatic compression tests and at least dynamic compression tests with a Split-Hopkinson-Pressure-Bar (SHPB). There was a linear increase in energy absorption capability with coating thickness for the absolute values and per foam thickness, but per

density or mass the energy absorption capability reached a saturation point. So there is an optimum in coating thickness.

As with uncoated aluminium foams there was an increase in plateau stress by decreasing the pore size. A decrease in pore size from 10 to 30 ppi more than doubled the energy absorption capability per foam thickness of coated foams. And there is a slight enhancement of energy absorption capability per mass. Other characteristics like compression strength and plateau stress showed a similar behaviour with respect to the energy absorption capability. Under dynamic loading there was also an increase in energy absorption capability by a factor of 10 for a coating thickness of 50  $\mu\text{m}$  in comparison to uncoated foams even at a very small foam thickness of 4 mm. The foams exhibited only little effect of strain rate sensitivity on plateau stress.

Fig. 3 shows the energy absorption capabilities per foam thickness of various non-coated aluminium foams and of aluminium foams of different pore sizes coated with different thicknesses of nano-Ni having a crystallite size of 43 nm. The energy absorption capability increases with a decrease in pore size and with the thickness of the coating layer.

#### **Example 7 – Absorption of electromagnetic waves by the metal foams of the invention**

The capability of open-porous aluminum- and nickel-coated aluminum foams to shield from and/or absorb electromagnetic waves was determined in a calorimetric microwave experiment. A ceramic crucible made of high purity  $\text{ZrO}_2$  was filled with an apolar oil (Julabo Thermal HS, maximum temperature range of from +20 to +250°C) as a heat transfer medium. Three experiments with a radiation power of the irradiated microwaves of 900 W and an irradiation time of 1 minute in each case were performed. Subsequently, the temperature increase of the oil was determined. In the first experiment, only the oil was irradiated. In the second experiment the an non-coated open-porous aluminum foam (available from m-pore, Dresden, Germany) with a pore size if 10 ppi and an edge length of 40 mm in the crucible was given to the oil, and in the third experiment, a aluminum foam cube coated with 100  $\mu\text{m}$  nickel particles of a cyrstallite size of about 40 nm was used. After the irradiation time of 1 minute the following temperature increases  $\Delta T$  were measured:

| Experiment                                        | $\Delta T / ^\circ\text{C}$ |
|---------------------------------------------------|-----------------------------|
| 1 (only oil)                                      | 11.7                        |
| 2 (oil + aluminum foam)                           | 15.9                        |
| 3 (oil + aluminum foam with 100 $\mu\text{m}$ Ni) | 23.3                        |

When a material absorbs microwave radiation, its temperature increases. The first experiment shows that the non-polar oil by itself absorbs only a small amount of radiation. The aluminum foam also absorbs only a small amount of radiation, the major part of the irradiated power passes the experiment without interaction. However, the coated foam absorbs microwave radiation to a greater degree and, therefore, heats up the oil more efficiently.

The relevant disclosure of all documents cited herein, such as patents, patent application and journal articles, is herewith incorporated by reference.

**Claims**

1. An open cell porous structure the cells of which are optionally filled with an elastomeric or thermosetting plastics, the open cell porous structure comprising a  
5 nanocrystalline metallic or nanocrystalline metal matrix composite coating wherein the nanocrystals have a crystallite size of from about 5 nm to about 150 nm.
2. The open cell porous structure of claim 1, wherein the crystallite size is from about 10 to about 100 nm.  
10
3. The open cell porous structure of claim 1 or 2, wherein the uncoated open cell porous structure comprises a material selected from one or more of a metal; a metal alloy; a metal foam, including aluminium foam, or metal alloy foam, including AlSi7Mg0.3 foam; a metal oxide, carbide and/or nitride; carbon; an organic polymeric material; a silicone; and a  
15 material derived from natural polymers and fibers; and combinations thereof.
4. The open cell porous structure of claim 3, wherein the uncoated open cell porous structure comprises a material selected from one or more of a metal; a metal alloy; a metal foam, including. aluminium foam, and/or metal alloy foam, including AlSi7Mg0.3 foam.  
20
5. The open cell porous structure of any of claims 1 to 4, wherein the metallic coating is selected from nickel, nickel alloys, zinc, tin, chromium, iron, copper, titanium, silver, gold, platinum, palladium, ruthenium, rhodium, iridium and osmium.
- 25 6. The open cell porous structure of any of claims 1 to 4, wherein the nanocrystalline metal matrix composite coating comprises one or more of the metals recited in claim 5 and a non-metal component selected from metal oxide, carbide, sulfide or nitride nanoparticles, nano-diamond particles, PTFE (polytetrafluoroethylene) nanoparticles or CNT (carbon nanotubes).  
30
7. The open cell porous structure of any of claims 1 to 6, wherein the cells are filled with an elastomeric or thermosetting plastics.

8. The open cell porous structure of any of claims 1 to 6 wherein the cells are not filled with an elastomeric or thermosetting plastics.

9. The open cell porous structure of any of claims 1 to 7, wherein the structure has a thickness of about 100  $\mu\text{m}$  or more, more than about 1 cm, more than about 2 cm, more than about 3 cm and more than about 4 cm and even about 5 cm.

10. The open cell porous structure of any of claims 1 to 9, wherein the nanocrystalline coating has a substantially uniform thickness of from 1  $\mu\text{m}$  to 1 mm.

11. The open cell porous structure of any of claims 1 to 10, wherein the thickness of nanocrystalline coating decreases from the outer region of the open cell porous structure to the inner region of the open cell porous structure.

12. The open cell porous structure of any of claims 1 to 10, wherein the thickness of nanocrystalline coating decreases from one side of the open cell porous structure to the other.

13. The open cell porous structure of any of claims 1 to 12, wherein on the coated open cell porous structure a further outer coating is applied.

14. A process for the production of the open cell porous structure of any of claims 1 to 13 comprising: coating the uncoated porous structure, if not made from an electrically conducting material, with an electrically conducting layer to form an electrically conducting intermediate open cell porous structure, and coating the electrically conducting uncoated or intermediate open cell porous structure with a metal, a metal alloy or a metal matrix composite by electroplating using a pulsed or a direct current or, in the case of a metal matrix composite, a pulse reverse current electroplating process, the cathode being the electrically conducting uncoated or intermediate open cell porous structure and the anode or anodes, which is/are positioned opposite to each outer surface of the uncoated or intermediate open cell porous structure is/are (a) sacrificial anode(s) comprising an inert conducting material and a sacrificial metal or metal alloy to be coated onto the uncoated or intermediate open cell porous structure to form the open cell porous structure coated with a nanocrystalline metallic coating;

and optionally filling the pores of the open cell porous structure with an elastomeric or thermosetting plastics.

15. The process of claim 13, wherein the anode has a cubic or or cuboidal cage-like  
5 form.
16. The process of claim 13, wherein the anode is a six-sided anode having interspaces between side walls.
- 10 17. The process of any of claim 14 to 16, wherein the thickness of the coating is controlled by the duration and the density of the pulsed, pulse reverse or direct current.
- 15 18. Use of the open-cell porous structure of any of claims 1 to 13 or prepared according to any of claims 14 to 17 for absorbing mechanical impact or stress or electromagnetic radiation.

Fig. 1

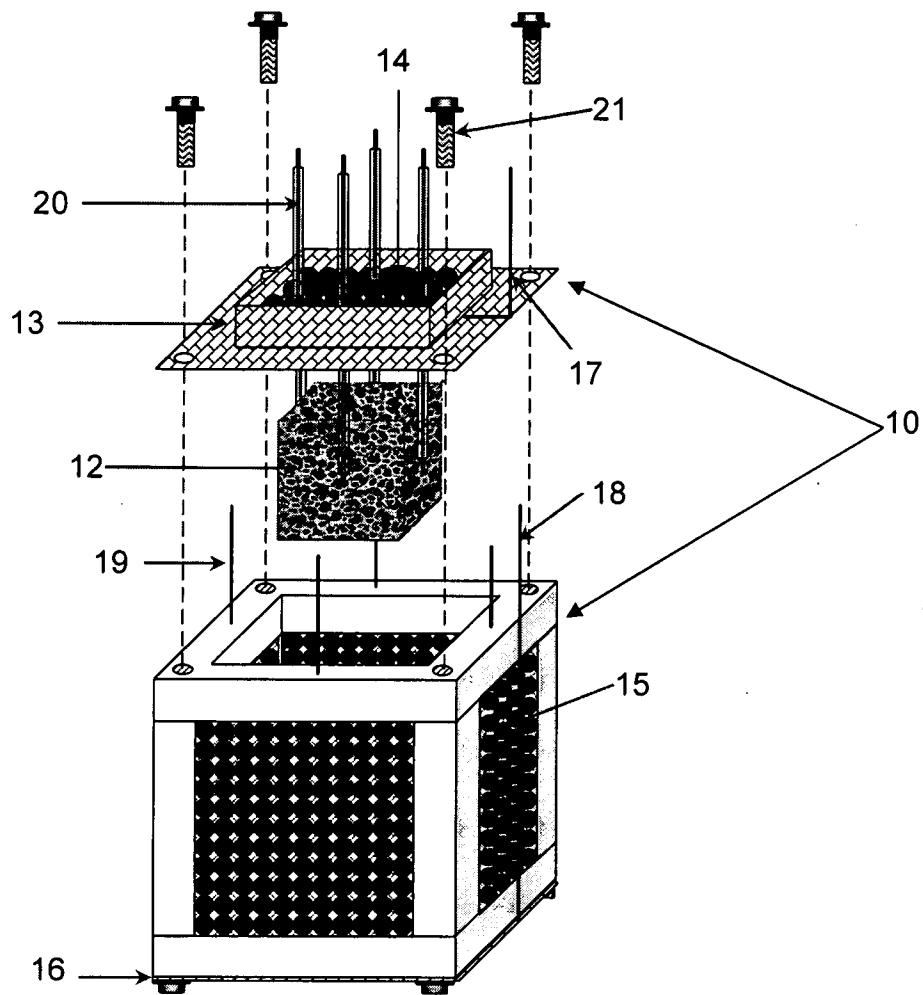




Fig. 2

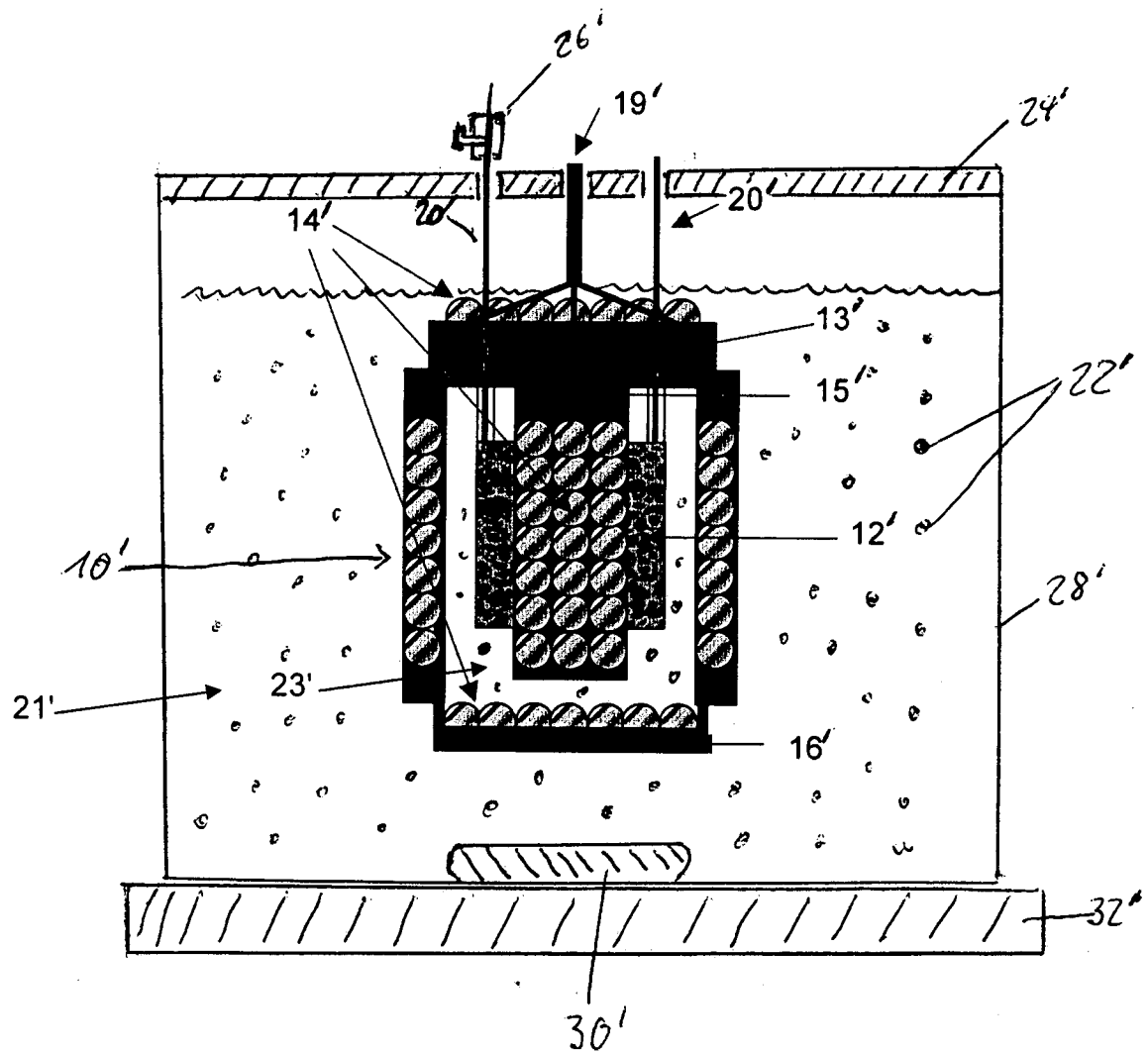
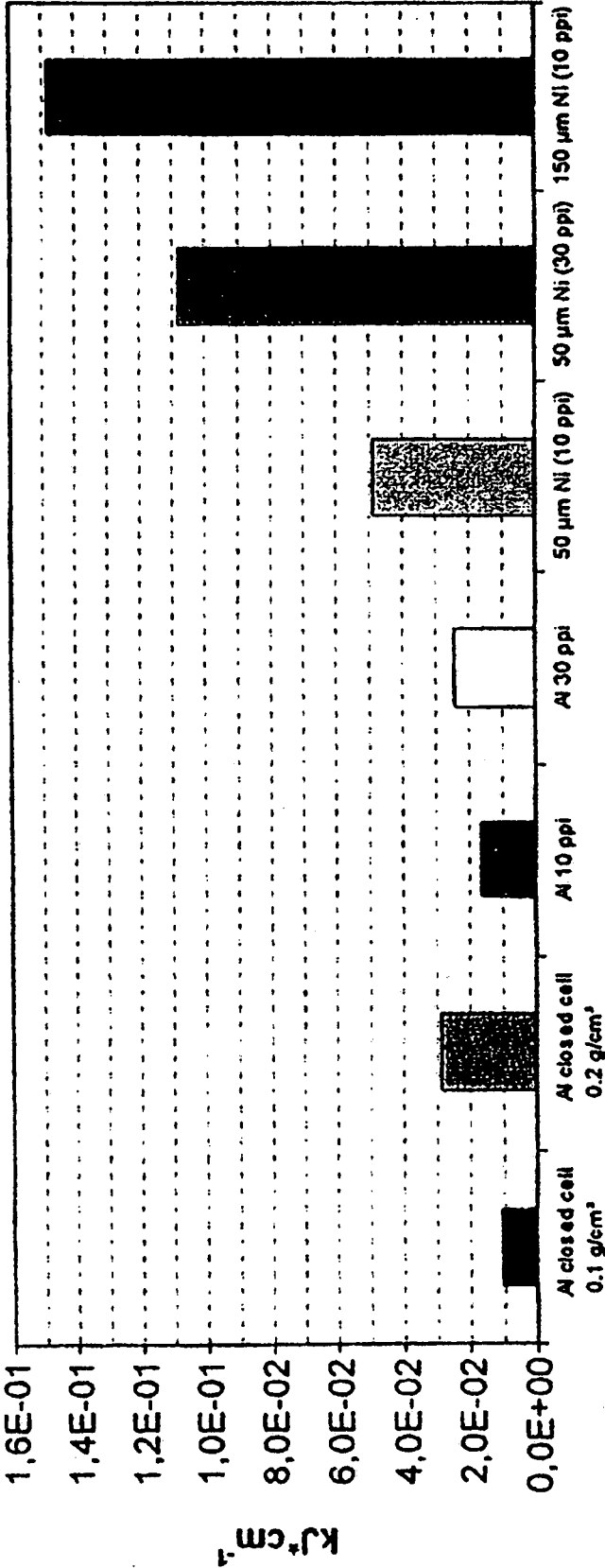


Fig. 3

Energy Absorption Capability per Foam Thickness



# INTERNATIONAL SEARCH REPORT

International application No  
PCT/EP2010/003464

## A. CLASSIFICATION OF SUBJECT MATTER

INV. C25D5/02 C25D5/18 C25D15/02  
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)  
C25D

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<br>Y    | US 6 217 732 B1 (SCHUH LOTHAR [DE] ET AL)<br>17 April 2001 (2001-04-17)<br>claims 1,2,9,12,24; figure 1<br>column 3, lines 21-25<br>column 3, line 47 - column 4, line 64<br>column 5, lines 49-67<br>column 7, lines 32-42<br>example 2                      | 1-6,<br>8-12,18<br>7,14-17 |
| X<br>Y    | US 2006/068026 A1 (HU MICHAEL Z [US] ET AL) 30 March 2006 (2006-03-30)<br>claims 8,11,12; figure 2<br>page 2, paragraphs 35,36<br>page 3, paragraphs 39,43,45<br>page 6, paragraph 75<br>page 6, paragraph 76 - page 7, paragraph 77<br>page 8, paragraph 108 | 1-3,5,18<br>7,14-17        |
|           | -----<br>-/-                                                                                                                                                                                                                                                  |                            |



Further documents are listed in the continuation of Box C.



See patent family annex.

\* Special categories of cited documents :

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- "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
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- "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.
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Date of the actual completion of the international search

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## C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

| Category* | Citation of document, with indication, where appropriate, of the relevant passages                                                                                                                                                                                                                                                                                                         | Relevant to claim No.        |
|-----------|--------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|------------------------------|
| X         | <p>YANG W ET AL: "Nanostructured palladium-silver coated nickel foam cathode for magnesium-hydrogen peroxide fuel cells"</p> <p>ELECTROCHIMICA ACTA, ELSEVIER SCIENCE PUBLISHERS, BARKING, GB, vol. 52, no. 1, 5 October 2006 (2006-10-05), pages 9-14, XP025168108</p> <p>ISSN: 0013-4686</p> <p>[retrieved on 2006-10-05]</p> <p>page 10, paragraph 2.1</p> <p>figure 1</p> <p>-----</p> | <p>1-5,8,9,<br/>11-13,18</p> |

# INTERNATIONAL SEARCH REPORT

Information on patent family members

International application No

PCT/EP2010/003464

| Patent document<br>cited in search report |    | Publication<br>date | Patent family<br>member(s) | Publication<br>date |
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|                                           |    |                     | US 2006280785 A1           | 14-12-2006          |