

(19) World Intellectual Property Organization
International Bureau



(43) International Publication Date
24 January 2008 (24.01.2008)

PCT

(10) International Publication Number
WO 2008/010747 A1

(51) International Patent Classification:

C23C 14/16 (2006.01) C23C 14/06 (2006.01)

C23C 14/34 (2006.01)

(21) International Application Number:

PCT/SE2006/000894

(22) International Filing Date: 19 July 2006 (19.07.2006)

(25) Filing Language:

English

(26) Publication Language:

English

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(81) Designated States (unless otherwise indicated, for every kind of national protection available): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BW, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, EG, ES, FI, GB, GD, GE, GH, GM, HN, HR, HU, ID, IL, IN, IS, JP, KE, KG, KM, KN, KP, KR, KZ, LA, LC, LK, LR, LS, LT, LU, LV, LY, MA, MD, MG, MK, MN, MW, MX, MZ, NA, NG, NI, NO, NZ, OM, PG, PH, PL, PT, RO, RS, RU, SC, SD, SE, SG, SK, SL, SM, SY, TJ, TM, TN, TR, TT, TZ, UA, UG, US, UZ, VC, VN, ZA, ZM, ZW.

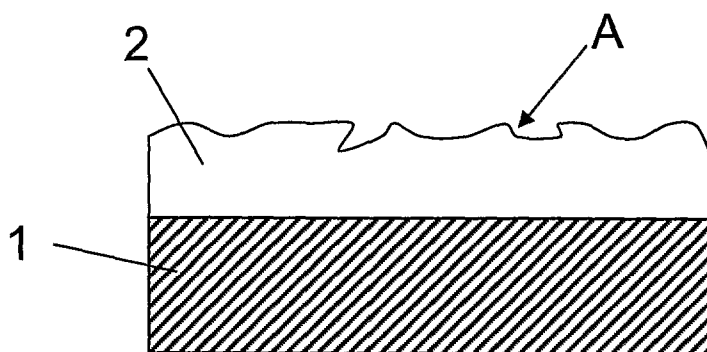
(84) Designated States (unless otherwise indicated, for every kind of regional protection available): ARIPO (BW, GH, GM, KE, LS, MW, MZ, NA, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IS, IT, LT, LU, LV, MC, NL, PL, PT, RO, SE, SI, SK, TR), OAPI (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).

Published:

— with international search report

For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.

(54) Title: METHOD OF PRODUCING A ROUGH SURFACE ON A SUBSTRATE



(57) Abstract: A method for producing metallic substrates with an adhesive surface is disclosed wherein a coating is applied to the substrate by means of electron beam evaporation. The gas pressure in the coating chamber is increased compared to normal coating pressure.

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METHOD OF PRODUCING A ROUGH SURFACE ON A SUBSTRATE

The present invention relates to a method according to the pre-characterizing
5 portion of claim 1.

Such a method is known from for example JP 1129958, wherein a method for
evaporating Ti is disclosed. The source is evaporated by the actuation of an
electron gun, thereby forming a titanium nitride film on a surface of a material,
10 such as steel grade SUS 304, to be treated.

Metallic laminates and fiber metal laminates (FMLs) are today used in several
different applications such as aerospace applications and armor applications.
The main reason for using this type of laminate structures in aerospace
15 applications is the reduction of weight. Furthermore, laminate structures have
high mechanical strengths, good fatigue strengths, works as thermal barriers, as
well as shock and damage barriers. These two latter features are also the reason
to use these types of laminates in armor applications since the multilayer
laminate structure will work as a shock absorber and limit the impact of a
20 projectile.

One possible way to improve the mechanical properties of these types of
laminates is to integrate stainless steel foils in the laminate structure. However, in
order to do so the stainless steel foils need to have a good adhesion to an
25 adjacent laminate layer, through an adhesive organic bonding layer.

The adhesion strength of stainless steel towards organic adhesives is however
not always sufficient during use in some applications. For example in the case of
FML, insufficient adhesive strength may lead to micro cracks or tendencies of
30 delaminations at the interface between the fiber layers and the metal foils. This

may be detrimental for the strength, and thereby the operation conditions and the service life, of the laminate.

The adhesion strength may also cause problems in certain decorative metallic laminates and painted stainless steels exposed to severe external mechanical stress. The difference in the coefficient of thermal expansion between steel and organic plastics is one cause for adhesion problems.

Moreover, the native chromium oxide present on stainless steel is also always impairing the adhesion strength. These factors are in fact limiting the use of stainless steel in certain lamination applications.

To enhance adhesion between stainless steel and organic adhesives, such as acrylics, polyesters, epoxies and various viscoelastic polymers, additional surface treatments are normally used. The objective of the surface treatment can both be to minimize the amount of oxide present on the surface and also to create a rough surface morphology that enhances adhesion strength due to a larger surface area. Various mechanical cleaning processes, such as brushing or blasting, as well as chemical cleaning and etching processes can be used for this purpose. For very high adhesion strengths multi-step processes may have to be used to create a surface with optimized cleanliness and surface structure.

Another approach is to apply a surface coating to the stainless steel that increases the wetting of the adhesive. This may be a simpler one-step method that with the application of a high surface energy coating to the stainless steel can create a very strong bond between steel and adhesive.

The object of the present invention is to provide a steel substrate with improved surface properties wherein said substrate is suitable for use in metallic laminates and fiber metal laminates (FML). More specifically, the object of the present

invention is to provide a steel substrate with improved adhesiveness to organic adhesives.

Summary of the invention

5

The stated object is achieved by a method as initially defined and having the features of the characterizing portion of claim 1.

10 A metallic substrate is provided with at least one coating layer comprising Ti by means of electron beam evaporation wherein the pressure in the coating chamber is increased at least 10 times, preferably at least 100 times, from normal pressure in the coating chamber. By utilizing this method, a metallic substrate can be provided with a coating having an excellent adherence to the substrate as well as an increased adherence to for example a further coating of a
15 paint or lacquer, or adjacent material in a laminate structure through an adhesive.

Brief description of the drawings

- 20 Figure 1 illustrates a coated substrate produced in accordance with the present invention.
- Figure 2 illustrates a coated substrate, having several coating layers, produced in accordance with the present invention
- Figure 3 illustrates a metallic laminate produced in accordance with the present invention.
- 25 Figure 4 illustrates a coated substrate produced in accordance with the present invention with an additional coating layer of a lacquer.
- Figure 5 illustrates an alternative metallic laminate produced in accordance with the present invention.
- 30 Figure 6 illustrates the change in contact angle of four samples with TiN_x coatings, with increasing pressure in the coating chamber.

Figure 7 illustrates the estimated surface energy of four samples with TiN_x coatings.

Figures 8a-d show SEM photographs of TiN_x coatings applied at different nitrogen pressures.

5 Figures 9a-h show SEM photographs of Ti coatings applied at different pressures and wherein the pressure is regulated with Ar.

In the figures 1-7 some dimensions may be exaggerated in order to clearly illustrate particular feature/features. The size of the different features in the
10 figures 1-7 should therefore not be considered limiting to the disclosure.

Detailed description of the invention

Electron beam evaporation is a physical vapor deposition process wherein
15 electrons are directed towards a source of material which is to be evaporated and thereby transferred to a substrate which is to be coated with the material. The kinetic energy of the electrons is transformed to heat at impact with the material causing the material to evaporate. Evaporation usually takes place under reduced atmosphere, i.e. vacuum. The specific pressure is adapted to the
20 material to be evaporated.

Electron beam evaporation can be used both as a batch process and a continuous process. An advantage with a continuous process is that the coating can be performed at a high production rate. Substrate speeds of 25-75 meters
25 per minute are not unusual. This allows a comparatively low substrate temperature since the substrate passes the coating chamber fairly quickly, causing minimal risk of distortion of the substrate as a result of the comparatively low thermal load during the deposition. Furthermore, a continuous process makes it possible to coat long objects, such as substrates up to 20 km long. A
30 continuous electron beam evaporation process is therefore recommendable in order to produce large scale objects in a cost effective manner.

A surface of a substrate 1 is coated by electron beam evaporation with at least one coating layer 2 comprising Ti, as shown in Figure 1. By increasing the pressure in the chamber at least 10 times, a coating having a high surface area A
5 can be achieved. The pressure in the chamber may be increased before the actual coating process begins, or during the coating process. The pressure may also be regulated during the coating process to ensure the desired gas to vapor ratio.

10 In most cases, the density of the coating decreases with increasing pressure in the chamber during coating. If low pressures are use in the evaporation process usually dense coatings are formed. The reason for this is simple, the energy of the evaporated metal, in the present case titanium, will less likely collide with gas molecules before condensation on the substrate surface. At any collision of the
15 vapor material on its way to the surface of the substrate it will lose energy by momentum transfer. This will give the metal vapor more reserved energy when it condensates on the surface to arrange the coating structure i.e. densify the coating. However, if the metal vapor has low energy when it impacts with the substrate surface it will less likely have enough energy to densify the coating i.e.
20 a low density coating with rougher sub-micrometer morphology is formed. Therefore, the higher the pressure in the coating chamber, the higher surface area of the coating. Hence, the pressure in the coating chamber is preferably increased at least 100 times, most preferably at least 1000 times, compared to normal coating pressure. The possible maximum pressure is mainly limited by
25 the equipment used.

Even though intended for steel substrates, the method according to the present invention may be used on any type of substrate which does not suffer substantial structural changes due to the temperature during the coating process. It is highly
30 appropriate for metallic substrates. Suitable metallic substrates are substrates of alloys based on any of the elements Fe, Al, Ti, Mg, Ni and Cu, preferably

stainless steel. By utilizing alloys based on these elements, a low weight metallic laminate may be produced which is suitable in applications requiring low weight structures having high mechanical strength. Examples of such applications are as constructional parts or body sheets for vehicles, such as cars, trucks, ships and aircrafts. Also, if low thermal expansion is required for the intended final product a suitable substrate may be Fe₆₄Ni₃₆, also known under the trade name Invar, which is a material with very low thermal expansion.

The substrate may be in form of a strip, foil, tube, wire, plate, bar etc. However, it may also be in more complex shapes. Preferably the substrate is in the shape of a strip due to the intended use in fiber metal laminates or metallic laminates. The form of a strip also enables the use of a continuous coating process, which is beneficial for *inter alia* economical reasons as mentioned earlier.

The coating metal is Ti, or an alloy based on Ti. This renders a coating comprising Ti. Ti is preferably chosen as the coating metal since it is a reactive metal which provides excellent adhesion to the substrate even if the coating layer should be highly porous. Furthermore, a coating based on Ti is ductile which enables further processing, such as bending, stretching or stamping, of the coated substrate without causing any spalling or cracking of the coating. Titanium metal is easily evaporated by electron beam evaporation and the pressures of the deposition process can be carefully monitored.

The pressure in the deposition chamber is increased by introduction of an appropriate volume of gas into the deposition chamber. The selection of gas can be tuned to fit the wanted process. If an oxidized porous structure is desired, the introduced gas can be purified air, oxygen, ozone or any other oxidizing gas. If a nitrided coating is needed, the gas can be any nitrogen containing gas, such as pure nitrogen, ammonia, hydrazine or even mixtures of N₂ and H₂. By increasing the gas pressure, part of the metal will react with the gas and form oxides or nitrides. Thereby, a non-stoichiometric metal oxide or nitride coating is provided

on the surface of the steel. It is also possible to increase the pressure by using other gases, for example a non-reactive gas such as Ar. Thereby, a coating consisting essentially of pure Ti or Ti alloy is accomplished.

- 5 The coating produced according to the method has a micro crystalline or an amorphous structure with sub-micrometer sized grains and is substantially hydrophilic. As a result of the large surface area, the contact area between the coated substrate and an adjacent coating of an adhesive is increased whereby the adherence is improved. Moreover, a surface with sub-micrometer sized
- 10 grains creates capillary forces in the surface pores and grain boundaries, which in turn improves the adherence of the surface further. This formed rough sub-micrometer size morphology will therefore be very good for adhesion of a laminate layer on to the coated steel substrate.
- 15 According to an embodiment the coated substrate is treated further. For example, the coated substrate may be subjected to a heat treatment to increase the mechanical strength of the substrate. The coated substrate may also be subjected to an oxidation step, preferably at an elevated temperature, directly after the coating step in order to provide the surface with a fully oxidized surface.
- 20 This may for example be beneficial in applications requiring anti-bacterial behavior, such as surfaces of TiO_2 for use in food processing or medical devices.

The substrate is preferably cleaned in a proper way to remove any oil residue or the like from previous manufacturing steps, such as rolling or drawing, before

25 coating in order to achieve a good adhesion of the coating to the substrate. A suitable method may for example be a degreasing bath followed by ion assisted etching. In the case of a continuous coating the ion assisted etching is preferably conducted in line with the coating process. In the case of a batch process, this step may preferably be conducted in the same chamber as the coating process if

30 the equipment to be used for the coating process so permits.

The electron beam evaporation process according to the present disclosure is not activated, such as by means of e.g. plasma, since this normally produces more dense coatings which would not give a rough enough surface morphology. Moreover, an activated process is less cost-effective, since the equipment is more expensive, and renders a slower deposition process. Also, the substrate is preferably not subjected to elevated temperatures directly before or during coating since a hot substrate may facilitate formation of bigger crystals in the coating in addition to causing structural changes of the substrate. Preferably, the temperature of the substrate is kept below 300 °C.

According to a specific embodiment of the invention, the metal to be evaporated is Ti and the pressure in the chamber is increased by means of nitrogen containing gas. In this case, the normal pressure in the chamber is approximately 10^{-6} mbar. For this specific example, the pressure in the chamber is increased to at least $5 \cdot 10^{-5}$ mbar, preferably at least $1 \cdot 10^{-4}$ mbar. However, the pressure may be increased up to an order of magnitude of 10^{-2} mbar.

According to another specific embodiment, the metal to be evaporated is Ti and the pressure in the chamber is increased by means of Ar. The pressure in the chamber should be at least $5 \cdot 10^{-5}$ mbar, preferably at least $1 \cdot 10^{-4}$ mbar. It could also be increased up to an order of magnitude of 10^{-2} mbar.

According to an embodiment of the invention, the substrate is provided with several coating layers by the method indicated above, as shown in Figure 2. The pressure while coating each layer may be the same or different. By using different pressure for each coating layer it is possible to achieve a density gradient in the coating, for example a dense layer at the steel surface and a porous layer at the opposite side of the coating. In Figure 2, the increasing density of the coating is indicated by the arrow D.

The produced coated steel strip is suitable for use in laminated structures, especially metallic laminated structures or fiber metal laminates. This is illustrated in Figure 3, showing two coated substrates 3 and one uncoated substrate 4. The coated substrates 3 and the uncoated substrates 4 are joined by an adhesive 6, such as a polymer based adhesive. The different substrates applied to the substrates in this embodiment may be of the same or of different compositions. For example, coated substrate 3 may be a stainless steel substrate provided with a Ti comprising coating and the uncoated substrate 4 may be of a Ni alloy.

10 Metallic laminates or fiber metal laminates may for example be used as constructional parts or body sheets for vehicles such as cars, busses, trucks, ship and aircrafts. One example of a suitable application is in laminates comprising at least two metal sheets, for example of steel, between which there are provided threads or fibers and wherein the metal sheets and the threads/fibers are bonded together by means of an adhesive. Such a laminate is for example disclosed in US 4 489 123 and may be used in aircraft or space applications.

Furthermore, the produced coated steel strip is suitable for constructional parts which should be painted/lacquered or otherwise surface treated and requiring high adherence of the painted coating to the substrate. This embodiment is illustrated in Figure 4, showing a coated substrate 3 having an additional coating layer of a lacquer 5. By utilizing a coated substrate produced according to the method of the invention the adherence of the paint/lacquer to the substrate is greatly improved, especially if the substrate is a metallic substrate to which it is difficult to affix the paint/lacquer.

The coated substrate may be used in many applications. Especially, it can be utilized in metallic laminates or FML used in armor applications. One example of yet another type of laminate is shown in Figure 5 wherein a coated substrate 3 produced in accordance with the present invention is attached to a corrugated

laminate layer 7 or a honeycomb shaped layer (not shown). Optionally, the corrugated laminate layer may be attached to further coated substrates produced in accordance with the present invention as shown in the figure. One example of this type of laminates is illustrated in US 5 874 153.

5

According to yet another embodiment, the substrate is a wire which should be used to manufacture a metallic web; the coated wire provides high adherence to an adjacent coated wire by means of an adhesive provided to the contact point.

- 10 In the case of the metal being Ti and an alloy based on Co, such as 75Co-25Cr or ASTM F-75, the method according to the present disclosure may also be used to produce components for biomedical applications, such as prostheses or implants. A porous coating in accordance with the present invention may provide a good bond to bone tissue and substantially reduce wear of a metal substrate.
- 15 Ti and Co based alloys are furthermore well known for their biocompatible properties.

Example 1

- 20 Four different samples, using a stainless steel substrate, were produced at four different pressures in the coating chamber. The metal to be coated was Ti and the pressure used was nitrogen pressure. Consequently, the coatings formed were of the type non-stoichiometric TiN_x with a deficit of N. The different samples are listed in Table 1. Sample 4 is a comparative example since the pressure used
- 25 in this case is normal for this operation.

The wetting properties was determined by measuring the contact angle with the surface of the samples of drops of three different liquids, distilled water (H_2O), ethylene glycol (hereafter also denoted EG) and diiodine methane (CH_2I_2).

- 30 Before testing, the samples were cleaned with pure ethanol in order to remove impurities and possible fingerprints.

Table 1

Sample	Coating composition	Coating pressure (mbar)
1	TiN _x	$1,2 \cdot 10^{-2}$
2	TiN _x	$2,2 \cdot 10^{-3}$
3	TiN _x	$3,0 \cdot 10^{-4}$
4	TiN _x	$3,6 \cdot 10^{-6}$

- 5 The measurements were conducted by means of Fibro DAT 1100 (dynamic absorption tests) by dropping drops of liquid from a height of 10 mm above the surface of the sample. The volumes of the drops were 4 µl for water and ethylene glycol, and 1,8 µl for diiodine methane. The drop was filmed from the side using a CCD camera. It was noted that after 10-20 seconds the contact angles of the
- 10 drops were stabilized and reached equilibrium. Unfortunately, contact angles less than 15° are outside the measuring range of the instrument used, whereby the exact equilibrium of these could not be determined. In four cases the contact angles was observed to be considerably less than 15°, therefore these were set to ~10°. The results are listed in Table 2 and illustrated in Figure 6.

15

Table 2

Sample	Contact angle θ (degrees)		
	H ₂ O	EG	CH ₂ I ₂
1	21	~10	~10
2	36	~10	17
3	54	~10	19
4	67	49	39

From the results above it is obvious that a higher pressure during coating improves the hydrophilic properties of the surface. This implies that it is easier for an additional coating of for example an adhesive to wet the surface of the coated substrate and therefore achieve a better adherence to the substrate.

5

Example 2

By measuring the contact angle between the surface and three different liquids, with known surface tension, it is possible to calculate the surface energy γ_{SV} . The basis is that the interaction between a liquid and a solid surface is dominated by van der Waals (hereafter denoted vdW) and acid-base interactions, respectively. Hence, the surface energy γ_{SV} can be calculated by the contribution of a polar component γ^{AB} and a dispersive component γ^{vdW} , as illustrated in Equation 1.

15

$$(Eq.1) \quad \gamma_{SV}^{tot} = \gamma^{AB} + \gamma^{vdW} \quad \text{wherein} \quad \gamma^{AB} = 2\sqrt{\lambda^+ \lambda^-}$$

It is therefore possible to calculate the surface energy by means of the equation system Equation 2a-c.

$$(Eq.2a) \quad \gamma_{LV1}(\cos \theta_{L1} + 1) = 2\sqrt{\lambda_{L1}^{vdW} \lambda_S^{vdW}} + 2\sqrt{\lambda_S^+ \lambda_{L1}^-} + 2\sqrt{\lambda_S^- \lambda_{L1}^+}$$

$$(Eq.2b) \quad \gamma_{LV2}(\cos \theta_{L2} + 1) = 2\sqrt{\lambda_{L2}^{vdW} \lambda_S^{vdW}} + 2\sqrt{\lambda_S^+ \lambda_{L2}^-} + 2\sqrt{\lambda_S^- \lambda_{L2}^+}$$

$$(Eq.2c) \quad \gamma_{LV3}(\cos \theta_{L3} + 1) = 2\sqrt{\lambda_{L3}^{vdW} \lambda_S^{vdW}} + 2\sqrt{\lambda_S^+ \lambda_{L3}^-} + 2\sqrt{\lambda_S^- \lambda_{L3}^+}$$

20 The contact angle is denoted θ ; and L, S, V stand for liquid, solid and vapor, respectively.

By utilizing the equilibrium contact angle measurements in Table 2 of Example 1, it is therefore possible to estimate the surface energy of the samples of Table 1 of Example 1. For those samples where the equilibrium contact angle could not be measured, the contact angle has been estimated to 10° as shown in Table 2.

25

Calculations wherein these contact angles are estimated to 5° , instead of 10° , result in less than 2% difference in the results of γ_{SV}^{tot} . In this case L1 is distilled water (H_2O), L2 is ethylene glycol (EG) and L3 is diiodine methane (CH_2I_2).

Known parameters used in the calculations are disclosed in Table 3. The results of the calculations are listed in Table 4 and illustrated in Figure 7.

Table 3.

Parameter	Value	Parameter	Value
γ_{LV,H_2O}	72,8 mN/m	$\gamma_{H_2O}^{vdW}$	21,8 mN/m
$\gamma_{LV,EG}$	48,0 mN/m	γ_{EG}^{vdW}	29,0 mN/m
γ_{LV,CH_2I_2}	50,8 mN/m	$\gamma_{CH_2I_2}^{vdW}$	50,8 mN/m
$\lambda_{H_2O}^+ = \lambda_{H_2O}^-$	25,5 mN/m	$\lambda_{CH_2I_2}^+ = \lambda_{CH_2I_2}^-$	~0 mN/m
λ_{EG}^+	1,9 mN/m	λ_{EG}^-	47,0 mN/m

10 Table 4.

Sample	$\gamma^{vdW} [mN/m]$	$\gamma^{AB} [mN/m]$	$\gamma_{SV}^{tot} [mN/m]$
1	50	1,9	52
2	49	2,2	51
3	48	5,4	53
4	40	0,2	40

Example 3

Four different samples, using a stainless steel strip substrate, were produced at four different pressures in the coating chamber. The metal to be evaporated was Ti and the coating pressure used was regulated with nitrogen gas. Consequently, the coatings formed were of the type non-stoichiometric TiN_x with a deficit of N. The different samples are listed in Table 5. The morphologies of the samples were investigated by Scanning Electron Microscope (SEM) and the results are shown in Figures 8a-d in the magnitude of 60000 times. It is clear from the photos that the difference in nitrogen pressure affects the surface structure of the produced coatings substantially. An increase of the process pressure renders more randomly oriented sub-micrometer sized grains which roughens the surface morphology and creates more pores and grain boundaries.

Table 5

Sample	Coating composition	Coating pressure (mbar)	Figure
5	TiN_x	$1 * 10^{-5}$	8a
6	TiN_x	$1,1 * 10^{-4}$	8b
7	TiN_x	$2,2 * 10^{-3}$	8c
8	TiN_x	$1,2 * 10^{-2}$	8d

Example 4

Four different samples, using a stainless steel strip as substrate, were produced at four different pressures in the coating chamber. The metal to be evaporated was Ti and the coating pressure used was regulated with Ar gas. The different samples are listed in Table 6, below. The morphologies of the samples were investigated by Scanning Electron Microscope (SEM) and are shown in Figures 9a-h at the magnitude of 20000 times and 60000 times, respectively.

Table 6

Sample	Coating composition	Coating pressure (mbar)	Figure
9	Ti	$1 * 10^{-5}$	9a (x20k) / 9e (x60k)
10	Ti	$1 * 10^{-4}$	9b (x20k) / 9f (x60k)
11	Ti	$1 * 10^{-3}$	9c (x20k) / 9g (x60k)
12	Ti	$1 * 10^{-2}$	9d (x20k) / 9h (x60k)

- Depending on the gas used for the pressure regulation of the evaporation process different coating morphologies were obtained. If comparing the samples given in Example 3, i.e. samples 5-8, with the samples from Example 4 i.e. the samples 9-12, it can clearly be seen that the utilization of the embodiment with Ar gives sub-micrometer sized grains which are larger than the grains produced using nitrogen as the regulating gas. This increased grain size will lead to an even rougher surface than the embodiment with N₂. Furthermore, the randomly oriented flake like grains of the Ar gas regulated coatings has a grain size of approximately 150 nm while the more triangular shape grains for the nitrogen gas regulated coating has a grain size of approximately 50 nm.

CLAIMS

1. Method of producing a coating comprising Ti on a metallic substrate by means of electron beam evaporation in a coating chamber characterized by using a pressure of at least 10^{-5} mbar in the coating chamber during coating.
2. Method according to claim 1 characterized by that Ti or an alloy based on Ti, is evaporated.
3. Method according to claim 1 characterized by that the pressure is increased by introduction of gas into the coating chamber.
4. Method according to claim 3 characterized by that the gas is a nitrogen containing gas, an oxidizing gas or a non-reactive gas.
5. Method according to claim 1 characterized by using a pressure of at least $5 \cdot 10^{-5}$ mbar, preferably at least $1 \cdot 10^{-4}$ mbar in the coating chamber during coating.
6. Method according to claim 1 characterized by that the electron beam evaporation process is a non-activated process.
7. Method according to any of the preceding claims characterized by that Ti is evaporated and that the pressure is increased to at least $5 \cdot 10^{-5}$ mbar, preferably $1 \cdot 10^{-4}$ mbar, by means of a nitrogen containing gas.
8. Method according to any of the claims 1-6 characterized by that Ti is evaporated and that the pressure is at least $1 \cdot 10^{-4}$ mbar and accomplished by means of Ar or any other inert gas or gas mixture.

9. Method according to any of the preceding claims characterized by that the surface of the substrate is cleaned, such as by a degreasing bath followed by ion-assisted etching, before coating.

5 10. Method according to any of the preceding claims characterized by that the temperature of the substrate is kept below 300 °C during coating.

11. Method according to any of the preceding claims characterized by that at least two coating layers are applied at an increased pressure, optionally at
10 different pressures.

12. Method according to any of the preceding claims characterized by that the electron beam evaporation process is conducted in an apparatus for continuous coating of a substrate.
15

13. Method according to any of the preceding claims characterized by that the coated substrate is treated further by heat treatment, mechanical treatment, such as bending, stretching or stamping or the like; or surface treated, such as painted with a lacquer or oxidized.
20

14. Method according to any of the preceding claims characterized by that the metallic substrate is Fe, Al, Ti, Mg, Ni, Cu or any alloy based of any of these elements.

25 15. Method according to claim 14 characterized by that the metallic substrate is stainless steel.

16. Method according to claim 14 characterized by that the metallic substrate is Fe₆₄Ni₃₆.
30

17. Method according to any of the preceding claims characterized by that the metallic substrate is in the form of a strip, foil, tube, wire, plate or bar.

18. Method according to any of the preceding claims characterized in that
5 the coating has sub-micrometer sized grains and is substantially hydrophilic.

19. Metallic substrate coated with a coating comprising Ti characterized in that the coating sub-micrometer sized grains and is substantially hydrophilic.

10 20. Metallic substrate according to claim 19 characterized in that the coating is non-stoichiometric titanium nitride with a deficiency of nitrogen.

21. Metallic substrate according to claim 19 characterized in that the coating consists essentially of Ti.

15

22. Metallic substrate according to any of the claims 19-21 characterized in that the substrate is Fe, Al, Ti, Mg, Ni, Cu or any alloy based of any of these elements.

20 23. Metallic substrate according to claim 22 characterized in that the substrate is stainless steel.

24. Metallic substrate according to claim 22 characterized in that the substrate is Fe₆₄Ni₃₆.

25

25. Metallic substrate according to any of claims 19-24 characterized in that a layer of adhesive or lacquer is provided in direct contact with the Ti comprising coating.

26. Method of producing a metal laminate or a fiber metal laminate characterized by incorporating at least one coated substrate produced in accordance with the method of any of the claims 1-18.

5 27. Metallic laminate characterized in that it comprises a coated substrate in accordance with any of the claims 19-25.

28. Fiber metal laminate characterized in that it comprises a coated substrate in accordance with any of the claims 19-25.

10

29. Biomedical device characterized in that it comprises a coated substrate in accordance with any of the claims 19-25.

15 30. Lacquered stainless steel product characterized in that it comprises a coated substrate in accordance with any of the claims 19-25.

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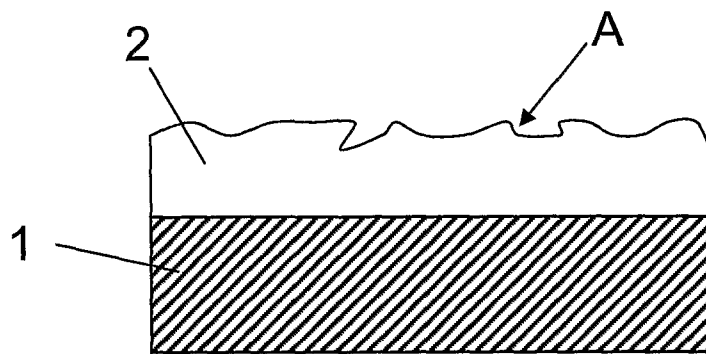


Fig. 1

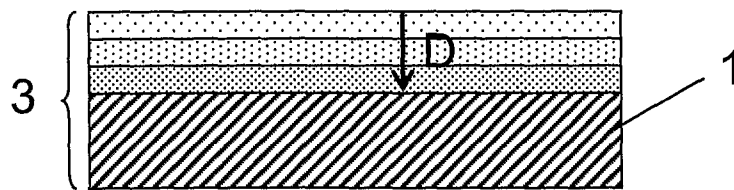


Fig. 2

2/9

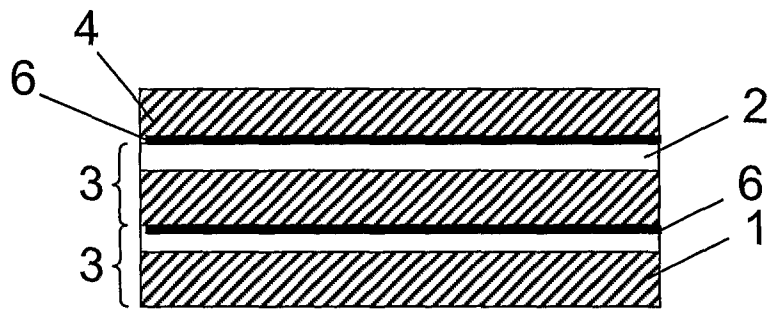


Fig. 3

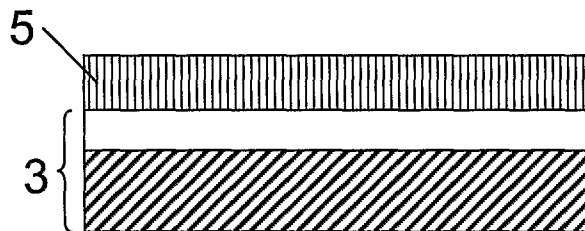


Fig. 4

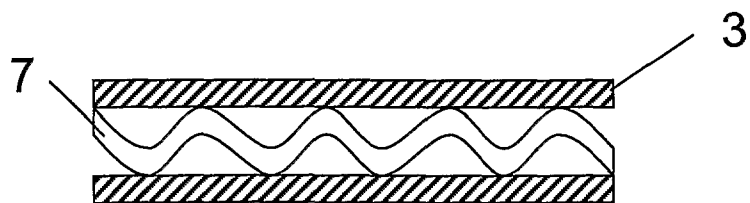


Fig. 5

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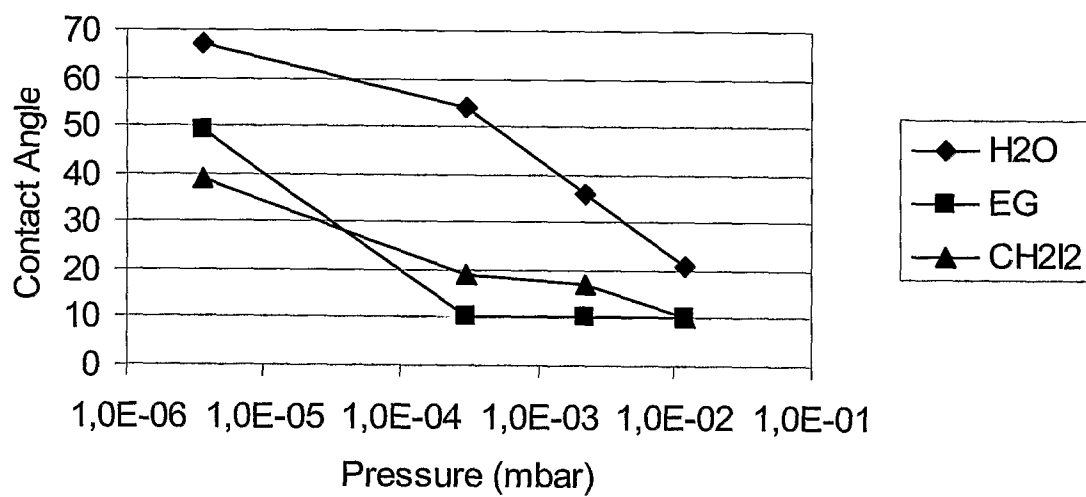


Fig 6.

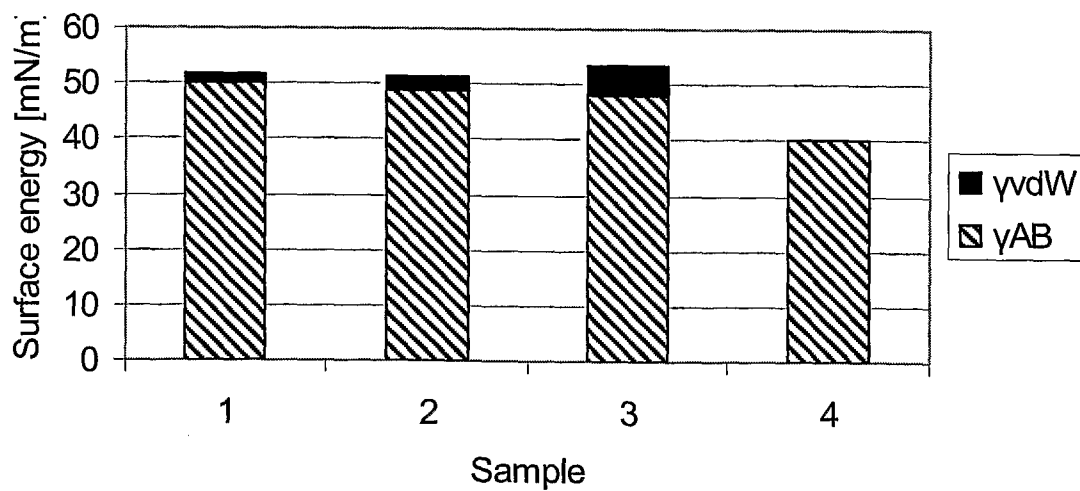


Fig 7.

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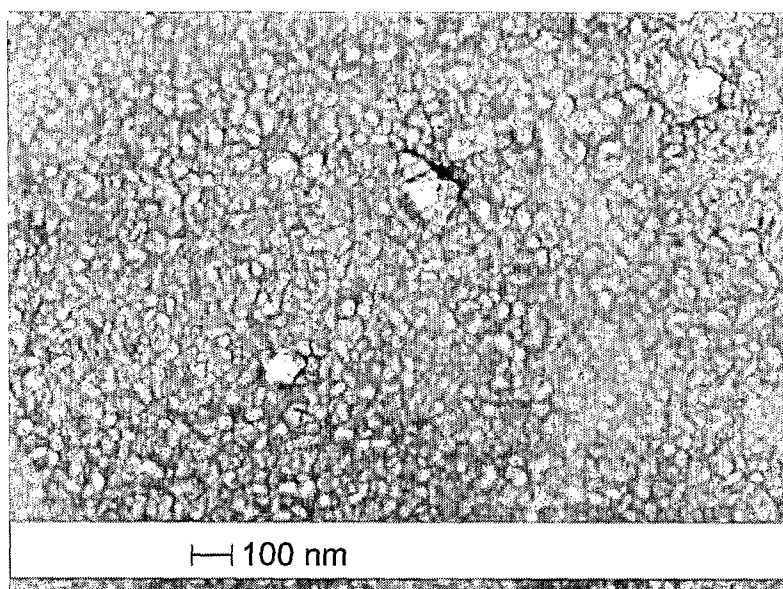


Fig 8a.

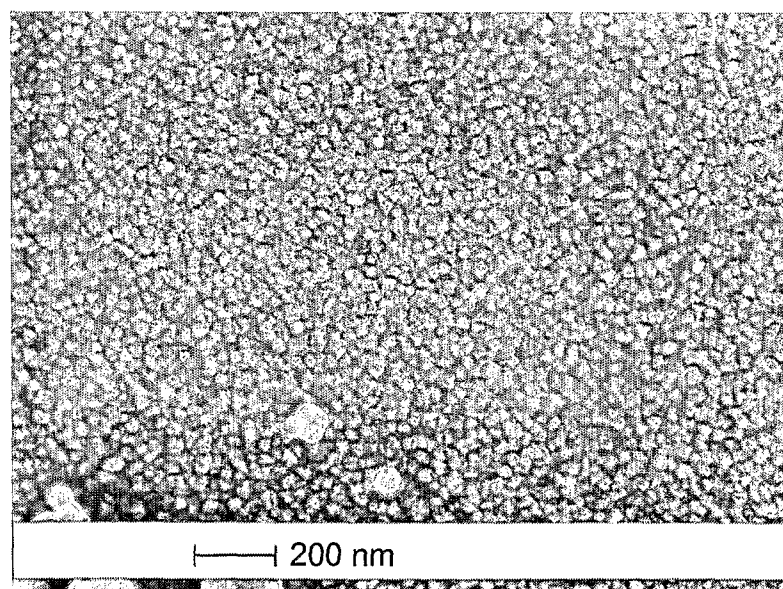


Fig 8b.

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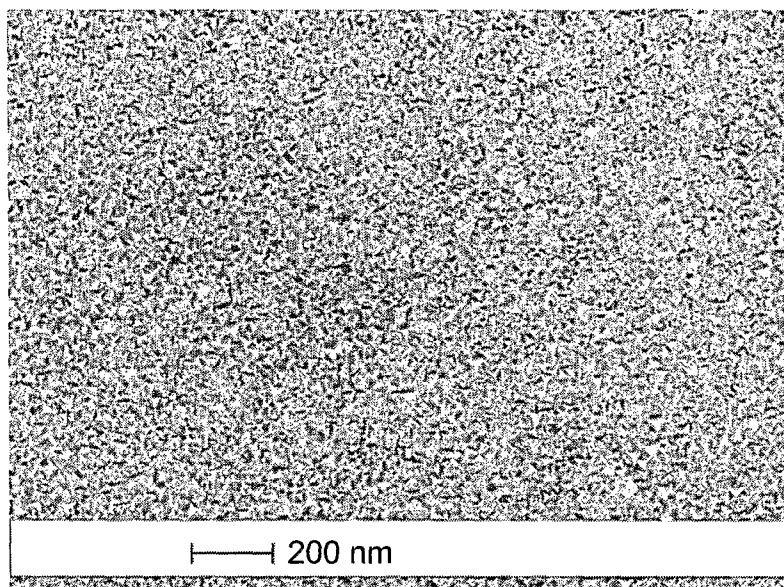


Fig 8c.

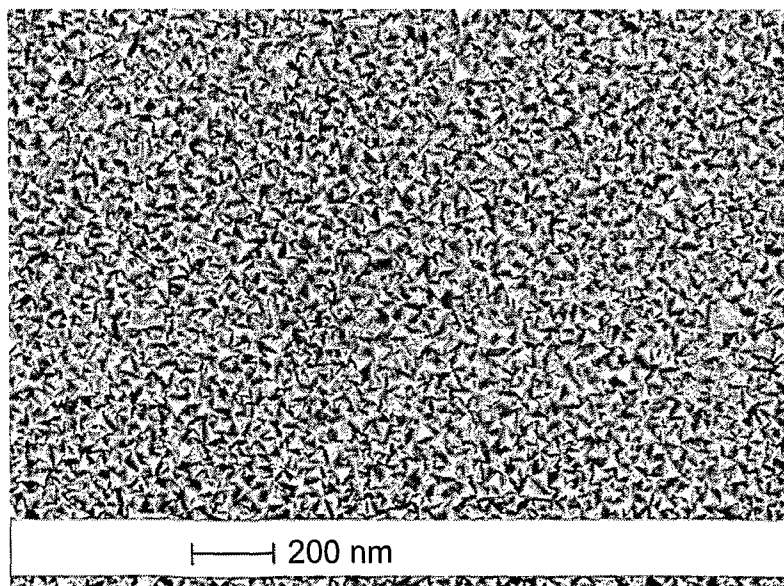


Fig 8d.

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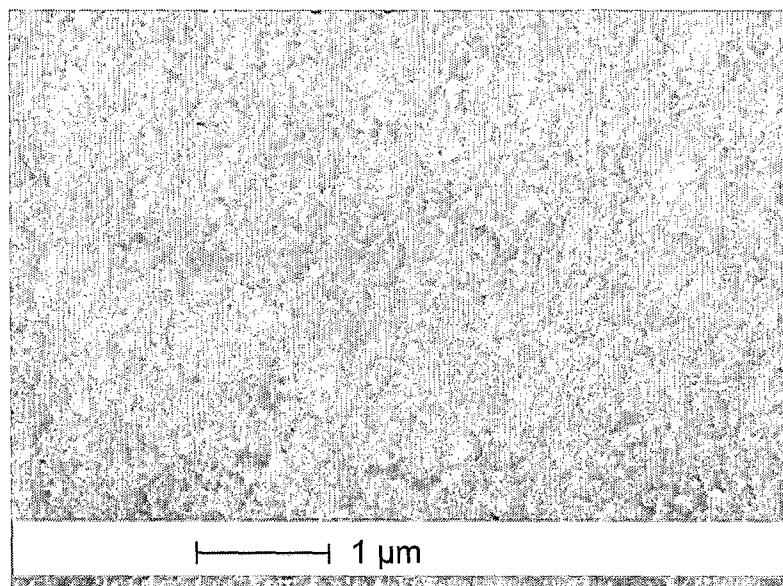


Fig 9a.

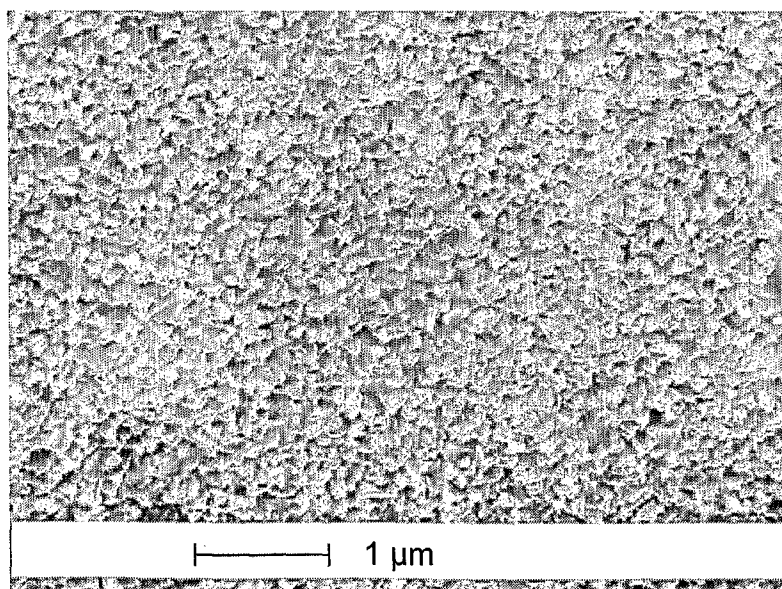


Fig 9b.

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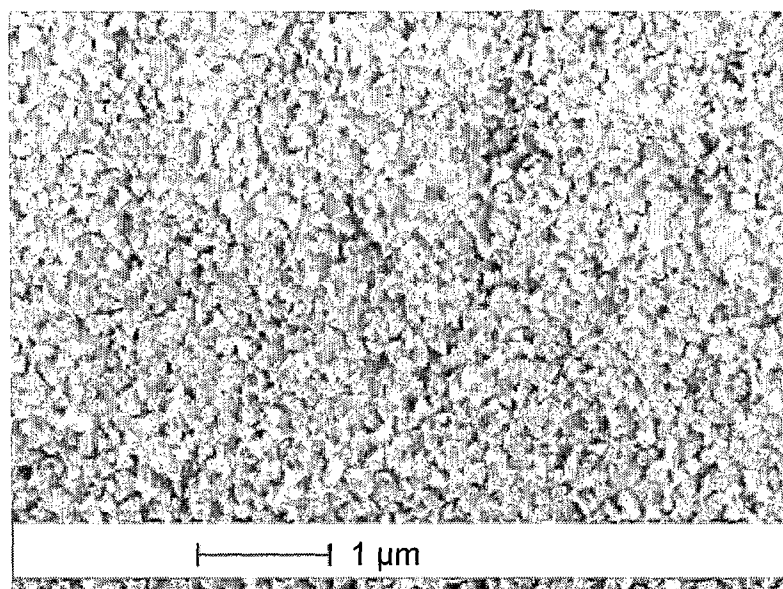


Fig 9c.

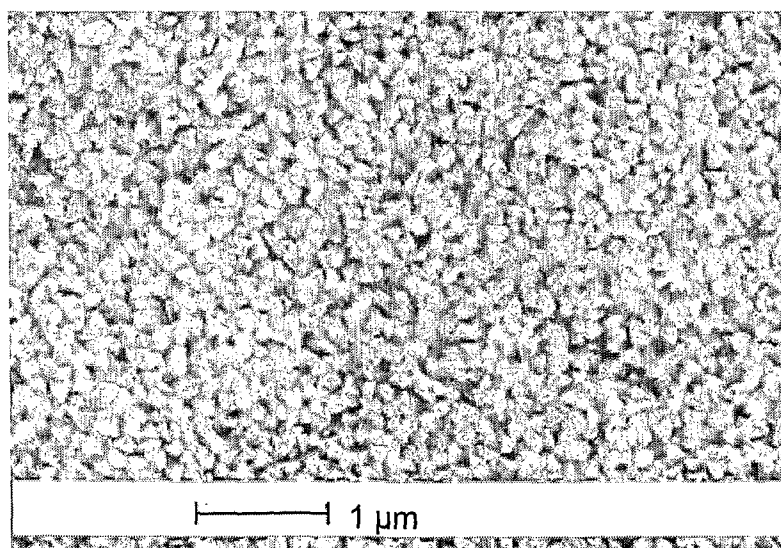


Fig 9d.

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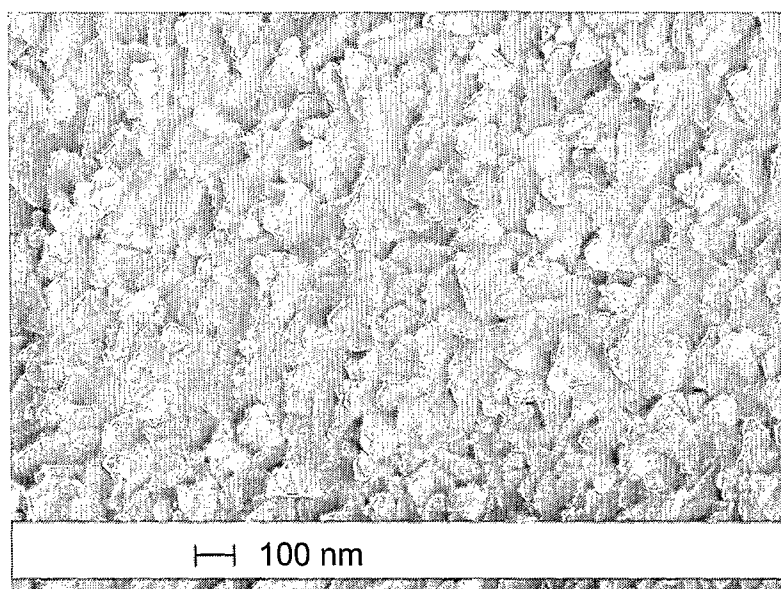


Fig 9e.

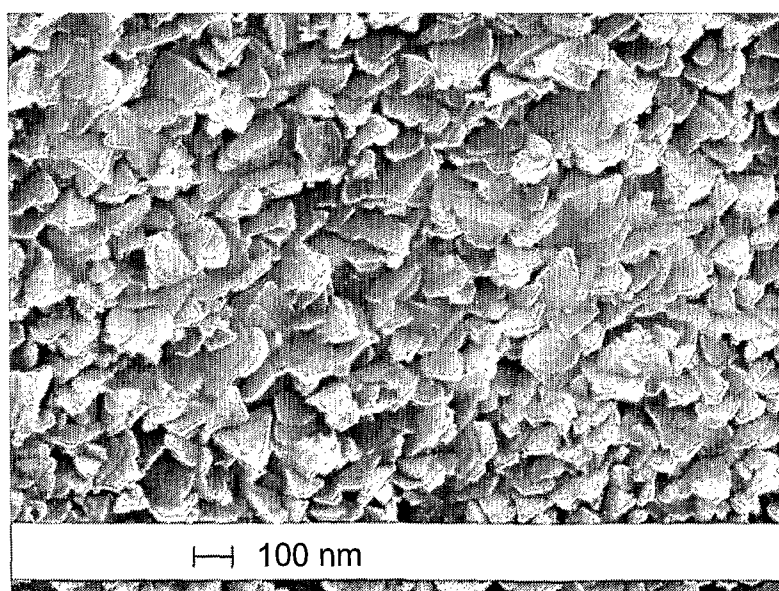


Fig 9f.

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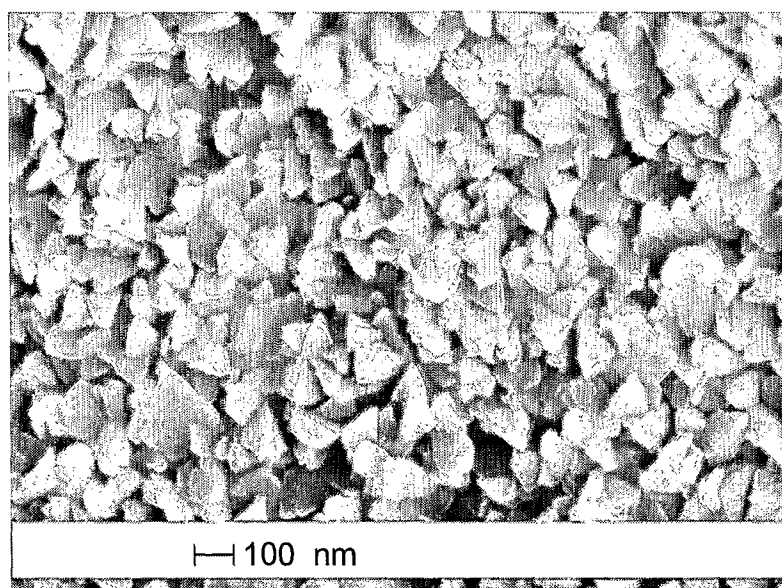


Fig 9g.

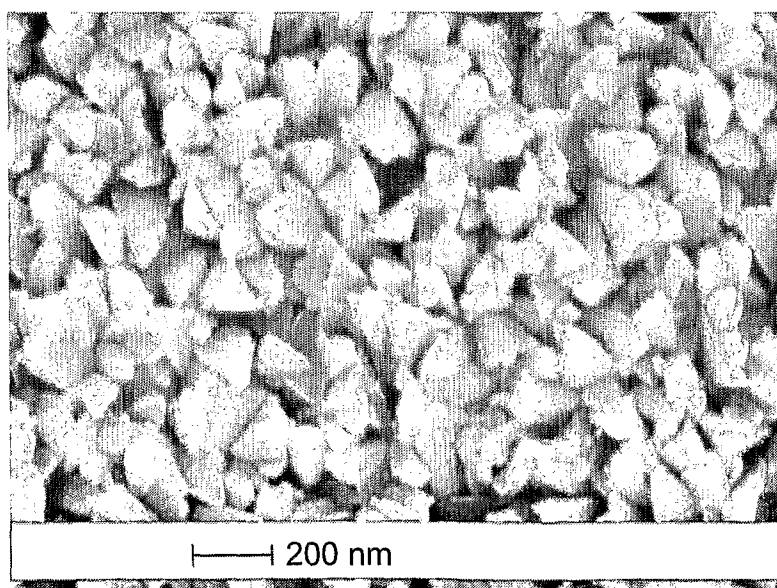


Fig 9h.

INTERNATIONAL SEARCH REPORT

International application No

PCT/SE2006/000894

A. CLASSIFICATION OF SUBJECT MATTER

INV. C23C14/16 C23C14/34 C23C14/06

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)
C23C

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

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X	EP 0 344 316 A1 (MATSUSHITA ELECTRIC IND CO LTD [JP]) 6 December 1989 (1989-12-06) page 2, line 45 - page 3, line 5; example 1; table 7	1-8, 10, 12-14, 17, 19-22, 26-29
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☒ Further documents are listed in the continuation of Box C.

☒ See patent family annex.

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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

12 March 2007

Date of mailing of the international search report

23/03/2007

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INTERNATIONAL SEARCH REPORT

International application No

PCT/SE2006/000894

C(Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

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International application No

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