



(11) **EP 1 818 431 A1**

(12) **EUROPEAN PATENT APPLICATION**

(43) Date of publication:
15.08.2007 Bulletin 2007/33

(51) Int Cl.:
D01D 5/00 (2006.01) C23C 18/02 (2006.01)

(21) Application number: **06425079.8**

(22) Date of filing: **13.02.2006**

(84) Designated Contracting States: AT BE BG CH CY CZ DE DK EE ES FI FR GB GR HU IE IS IT LI LT LU LV MC NL PL PT RO SE SI SK TR Designated Extension States: AL BA HR MK YU (71) Applicant: CRF Societa' Consortile per Azioni 10043 Orbassano (Torino) (IT) (72) Inventors: • Carotenuto, Gianfranco C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT) • Martorana, Brunetto C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT)	• La Peruta, Gianluca C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT) • Butera, Francesco C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT) • Perlo, Piero C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT) • Innocenti, Gianfranco C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT) • Nicolais, Luigi C.R.F. Soc. Consortile Azi. 10043 Orbassano (Torino) (IT) (74) Representative: Freyria Fava, Cristina Buzzi, Notaro & Antonielli d'Oulx Srl Via Maria Vittoria, 18 10123 Torino (IT)
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(54) **Process for the manufacture of a noble metal having fibrous morphology**

(57) A process for the manufacture of a noble metal having fibrous morphology comprising the phases of:
i) preparation of a colloidal suspension of a metal in the elementary state in the presence of a polymer;
ii) separation of the metal in the elementary state and the

polymer to obtain a metal-polymer nanocomposite; and
iii) combustion of the metal-polymer nanocomposite with consequent elimination of the polymer phase to obtain a metal having fibrous morphology.

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Description

[0001] The present invention concerns a new process for the manufacture of metals with fibrous morphology, in particular a metallic material with fibrous morphology having fibres of nanometric thickness.

TECHNICAL BACKGROUND OF THE INVENTION

[0002] The marked difficulty of handling and using metallic nanostructures is chiefly connected to their very marked tendency to aggregation.

[0003] In practice almost all the atoms contained in a metallic nanoparticle system lie on the surface and therefore possess high mobility, which causes rapid welding of their metal surfaces -- when these come into contact -- through mechanisms of solid-phase atomic diffusion. It should also be said that, according to different thermodynamic theories that have been verified experimentally, metallic phases of nanometric dimensions present melting points that are significantly lowered compared to the corresponding massive metals, and it has sometimes been hypothesised that these systems are in a condition fluctuating between the solid and the liquid [1-4].

[0004] The aggregation of metallic nanoparticles represents a considerable drawback since it involves the complete loss of the mesoscopic characteristics (e.g. plasma absorption, fluorescence, etc.) and small metallic masses of sub-micrometric dimensions are formed that are arborescent (dendrites) that cannot in practice be used for any technological application.

[0005] The aggregation of metallic nanoparticles, if appropriately controlled, may bring about the development of particular fibrous structures that can have significant technological applications in various sectors (e.g. electrodes for batteries [9-11], electrostatic filters [12], oxygen sensors [13], sterilisers for the air [14], devices to dose ozone [15], heterogeneous catalysts [16], heat exchangers [17], membranes for ultrafiltration of biological liquids [17], etc). These materials also enable the welding characteristics of electric contacts to be improved, reducing contact resistance and, thus, reducing wastage of electricity [18].

[0006] The possibility of sintering ceramic powders at low temperature (800°C-1200°C) making use of powders of nanometric dimensions has been widely investigated and has been one of the chief motivations for the study of colloidal chemistry [19]. This sintering technique is based on the preparation of a precursor comprising the ceramic powder held together by a polymeric bonding agent suitably softened with appropriate plasticisers.

[0007] The polymeric bonding agent plays a very important role and is frequently comprised of polyvinyl pyrrolidone (PVP). PVP is an amorphous polymer that decomposes rapidly and quantitatively at relatively low temperatures (ca. 350-500°C). For this particular characteristic its use is widespread in the sector of sintering ceramic powders at low temperature [19-21]. In particular,

the material is used as a bonding agent for fine-grain ceramic powders, whereby a precursor tape can be made, subsequently heated in air at 250-300°C to completely burn the polymer bonding agent and then heated to 900-1400°C to conclude the sintering-densification of the ceramic material. The polymer burns in air without leaving any type of solid residue such that, at the completion of its combustion, the result is an intimately aggregated powder. Few other polymers present analogous characteristics (e.g. polyvinyl alcohol, PVA) and may thus be used in its place.

[0008] Special inks to metallise ceramic and glass substrata (a process known as *electroless plating* [22]) have been proposed, combining polymers (e.g. PVP, PVA) with very fine grain gold or silver powder.

DESCRIPTION OF THE INVENTION

[0009] The purpose of the present invention is to develop a new economic and innovative process for the manufacture of a metallic material with fibrous morphology.

According to the present invention, this purpose is achieved thanks to the solution described specifically in the attached claims. The claims form an integral part of the technical instruction provided here in regard to the invention.

The invention relates to a process for the manufacture of a metallic material of fibrous morphology and comprises the phases of:

- i) preparation of a colloidal solution of a metal in the presence of a polymer;
- ii) separation of metal and polymer from the colloidal suspension to obtain a metal-polymer nanocomposite; and
- iii) combustion of the metal-polymer nanocomposite to obtain a metal with fibrous structure.

The fibres present nanometric thickness and thus the surface development of the solid metal is the maximum that can be achieved for a porous structure.

DETAILED DESCRIPTION OF THE INVENTION

[0010] The invention will now be described in detail, purely as an example and without limiting intent, in reference to the attached figures, in which:

- figure 1 shows a TEM micrograph of an Ag-PVP nanocomposite. The inset shows the granulometric distribution of the particles;
- figure 2 shows a TEM micrograph of an Ag-PVP nanocomposite. The inset shows the granulometric distribution of the particles;
- figure 3 shows an XRD diffractogram of the Ag/PVP nanocomposite (a) and of a metallic silver standard (foil) (b);

-- figure 4 shows a TGA thermogram of an Ag/PVP nanocomposite heated in a flow of nitrogen from 25°C to 600°C at 10°C/min (a) and an EDS spectrum of the residue (b);-- figure 5 shows a TGA thermogram of an Ag/PVP nanocomposite heated in a flow of air from 25°C to 600°C at 10°C/min (a) and an EDS spectrum of the residue (b);-- figure 6 shows a series of four SEM micrographs of the residue of pyrolysis (a) and of combustion (from b to d) of an Ag/PVP nanocomposite;-- figure 7 shows an SEM micrograph of the residue of pyrolysis of an Ag/PVP nanocomposite containing clusters of silver of a few nanometres. In an embodiment that is preferred at present, the process according to the present invention comprises three distinct phases.

The first phase consists in the preparation of a colloidal suspension of the metal by alcohol reduction of an ionic precursor in the presence of a protective polymeric agent. The second phase entails isolating the metal-polymeric protector agent nanocomposite by co-precipitation of the two components from the colloidal suspension, and lastly the third phase entails combustion of the organic component of the nanocomposite such as to obtain a metallic material with fibrous structure.

[0011] However, the fibrous morphology is only produced when the nanocomposite presents a relatively reduced nano-load of metal (approximately 5% by weight).

[0012] The fibrous metallic structure, corresponding to a sort of metallic wool, has been obtained by burning a particular hybrid organic-inorganic nanostructured system in air, that is by burning a metal-polymer nanocomposite. From the structural standpoint this precursor is constituted of spherical metal nanoparticles with mean particle size of approximately 3-15 nm, not aggregated but dispersed uniformly within a continuous polymeric matrix in general comprised of polyvinyl pyrrolidone (PVP) of low molecular weight (10,000 u.m.a.).

[0013] Two-phase systems of this type (which can be defined as metal-polymer nanocomposites) may be produced with a very high degree of purity, as will be described below. Numerous catalytically-active noble metals (e.g. Au, Ag, Pd, Pt, Rh, etc.) may be produced in the form of a colloidal suspension by reduction of the corresponding ions with alcohols [5-8,23]. These ions originate from the disassociation of electrolytes (ionic solids) typically consisting of inorganic salts (sulphates and nitrates) or organic salts (acetates). As reducing agent, vicinal diols are usually preferred, since these chemical compounds possess a much greater reducing power than simple alcohols and thus the reduction may also be carried on at ambient temperature.

[0014] Usually the reducing agent is introduced in larger than stoichiometric quantities, since it also acts as organic solvent in which the reaction takes place and is thus also the means of growth of the nanometric solid metallic phase. A frequently-used reducing agent is eth-

ylene glycol (1,2-ethanediol). With some metal salts (e.g. AgNO₃) the reduction reaction may easily be performed at ambient temperature and consists in dehydration of the glycol with formation of acetaldehyde and subsequent reduction of the metal ion by the acetaldehyde with formation of metallic atoms and molecules of acetal.

[0015] The metal atoms form metallic clusters (aggregations of a small number of metal atoms) once the system exceeds the saturation limit.

[0016] The reduction reaction is carried on in presence of a protective agent whose function is to become adsorbed onto the surface of the metal particles, stabilising the surface and thus preventing particle aggregation, which would otherwise be made possible by their frequent collisions in the reaction environment due to Brownian motion.

[0017] These stabilising agents are in general organic molecules able to be adsorbed with varying degree of stability onto the surface of the metal particles so as to comprise an organic coating. Polymeric protective agents are particularly valid. Among these, those most frequently used are poly(vinyl pyrrolidone) (PVP) and polyvinyl alcohol (PVA). That is, the same polymers that are used as bonding agents in the sinteration of hyper-fine ceramic powders.

[0018] Ethylene glycol also shows some capability to be adsorbed onto metal surfaces; however, the protective power of this molecule is quite limited and thus inadequate in the presence of high concentrations of particles. Furthermore, the polymeric stabiliser is also able to favour the reduction reaction of the colloidal metal and the phase separation process.

[0019] At the end of the synthesis process, the metallic nanoparticles may be isolated from the liquid medium in which they are dispersed, for example, through the co-precipitation technique, that is to say precipitation together with the polymeric stabiliser. In particular, since the metal particles are linked to the polymeric stabiliser in a stable fashion through a co-ordination link involving numerous lateral polar groups of the polymer, the particles are completely precipitated together with the polymer by varying the polarity of the liquid dispersing medium.

[0020] The polarity of ethylene glycol may be substantially varied by the addition of acetone. The two solvents are miscible in all proportions and successive additions of acetone gradually lower the polarity of the resulting binary mixture. From this liquid phase that gradually becomes less polar, PVP ends up by precipitating, taking with it the metal nanoparticles, which are stably linked to its structure by non-bond interactions.

[0021] The phase that coagulates (coacervates) initially consists of a sort of soft semisolid due to the presence of a large quantity of ethylene glycol that plasticises the PVP. However, if separated and washed repeatedly with acetone, if necessary applying ultrasound with a sonicating bath, this material gradually becomes more solid as the last molecules of ethylene glycol diffuse outwards.

[0022] Lastly, when the metal/PVP nanocomposite material is left to dry in the air and the acetone is completely eliminated, a rigid polymeric solid is obtained. This material is absolutely stable, but must be stored in an anhydrous environment (desiccator) to prevent it from absorbing water, before it is converted into metallic wool by thermolysis.

[0023] Figures 1 and 2 show the microstructures of two polymeric Ag/PVP nanocomposites obtained starting from different quantities of silver salt. Figure 3a shows the XRD diffractogram of the Ag/PVP nanocomposite after drying, whereas figure 3b shows the diffractogram of a metallic silver standard; as may be seen, the metal produced by alcohol reduction of the corresponding salts is crystalline and nanometric (reflection broadening).

[0024] The dried nanocomposite material is then burned in air. In particular, since the temperature required for combustion is relatively low (350°C-400°C), the process is conducted using a simple quartz kiln (or tubular quartz oven) operating in air flow.

[0025] In order to establish the thermal threshold required for combustion of the material, a specimen of nanocomposite of approximately 15 mg was placed inside a thermogravimetric balance (TGA, TA-Instrument Mod.Q500) and the material was subjected to thermal scanning from ambient temperature to 600°C at 10°C/min. Tests in nitrogen flow were also carried out under the same heating conditions.

[0026] Figure 4a shows the TGA thermogram of a specimen of Ag/PVP heated in a flow of nitrogen (pyrolysis). As may be seen, decomposition began at 350°C and was practically complete at approximately 470°C, with a single weight loss. The residual weight was equal to 16% of the initial mass, and was found to be higher than the value obtained by combustion of the specimen in air under the same heating conditions. This may be attributed to the formation of carbon residue produced by thermal decomposition (pyrolysis) of the polymer. The presence of this product of pyrolysis was confirmed by elemental analysis carried out on the residue through an X-ray microprobe (EDS, LINK AN10000) (see Figure 4b). EDS analysis carried out on the residue showed the presence of elements that constitute the polymeric matrix (PVP), principally carbon and traces of nitrogen, in addition to the signal for silver.

[0027] Figure 5a shows the TGA thermogram of the Ag/PVP nanocomposite burned in air under the same conditions. In this case, a double weight loss was observed, respectively centred around 410°C and 490°C. Combustion of the Ag/PVP nanocomposite in air left a residue equal to 4% of the initial mass, suggesting complete decomposition of the polymeric matrix. Indeed, subsequent elemental analysis performed by EDS showed that the residue was exclusively comprised of metallic silver (see figure 5b).

[0028] The particular fibrous morphology of the product of thermal decomposition of the Ag/PVP nanocomposite was visualised with the aid of a scanning electron

microscope (SEM, Cambridge S360). Figure 6a shows the residue of the Ag/PVP specimen burned in nitrogen (pyrolysis). The material presents a porous structure, but highly irregular. Particles of silver cannot be distinguished and thus must still be englobed in the carbon matrix generated during pyrolysis. Combustion of the nanocomposite in air, on the contrary, brought about the formation of a fibrous metallic structure, shown in figures 6a, 6c and 6d. The fibres are practically continuous and have a diameter of approximately 2 µm. Furthermore, they are linked together to produce a network the average size of whose mesh is below 10 µm in diameter.

[0029] By controlling the nucleation conditions (reaction temperature close to 40°C) of the metallic phase in the PVP/ethylene glycol system it is possible to generate a high quantity of silver particles of very small dimension. These Ag/PVP nanocomposites are able by combustion to produce silver fibres of a diameter of a few hundred nm (see figure 7).

[0030] Combustion in air of Ag/PVP nanocomposites having a reduced nanometric metallic load (approximately 5% by weight) leads to a fibrous-networked structure constituted of metal alone.

[0031] Naturally, the details of the process and its embodiments may be widely varied with regard to what is described and illustrated here without thereby departing from the sphere of protection of the present invention, as defined in the attached claims.

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Claims

1. Process for the manufacture of a metal having fibrous morphology comprising the phases of:

- i) preparation of a colloidal suspension of a metal in the elementary state in the presence of a polymer;
- ii) separation of the metal in the elementary state and of the polymer, to obtain a metal-polymer

nanocomposite;

iii) combustion of the metal-polymer nanocomposite, to obtain a metal having fibrous morphology.

2. Process according to claim 1, **characterised in that** said colloidal suspension is prepared by reduction of a salt of the metal by means of a reducing agent in a solvent, such as to obtain a colloidal suspension of the metal in the elementary state in said solvent.
3. Process according to claim 2, **characterised in that** said solvent and said reducing agent present the same composition.
4. Process according to claim 2, **characterised in that** said reducing agent is an alcohol, preferably a vicinal diol.
5. Process according to claim 4, **characterised in that** said vicinal diol is 1,2-ethanediol.
6. Process according to any of the claims from 2 to 5, **characterised in that** said reducing agent is used in greater quantities than those of the stoichiometric relationship between metal and reducing agent.
7. Process according to any of the above claims, **characterised in that** said polymer is soluble in said solvent.
8. Process according to claim 7, **characterised in that** said polymer is selected from among polyvinyl pyrrolidone and polyvinyl alcohol.
9. Process according to any of the above claims, **characterised in that** said phase i) of preparation of the colloidal suspension is carried out at a temperature in the range 25-50°C, preferably 35-45 °C.
10. Process according to any of the above claims, **characterised in that** said metal-polymer nanocomposite contains a quantity of metal below 10% by weight.
11. Process according to any of the above claims, **characterised in that** said metal-polymer nanocomposite contains a quantity of metal less than 7% by weight.
12. Process according to any of the above claims, **characterised in that** said metal-polymer nanocomposite contains a quantity of metal equal to 5% by weight.
13. Process according to any of the above claims, **characterised in that** said phase ii) of separation of the metal in the elementary state and of the polymer from the suspension involves co-precipitation of the metal in the elementary state and of the polymer.

14. Process according to claim 12, **characterised in that** said phase ii) of separation is achieved by varying the polarity of the suspension.
15. Process according to claim 13, **characterised in that** said phase ii) of separation of the metal-polymer nanocomposite also includes a phase of drying the metal-polymer nanocomposite that has been coprecipitated. 5
16. Process according to any of the above claims, **characterised in that** is said phase iii) of combustion of the metal-polymer nanocomposite is conducted at a temperature between 300 and 500°C. 10
17. Process according to any of the above claims, **characterised in that** is said phase iii) of combustion of the metal-polymer nanocomposite is conducted in air. 15
18. Process according to any of the above claims, **characterised in that** said metal is selected from among Au, Ag, Pd, Pt, Rh, Ir. 20
19. Process according to any of the claims from 2 to 18, **characterised in that** said metal in the elementary state presents a particulate morphology. 25
20. Process according to any of the claims from 2 to 19, **characterised in that** said metallic particles present a mean diameter between 1 and 20 nm. 30
21. Metallic material having fibrous morphology obtained with the process according to any of the claims from 1 to 20. 35
22. Metallic material according to claim 21, **characterised in that** it presents continuous fibres with diameter below 5 micron. 40
23. Metallic material according to claim 22, **characterised in that** said diameter is equal to approximately 2 micron.
24. Metallic material according to any of the claims from 21 to 23, **characterised in that** it presents a networked structure 45

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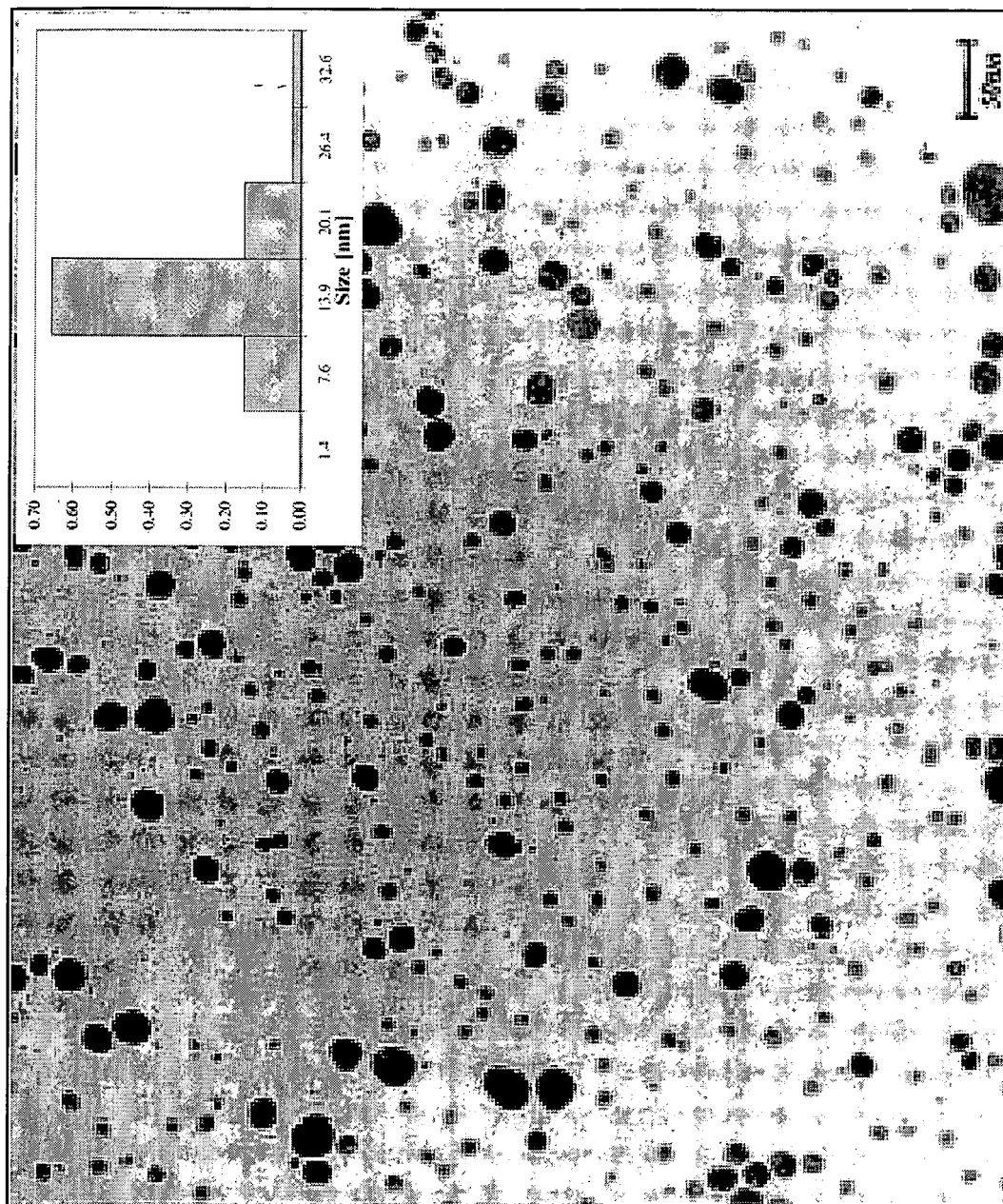


Fig. 1

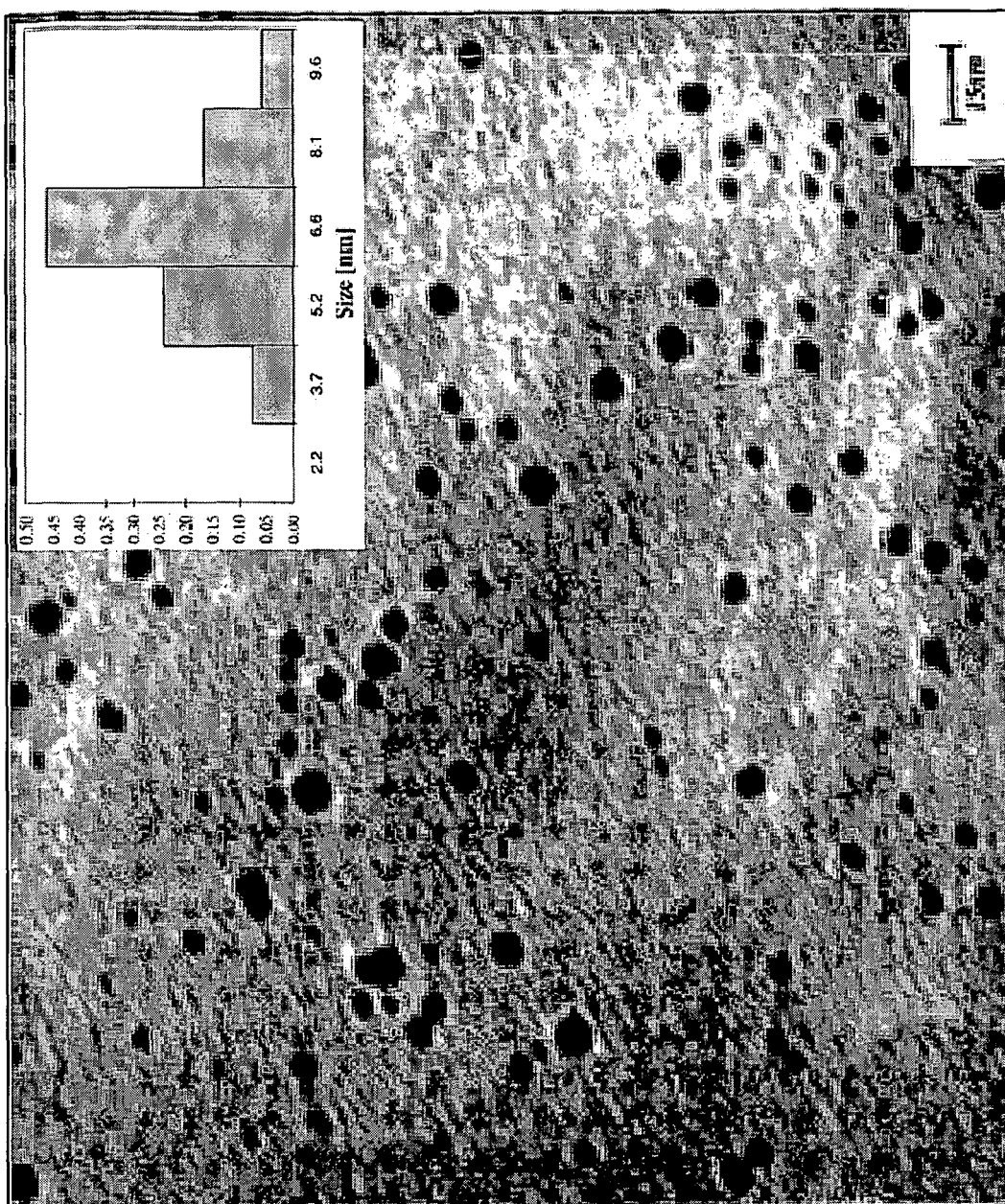


Fig. 2

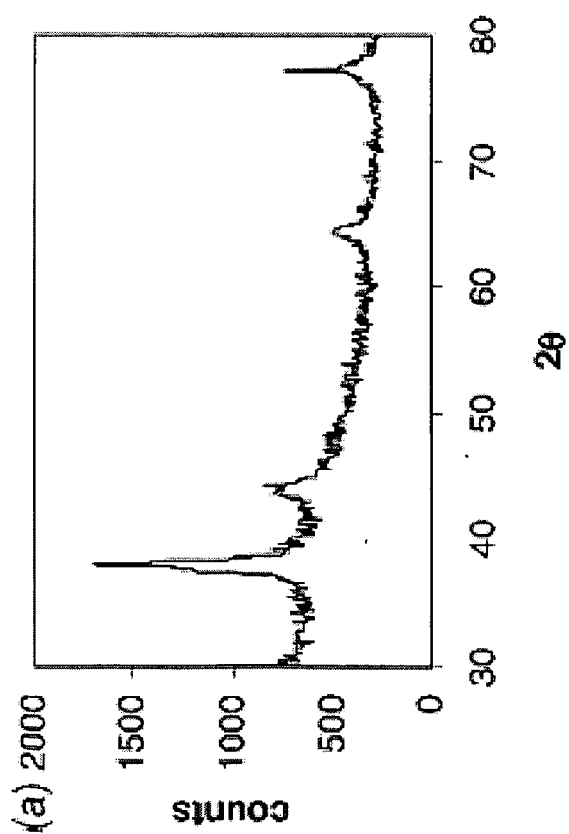


Fig. 3a

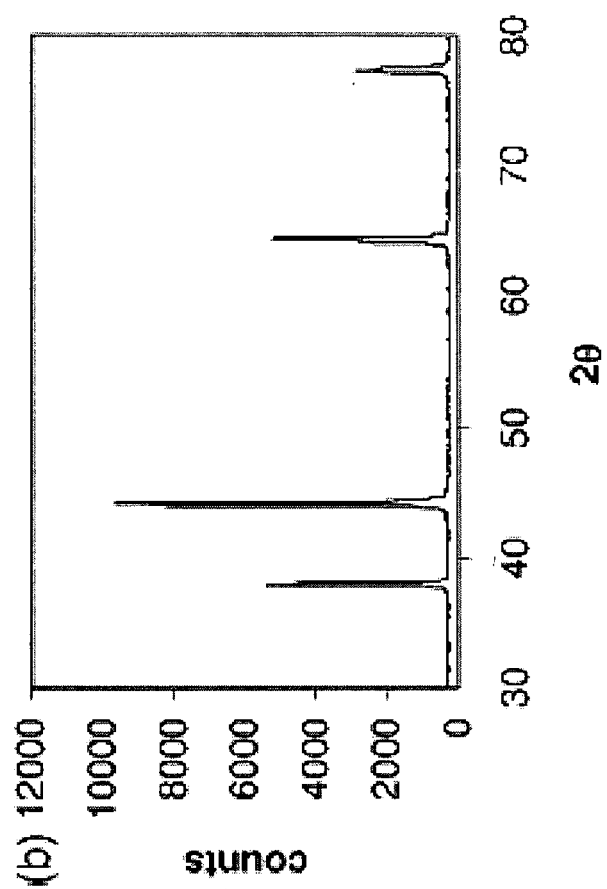


Fig. 3b

Fig. 4a

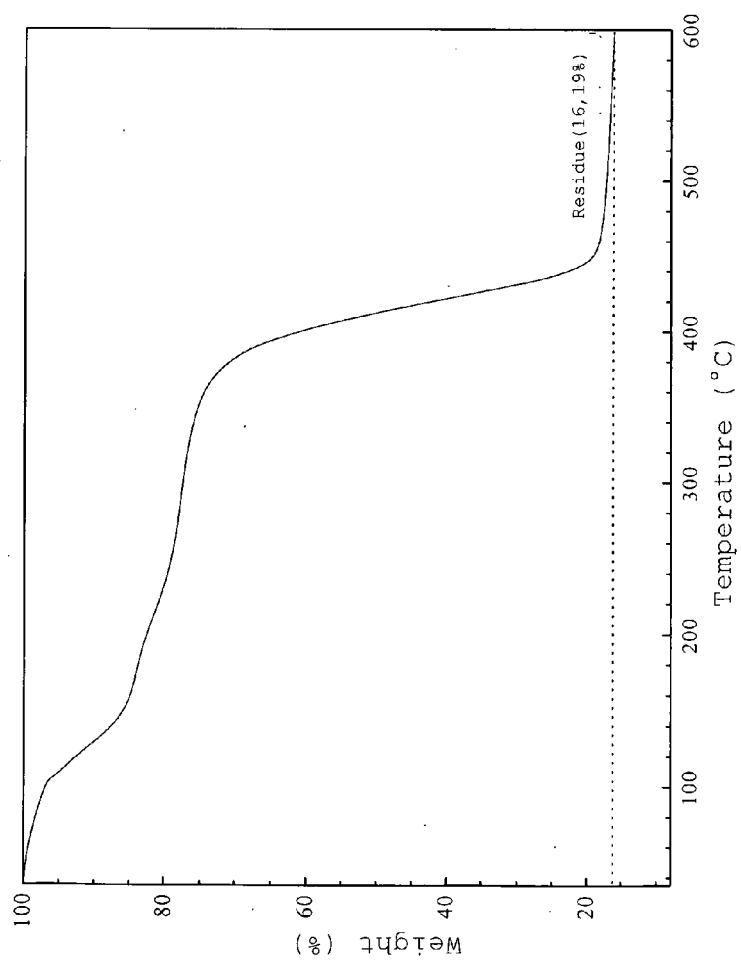
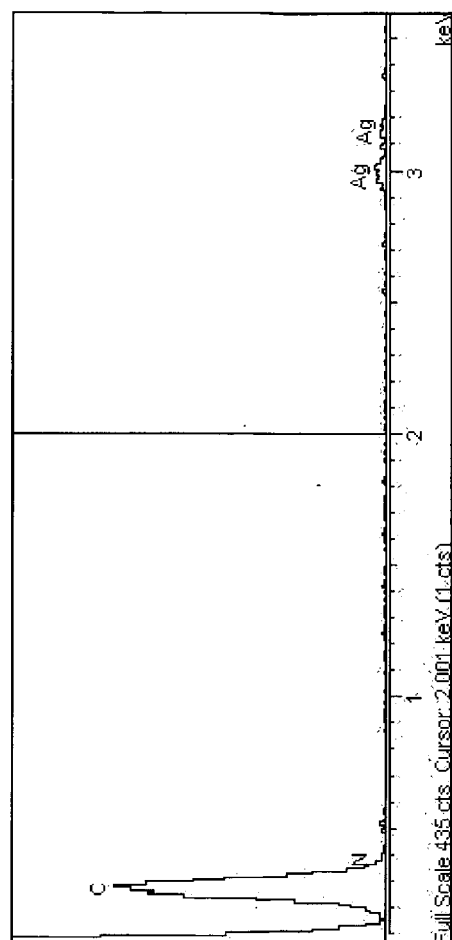


Fig. 4b



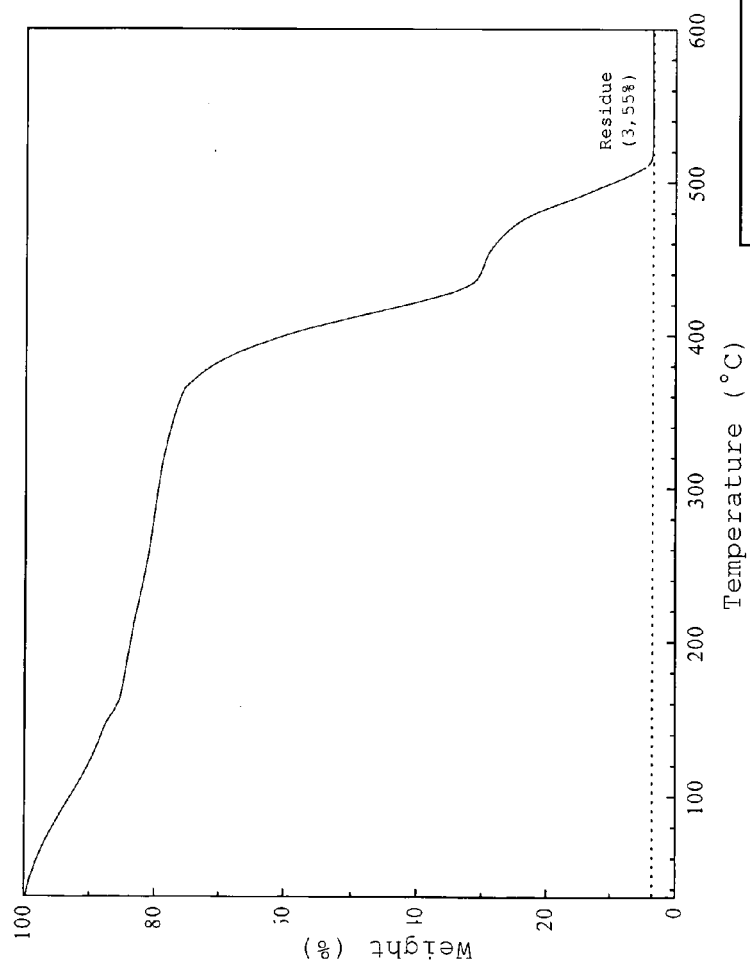


Fig. 5a

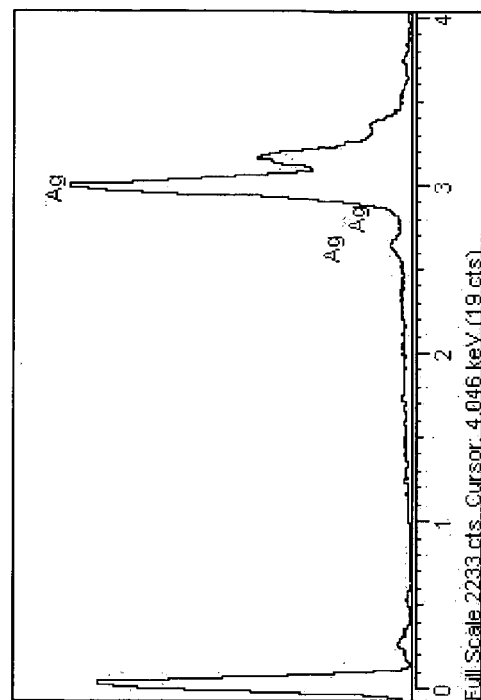


Fig. 5b

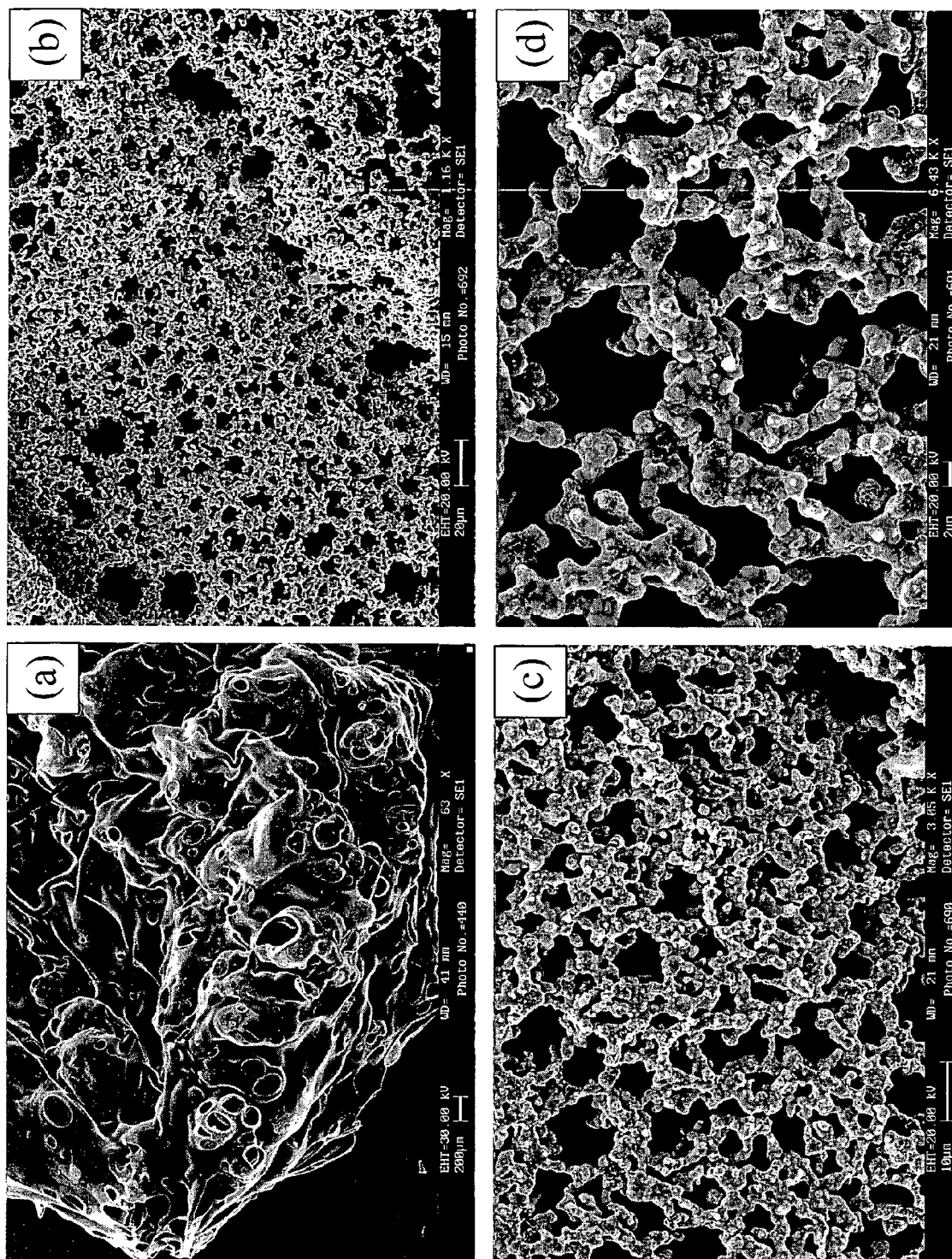


Fig. 6

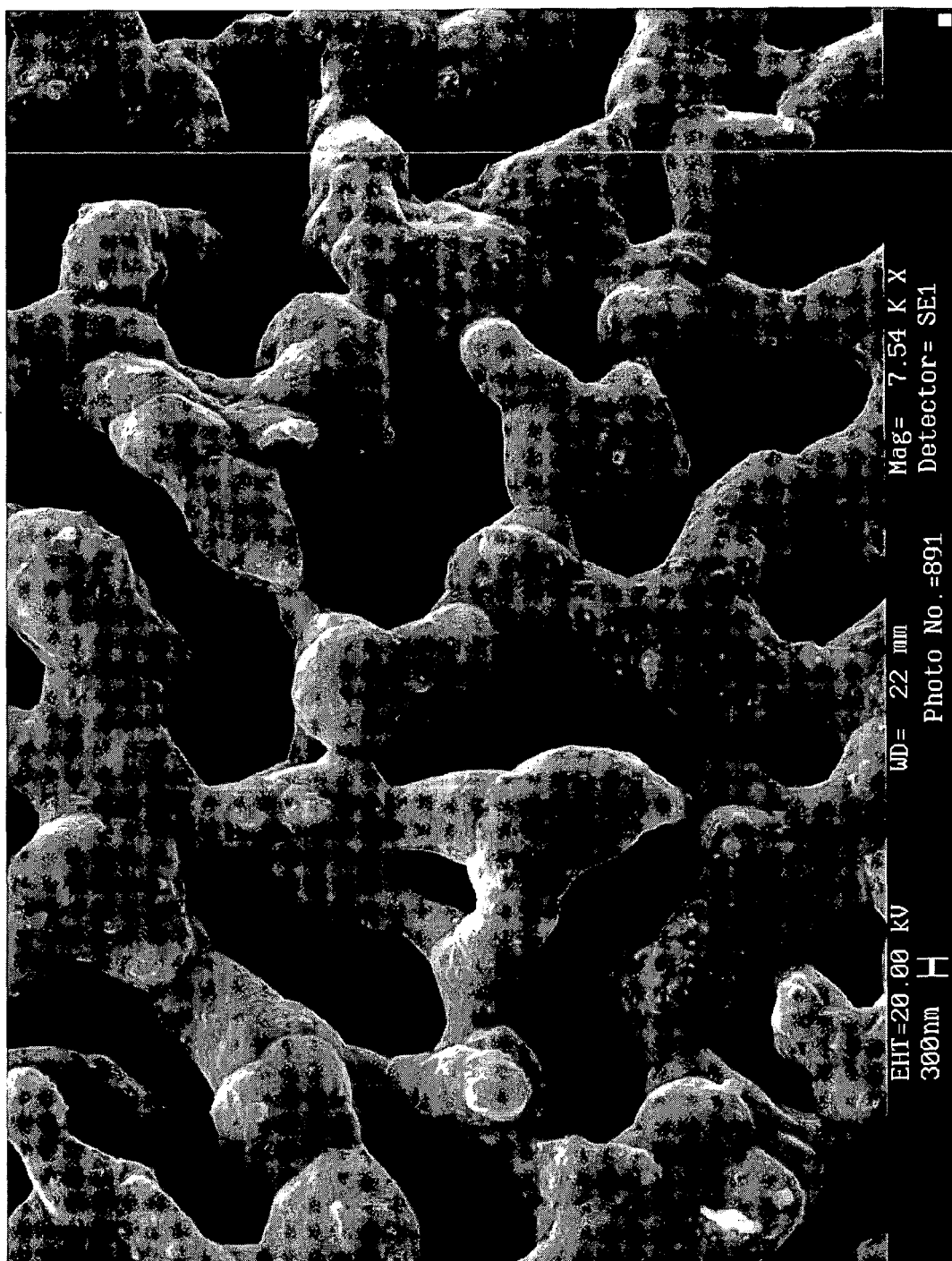


Fig. 7



European Patent
Office

EUROPEAN SEARCH REPORT

Application Number
EP 06 42 5079

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (IPC)
X	DE 196 39 632 A1 (ZENNECK, ULRICH, PROF. DR., 91301 FORCHHEIM, DE; ZENNECK, ULRICH) 9 April 1998 (1998-04-09) * the whole document *	1-24	INV. D01D5/00 C23C18/02
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			TECHNICAL FIELDS SEARCHED (IPC)
			D01D C23C
The present search report has been drawn up for all claims			
Place of search Munich		Date of completion of the search 18 July 2006	Examiner Ramos Flores, C
CATEGORY OF CITED DOCUMENTS X : particularly relevant if taken alone Y : particularly relevant if combined with another document of the same category A : technological background O : non-written disclosure P : intermediate document		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons & : member of the same patent family, corresponding document	

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

EP 06 42 5079

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18-07-2006

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
DE 19639632	A1	09-04-1998	NONE	
US 6346136	B1	12-02-2002	NONE	
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