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(71) **Applicant** *(for all designated States except US)*: **EL-MARCO s.r.o.** [CZ/CZ]; V Horkach 76, 46007 Liberec (CZ).

(72) **Inventors; and**
(75) **Inventors/Applicants** *(for US only)*: **DUCHOSLAV, Jiri** [CZ/CZ]; Cpakova 703, 25601 Benesov (CZ). **KAVAN, Ladislav** [CZ/CZ]; Na Slovance 34, 18200 Praha (CZ). **RUBACEK, Lukas** [CZ/CZ]; Na Drahach 476, 54233 Ryne v Podkrkonosi (CZ). **ZUKALOVA, Marketa** [CZ/CZ]; Kankovseho 1236, 18200 Praha (CZ). **PROCHAZKA, Jan** [CZ/—]; Kamenne Zehrovice 23, 27301 Kamenne Zehrovice (CZ).

(74) **Agent**: **MUSIL, Dobroslav**; Cejl 38, 60200 Brno (CZ).

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(54) **Title**: METHOD FOR PRODUCTION OF ANORGANIC NANOFIBRES AND/OR NANOFIBROUS STRUCTURES COMPRISING TIN, ANORGANIC NANOFIBRES AND/OR NANOFIBROUS STRUCTURES COMPRISING TIN

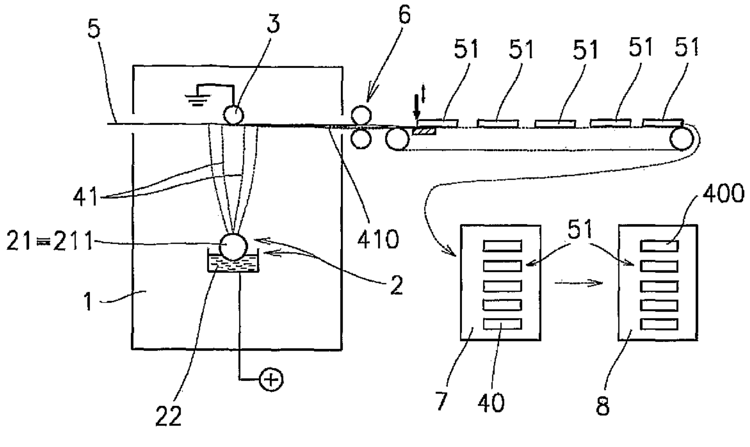

Fig. 1

(57) **Abstract**: The invention relates to the method for production of anorganic nanofibres and/or nanofibrous structures comprising TiN from a polymer matrix containing titanium alkoxide dissolved in a solvent system on basis of alcohol containing chelating agent, poly(vinylpyrrolidone) and addition of concentrated hydrochloric acid are through electrostatic spinning produced the organic/anorganic nanofibres, which are subject to calcination in the air atmosphere at the temperature from 350 to 800 °C and the produced $Ti0_2$ nanofibres are annealed in a stream of NH3 atmosphere at the temperature from 400 to 900 °C, by which the TiN nanofibres are created without the residual TiO_2.

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Method for production of anorganic nanofibres and/or nanofibrous structures comprising TiN, anorganic nanofibres and/or nanofibrous structures comprising TiN

Technical field

The invention relates to the method for production of anorganic nanofibres and/or nanofibrous structures comprising TiN.

Next to this, the invention relates to anorganic nanofibres and/or nanofibrous structure comprising TiN.

Background art

TiN excels with high hardness of cca 85 of Rockwell scale, high wear resistance, chemical stability and further special physical properties. It is used for surface finish of alloys of titanium, steels, aluminium and further materials for the purpose to improve their utility properties. Mostly this is applied as coating on surfaces of drills, lathe tools, screw cutters and similar tools by which they increase their service life up to several times. They provide the same effect on pressing tools, they prolong the life of forms for pressing of plastics and thanks to parameters of surface they also increase the quality of pressings. TiN coatings are produced directly through the PVD or CVD methods. Another property of TiN is electrical conductivity, resistance against corrosion and IR reflectivity. TiN features a gold-like colour, therefore it is often used for decoration purposes in jewellery, as a coating for spectacle frames, etc. It is hardly recognizable from gold coatings, but it features many times higher abrasion resistance. Recently the TiN coatings appear also on surgical instruments, at which they increase, besides their life, also the smoothness of cuts, moreover the TiN coating features antibacterial effects.

TiN in micro or nano form is advantageous from the point of view of high specific surface, at the same time of a minimum size, thanks to which it can be better incorporated into the structure of treated surfaces and composites. At present it is being produced only in a form of nano-powders or thin TiN layers.

Nanofibrous morphology of TiN, with thickness of fibres from tens to hundreds of nanometers, has a number of further important attributes at simultaneous keeping of all the above mentioned properties of TiN. Besides the high specific surface it features a distinct improvement in accessibility of surface.

For the time being, no other production methods of pure TiN nanofibres without further admixtures are known. For example patent JP1215718 discloses production of TiN nanofibres through annealing of TiO_2 nanofibres in NH3 atmosphere, nevertheless the resultant nanofibres whose length is within the range from 300 to 2000 nm and the ratio of their length and diameter from 3 to 200, contain up to 40 % of residual O_2, or more precisely they contain the residual TiO_2.

There are also known production methods of nanoparticles of a pure TiN through annealing of TiO_2 in NH_3, nevertheless in the resultant product remain the residual structures of TiO_2. Phase-pure TiN is usually created at high temperatures when it is difficult to keep the fibrous morphology of the product.

The goal of the invention is to develop a production method of anorganic nanofibres and/or nanofibrous structures comprising TiN in pure state without residual TiO_2. At the same time the goal of the invention is to develop anorganic nanofibres and/or nanofibrous structures comprising TiN in pure state without residual TiO_2.

The principle of invention

The goal of the invention has been achieved through the metod for production of anorganic nanofibres and/or nanofibrous structures comprising TiN, whose principle consists in that, from the polymer matrix containing titanium alkoxide dissolved in a solvent system on basis of alcohol containing a chelating agent, poly(vinylpyrrolidone) and addition of concentrated hydrochloric acid are through electrostatic spinning produced the organic/anorganic nanofibres arranged in a nanofibrous structure, which are subject to calcination in the air atmosphere at the temperature from 350 to 700 °C and the produced TiO_2 nanofibres arranged in a nanofibrous structure are annealed in stream of NH_3 atmosphere at the temperature from 400 to 900 °C, by which TiN nanofibres are created without residual TiO_2.

The method according to the invention represents a low-temperature conversion of TiO_2 polycrystallic nanofibres with a high accessibility of surface to TiN. The synthesis runs in ammonia atmosphere at low temperatures along full keeping of the nanofibrous structure and it is a complete one, so that the resultant product does not contain TiO_2. Anorganic nanofibres or anorganic TiN nanofibrous structures without any further additions and especially without TiO_2, represent a new form of TiN and provide new possibilities how to utilise properties of TiN in many branches.

To reach a high quality of anorganic nanofibres and/or anorganic nanofibrous structures it is advantageous, if the calcination temperature of organic/anorganic nanofibres lies within an interval from 500 to 700 °C and the temperature of annealing in NH_3 atmosphere within an interval from 500 to 800 °C.

At the same time it is preferred if the alcohol in the solvent system is selected from group of ethanol, 1-propanol, 2-propanol or of their mixtures.

Further it is preferred if the poly(vinylpyrrolidone) has the molecular weight of 1300000 g/mol and its weight concentration in the solution is within the range from 4 to 9 %.

At the same time it is preferred, if the chelating agent is beta - diketone, which is according to the claim 6 preferably acetylacetone.

At all above mentioned methods of production it is preferred, if the titanium alkoxide is selected from the group of titanium tetrabutoxide, titanium tetraisopropoxide.

Further, at all above mentioned methods it is preferred, if molecular ratio of alkoxide and chelating agent in the solution is within the range of 1:0,8 to 1:2,2.

The goal of the invention has been achieved by anorganic nanofibres, whose principle consists in that, they are formed of TiN without residual TiO_2. TiN nanofibres of such purity have not been produced yet, and their application will be based especially on their electrical conductivity, high specific surface and high accessibility of this surface.

Anorganic nanofibres are polycrystalline ones and at the same time they may be hollow or compact, according to the manner of their desired application.

The goal of the invention has also been achieved by anorganic nanofibrous structure comprising the TiN nanofibres, whose principle consists in that, it is totally formed of the TiN anorganic nanofibres without residual TiO_2. This anorganic nanofibrous structure may be formed, according to the requirements to application of the resultant product, of polycrystalline compact or hollow anorganic nanofibres.

One of advantages of such anorganic nanofibrous structure consists in that, its high sintering ability is kept. This ability may be e.g. used after grinding the fibres into individual particles and their further application for production of compact parts. At increasing the temperature above the temperature for preparation of nanofibres, the TiN nanocrystals are easy to sinter into greater aggregates and enable creation of dense and strong formations.

The anorganic nanofibrous structure shown above is according to the claim 15 able of low-temperature reversible reaction of TiN to TiO_2 and back to TiN with high cycling ability at simultaneous keeping the initial structure in the temperature interval of 400 - 900°C, that means the nanofibrous structure with high specific surface or sintered nanofibrous structure. Utilisation of this reaction may be expected in physical and/or chemical processes, at which e.g. a change in colour and electrical conductivity may be utilised.

At the same time it is preferred if the temperature interval lies within 450 to 600 °C.

According to the claim 17 the anorganic nanofibrous structure is a part of a composite, which is preferably a bullet-proof material or material with high wear resistance.

Due to its high specific surface and accessibility of this surface, the anorganic nanofibrous structure presents supporting structure for catalysis.

Thanks to its electrical conductivity the anorganic nanofibrous structure is preferably a part of electrodes of electrochemical cells.

According to the claim 23, the anorganic nanofibrous structure is preferably a part of solar cells.

Description of the drawings

To better understand the principle of the invention, the Fig. 1 schematically represents one of the applicable devices for production of precursor organic/anorganic nanofibres through electrostatic spinning. Fig. 2 represents the nanofibrous layer of precursor of TiO_2 nanofibres, the Fig. 3 represents TiO_2 nanofibres for TiN synthesis, the Fig. 4a shows keeping of morphology of nanofibres during the TiN synthesis, the Fig. 4b represents the size of nanofibres, the Figs. 4c, 4d indicate the size of TiN crystals and type of porosity. The Fig. 5a shows keeping of morphology of nanofibres during TiN synthesis, the Fig. 5b represents the size of nanofibres. Figs. 5c, 5d indicate the size of crystals, a dense sinter of TiN crystals and type of porosity of hollow fibres.

Examples of embodiment

Exemplary embodiment of a device for electrostatic spinning of polymer matrices is schematically represented in the Fig. 1 and it comprises a spinning chamber 1, in which there are against each other arranged a spinning electrode 2 and a collecting electrode 3. The spinning electrode 2 comprises the spinning mean 21 formed in the represented embodiment according to the CZ patent 294274 of rotatably mounted cylinder 211, extending by a section of its circumference into the polymer matrix 4 being situated in the reservoir 22 of polymer matrix. Rotating cylinder 211 carries out thanks to its rotation the polymer matrix into electrostatic field, which is induced between the spinning electrode 2 and collecting electrode 3, while a portion of surface of the rotating cylinder 211 positioned against the collecting electrode 3 represents an active spinning zone of the spinning means 21. During spinning thus the polymer matrix 4 is to be found in electrostatic field on surface of active spinning zone of the spinning mean 21 of the spinning electrode. Between the active spinning zone of the spinning mean 21 of the spinning electrode and collecting electrode 3 a substrate material 5 led.

The substrate material 5 is mostly formed of non-woven fabric of suitable properties, nevertheless it may be formed of other suitable fabric, foil or paper. The spinning electrode 2, respective its spinning mean 21, may be formed also of different embodiment, for example according to CZ PV 2006-545 or CZ PV 2007-485 or in other suitable manner, while especially for discontinuous production is even not excluded usage of jet or needle spinning electrodes. Similarly, the collecting electrode 3 may be formed of a cylindrical rod or of a plate or according to CZ PV 2006-477 or according to CZ PV 2007-108 as a corona emitting, or also according to CZ PV 2007-727, eventually in other suitable manner.

Polymer matrix 4 containing titanium alkoxide dissolved in the solvent system on basis of alcohol comprising a chelating agent, poly(vinylpyrrolidone) and additive of concentrated hydrochloric acid is in a known, not represented manner, brought into the reservoir 22 of polymer matrix, out of which is, in example of embodiment according to the Fig. 1, carried out by a circumference of the rotating cylinder 211 into the electrostatic field induced between the spinning electrode 2 and the collecting electrode 3, in which on the active spinning zone of the rotating cylinder 211 the organic/anorganic nanofibres 41 are produced, which are drifted towards the collecting electrode 3 and which are deposited on the substrate material 5, formed of non-woven fabric of organic fibres (microfibres), on which they create the nanofibrous structure 410 having the thickness of layer up to several hundreds of micrometers. This nanofibrous structure 410 is together with the substrate material 5 in a known manner drawn off from the spinning chamber 1 by means of take-up device 6 and behind it is deposited on a conveyor 61, and in a known manner, e.g. by means of a knife and pad, is divided into fabric formations **51** of required length or shape. Organic/anorganic nanofibres **41** are formed of organic polymer, in which a anorganic component formed of complex titanium compounds. is dispersed.

Fabric formations **51** comprising the nanofibrous structure **410** formed of organic/anorganic nanofibres **41** and the substrate material **5** are removed form the conveyor and consequently inserted into the calcining furnace **7**, in which they are subjected to calcination in air atmosphere at the temperature from 350 to 800 °C, through which the substrate material **5** and organic components are removed from organic/anorganic nanofibres **41** so that the nanofibrous structure **410** contains only the anorganic nanofibres **40** of TiO_2, which are polycrystalline and have a high accessibility of surface. Optimum temperature of calcination lies within interval from 500 to 700 °C.

Before inserting into the calcining furnace **7** at not represented embodiment the substrate material **5** may be removed from the fabric formations **51**, so that only a part of fabric formations formed of nanofibrous structure **410** is subjected to calcination.

According to another not represented example of embodiment the fabric formations **51** or their parts formed of nanofibrous structures **410** are subjected to calcination continually.

Once the calcination is finished, the nanofibrous structure **410** formed of TiO_2 nanofibres is inserted or is brought into annealing furnace **8** with streaming NH_3 atmosphere and temperature from 400 to 900 °C, in which total conversion of TiO_2 nanofibres **40** to TiN nanofibres **400** runs while fully keeping the nanofibrous structure and high accessibility of surface of nanofibres. The resultant nanofibrous structure does not contain TiO_2. Optimum temperature of annealing lies within interval from 500 to 800 °C. Streaming of NH_3 atmosphere through the nanofibrous structure contributes especially to ideal conversion.

The obtained TiO_2 nanofibres were e.g. after calcination warmed in streaming NH_3 atmosphere at the temperature of 500 °C, for a period of two hours. Upon this process the TiO_2 nanofibres were completely converted into pure TiN nanofibres without the residual TiO_2. Diameter of obtained nanofibres was within the range from 30 to 1000 nanometers. The specific surface of this structure was 46 m^2/g, which corresponds to average size of individual TiN crystals about 25 nanometers.

The obtained nanofibres kept their dimensions with respect to the initial TiO_2 nanofibres. Keeping of morphology of nanofibres during the TiN synthesis, the size of nanofibres, size of TiN crystals and type of porosity are witnessed by Figs. 4a - d.

Example 1

The polymer matrix for spinning was prepared by dissolution of 100 g of titanium tetrabutoxide in a mixture of 250 g of ethanol and 29,4 g of acetylacetone. After homogenising the obtained solution was carefully mixed with solution of 35,2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 758,8 g of ethanol and after then acidified with concentrated hydrochloric acid. The polymer matrix for spinning thus in this example contained titanium tetrabutoxide dissolved in the solvent system containing ethanol, acetylacetone, poly(vinylpyrrolidone) and additive of concentrated hydrochloric acid.

From this polymer matrix through the electrostatic spinning the organic/anorganic nanofibres containing poly(vinylpyrrolidone) were produced, which comprised the complex titanium compounds. From these organic /anorganic nanofibres on the substrate material there was created the nanofibrous structure, which was removed from the substrate material and consequently calcinated in furnace in the air atmosphere at the temperature of 500°C upon production of pure polycrystalline TiO_2 nanofibres with the size of surface being $50m^2/g$. Such TiO_2 nanofibres are shown in the Fig. 3. The nanofibrous structure of organic/anorganic nanofibres formed on the substrate material could be calcinated also together with substrate material, which would burn at the same time, so that the result would again be the nanofibrous structure from pure polycrystalline TiO_2 nanofibres.

Alternatively the following polymer matrices were subjected to spinning through electrostatic method .

a) for production of polymer matrix for production of TiO_2 nanofibres the mixture of 250 g of 2-propanol and 29,4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenising the obtained solution was mixed with solution of 35,2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 758,8 g of ethanol, and after then acidified with concentrated hydrochloric acid. Through electrostatic spinning from this polymer matrix a layer of organic/anorganic nanofibres was produced, which was consequently calcinated at the temperature of 600°C.

b) for production of polymer matrix for production of TiO_2 nanofibres the mixture of 250 g of 1-propanol and 29,4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenising the obtained solution was mixed with solution of 35,2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 758,8 g of ethanol, and after then acidified with concentrated hydrochloric acid. Through electrostatic spinning from this polymer matrix a layer of organic/anorganic nanofibres was produced, while the layer of organic/anorganic nanofibres was consequently calcinated at the temperature of 700 °C.

c) for production of polymer matrix for production of TiO_2 nanofibres the mixture of 250 g of ethanol and 58,8 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide. was dissolved. After homogenising the obtained solution was mixed with solution of 35,2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 729,4 g of ethanol, and after then acidified with concentrated hydrochloric acid. Through electrostatic spinning from this polymer matrix a layer of organic/anorganic nanofibres was produced, while the layer of organic/anorganic nanofibres was consequently calcinated at the temperature of 400 to 800°C.

d) for production of polymer matrix for production of TiO_2 nanofibres the mixture of 150 g of ethanol and 29,4 g of acetylacetone was used, in which 100 g of titanium tetrabutoxide was dissolved. After homogenising the obtained solution was mixed with solution of 35,2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 272,1 g of ethanol and after then acidified with concentrated hydrochloric acid. Through electrostatic spinning from this polymer matrix a layer of organic/anorganic nanofibres was produced, while the layer of organic/anorganic nanofibres consequently calcinated at the temperature of 400 to 800°C.

e) for production of polymer matrix for production of TiO_2 nanofibres the mixture of 250 g of ethanol and 35,2 g of acetylacetone was used, in which 100 g of titanium tetraisopropoxide was dissolved. After homogenising the obtained solution was mixed with solution of 42,2 g of poly(vinylpyrrolidone) having molecular weight of 1300000 g/mol in 977,7 g of ethanol and after then acidified with concentrated hydrochloric acid. Through electrostatic spinning from this polymer matrix a layer of organic/anorganic nanofibres was produced, while the layer of organic/anorganic nanofibres consequently calcinated at the temperature of 500 to 700°C.

In all cases a long-term continuous spinning process was achieved and thickness of produced nanofibres was within the range from 30 to 1000 nanometers.

Example 2

TiO_2 nanofibres obtained in the same manner as in the example 1 were warmed in streaming NH_3 atmosphere at the temperature of 500 °C. After two hours the temperature was increased to 800°C at a rapid increase, and after thirty minutes the annealing furnace was switched off. At this process, there occurred a complete conversion of TiO_2 nanofibres to pure TiN nanofibres without residual TiO_2. Nanofibrous morphology was kept, but fibres consisting of TiN nanocrystals were of more compact character. Specific surface of this anorganic nanofibrous structure was 20,3 m^2/g, which corresponds to an average size of individual TiN crystals being 53 nanometers.

The obtained hollow fibres were created of a compact TiN. Keeping of morphology of nanofibres during the TiN synthesis, the size of nanofibres, size of TiN crystals, the dense sintering of TiN crystals and type of porosity of hollow nanofibres are witnessed by Figs. 5a - d.

Example 3

TiN nanofibres obtained in the same manner as in the example 2 were warmed upon presence of air at the temperature of 450 °C for a period of thirty minutes. At his process, there occurred a complete reverse conversion of TiN nanofibres to pure TiO_2 nanofibres without residual TiN. Nanofibrous morphology was kept also at this reversible reaction.

TiO_2 nanofibres obtained in this manner were warmed in streaming NH_3 at 550°C upon simultaneous production of TiN nanofibres without residual TiO_2. The original structure of nanofibres was still kept.

Said procedure of reverse conversion to TiO_2 and backwards to TiN was repeated in cycles at simultaneous keeping the original structure of nanofibres both of TiN and of TiO_2.

Example 4

TiO_2 nanofibres obtained in the same manner as in the example 1 were warmed upon presence of air at the temperature of 600° C for a period of 6 hours. The initial structure of nanofibres was kept, only sintering of crystals occurred. The resultant product contained anatase with cca 5% of rutile (Figs. 6, 7). In parallel TiO_2 nanofibres were cyclically subjected to calcination in the stream of NH_3 at the same temperature and for the same period. Phase-pure TiN nanofibres with the same nanofibrous morphology were produced. These nanofibres were used for cycling of TiN-TiO_2 and backwards. There were performed 6 cycles, while oxidation was performed at presence of air at 450° C for 30 minutes and reduction in stream of NH_3 at 600°C for 6 hours. This process was fully reversible.

Industrial applicability

Pure TiN in nanofibrous form, especially in the form of anorganic nanofibrous structure, that has not existed to date, may be used in many industrial branches. Electrical conductivity and a high specific surface enable a perfect distribution of electrons, which enables application at production of more efficient electrodes. TiN nanofibres substantially improve mechanical properties of composite materials and products made of them, and simultaneously improve their anticorrosion properties. Inertness, high specific surface and accessibility of this surface enable usage of nanofibrous structure of TiN as a support structure for catalysts. Further possibilities of application appear in devices for conversion and storage of energy, like solar cells and electrodes for electrochemical cells.

CLAIMS

1. A method for production of anorganic nanofibres and/or nanofibrous structures comprising TiN, **characterised in that,** from a polymer matrix containing titanium alkoxide dissolved in a solvent system on basis of alcohol containing chelating agent, poly(vinylpyrrolidone) and addition of concentrated hydrochloric acid are through electrostatic spinning produced organic/anorganic nanofibres arranged in a nanofibrous structure, which are subject to calcination in the air atmosphere at the temperature from 350 to 800 °C and the created TiO_2 nanofibres arranged in the nanofibrous structure are annealed in a stream of NH_3 atmosphere at the temperature from 400 to 900 °C, by which TiN nanofibres are created without the residual TiO_2.

2. Method according to the claim 1, **characterised in that, the** temperature of calcination of organic/anorganic nanofibres lies within an interval from 500 to 700 °C and the temperature of annealing in NH_3 atmosphere lies within an interval from 500 to 800 °C.

3. Method according to the claim 1 or 2, **characterised in that, the** alcohol in the solvent system is selected from the group of ethanol, 1-propanol, 2-propanol or of their mixtures.

4. Method according to any of claims 1 to 3, **characterised in that, the** poly(vinylpyrrolidone) has the molecular weight of 1300000 g/mol and its weight concentration in solution is within the range from 4 to 9 %.

5. Method according to any of claims 1 to 4, **characterised in that, the** chelating agent is acetylacetone.

6. Method according to any of claims 1 to 5, **characterised in that, the** titanium alkoxide is selected from the group of titanium tetrabutoxide, titanium tetraisopropoxide.

7. Method according to any of claims 1 to 6, **characterised in that, the** molecular ratio of alkoxide and chelating agent in the solution is within the range of 1:0,8 to 1:2,2.

8. Anorganic nanofibres produced through the method according to any of claims 1 to 7, **characterised in that, they** are formed of TiN without residual TiO_2.

9. Anorganic nanofibres according to the claim 8, **characterised in that, the** nanofibres are polycrystalline ones.

10. Anorganic nanofibres according to the claim 8, **characterised in that, the** nanofibres are hollow ones.

11. Anorganic nanofibrous structure comprising the TiN nanofibres, produced through the method according to any of claims 1 to 7, **characterised in that,** it is completely formed of anorganic nanofibres of TiN without residual TiO_2.

12. Anorganic nanofibrous structure according to the claim 11, **characterised in that,** it is formed of hollow anorganic nanofibres.

13. Anorganic nanofibrous structure according to the claim 11, **characterised in that,** it is formed of compact anorganic nanofibres.

14. Anorganic nanofibrous structure according to any of claims 11 to 13, **characterised in that, the** anorganic TiN nanofibres are formed of TiN crystals, which have high sintering ability.

15. Anorganic nanofibrous structure according to any of claims 11 to 14, **characterised in that,** it is able of low-temperature reversible reaction of TiN to TiO_2 and back to TiN with high cycling ability at simultaneous keeping the initial nanofibrous structure in the temperature interval of 400 - 900°C.

16. Anorganic nanofibrous structure according to the claim 15, **characterised in that, the** low-temperature reversible reaction of TiN to TiO_2 and backwards to TiN runs in temperature interval from 450 to 600 °C.

17. Using of anorganic nanofibrous structure according to any of claims 11 to 16, **characterised in that, it** is a part of a composite.

18. Using of anorganic nanofibrous structure according to the claim 17, **characterised in that, the** composite is a bullet-proof material.

19. Using of anorganic nanofibrous structure according to the claim 17, **characterised in that, the** composite is material having a high wear resistance.

20. Using of anorganic nanofibrous structure according to any of claims 11 to 13 and 15 to 16, **characterised in that,**it creates supporting structure with high accessible specific surface for catalysis.

21. Using of anorganic nanofibrous structure according to any of claims 11 to 16, **characterised in that,** it is a part of electrodes.

22. Using of anorganic nanofibrous structure according to the claim 21, **characterised in that, the** electrodes are the electrodes of electrochemical cells.

23. Using of anorganic nanofibrous structure according to any of claims 11 to 16, **characterised in that,** it is a part of solar cells.

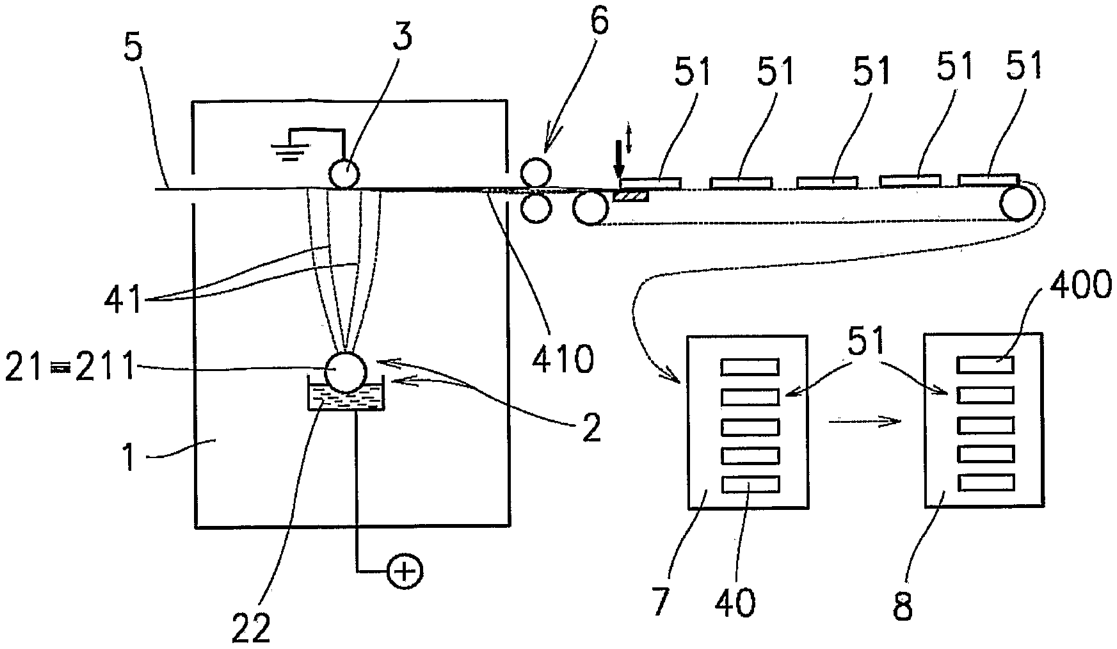

Fig. 1

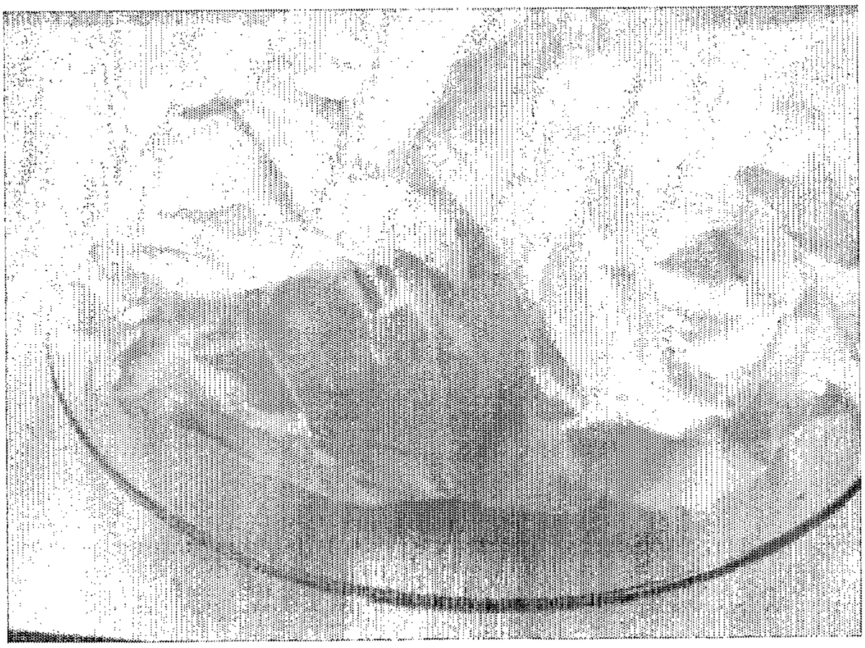

Fig. 2

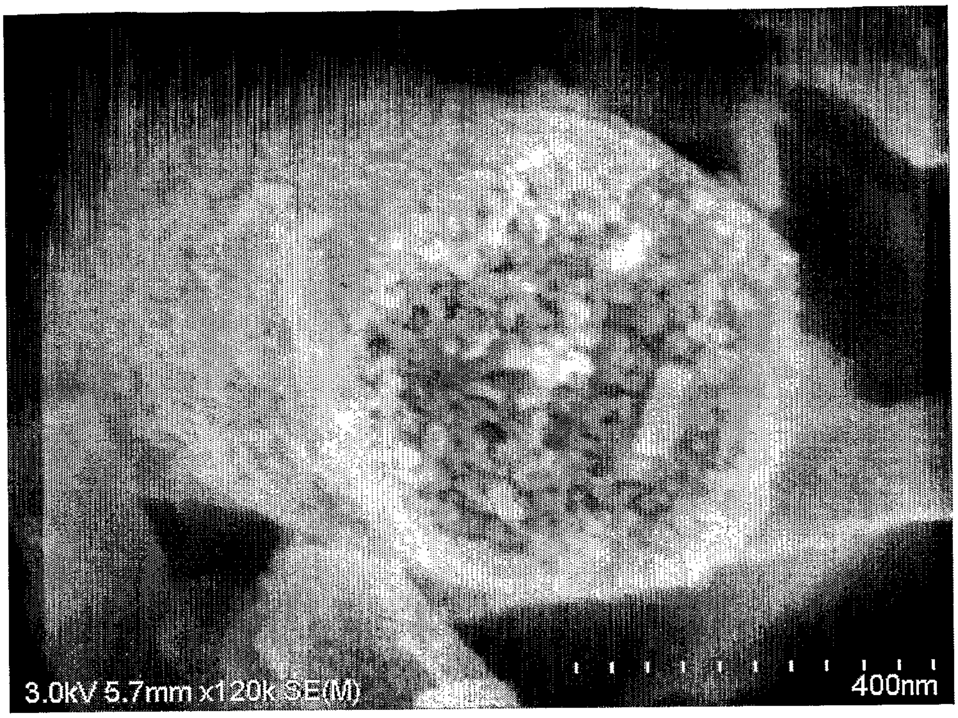

Fig. 3

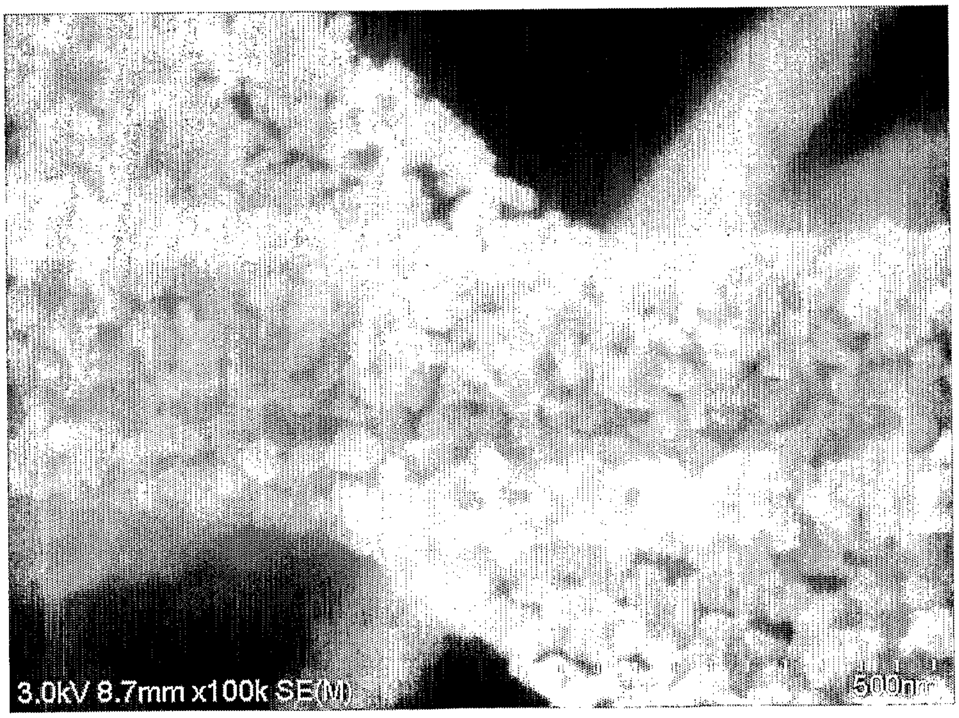

Fig. 4a

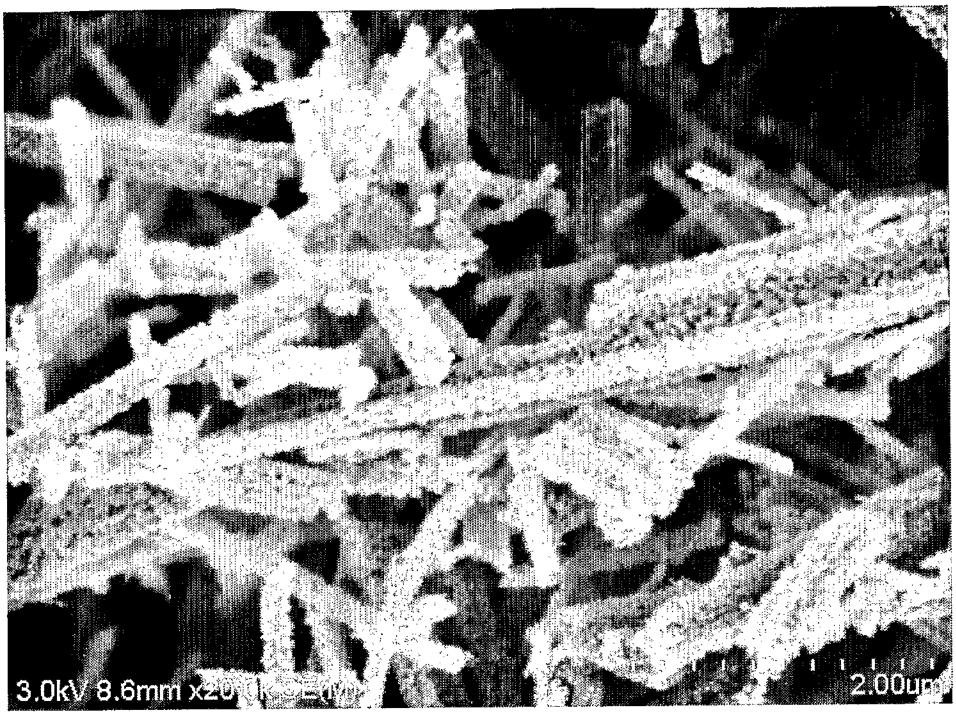

Fig. 4b

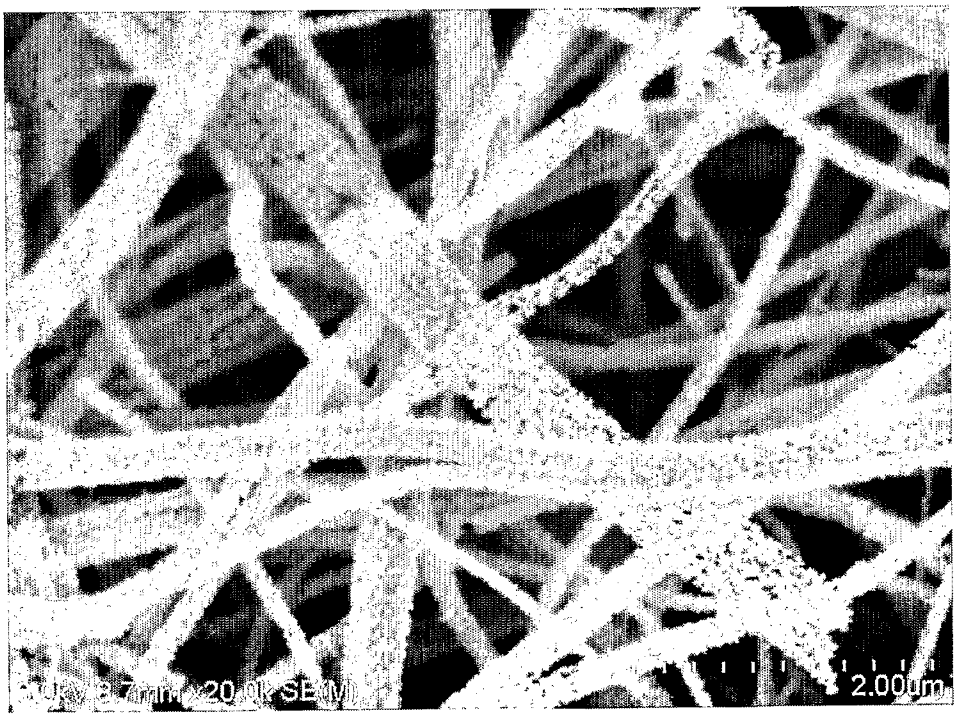

Fig. 4c

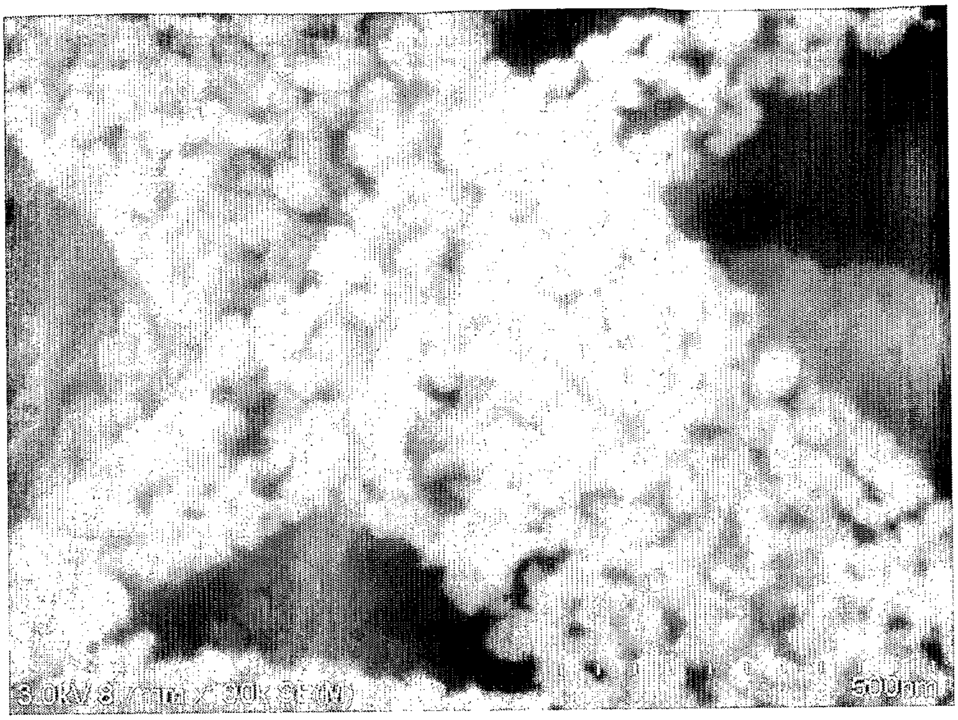

Fig. 4d

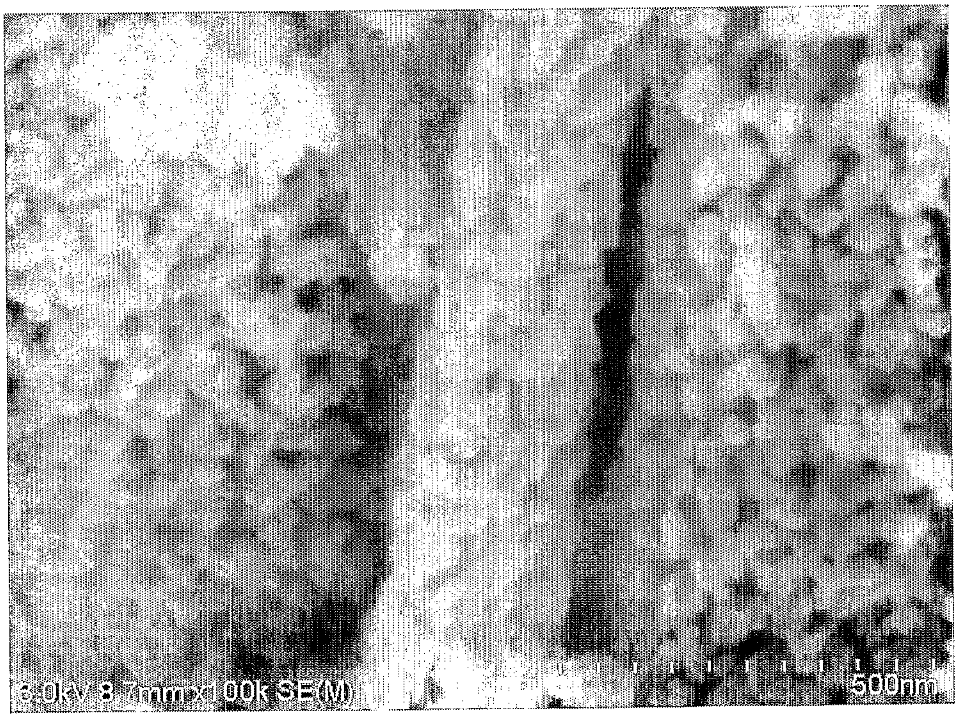

Fig. 5a

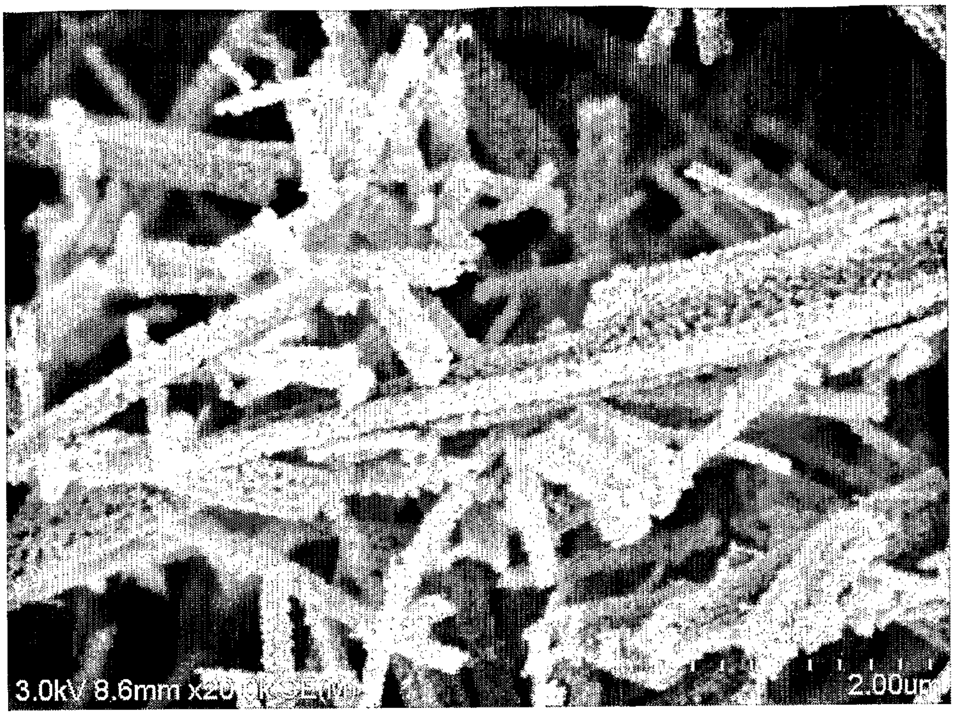

Fig. 5b

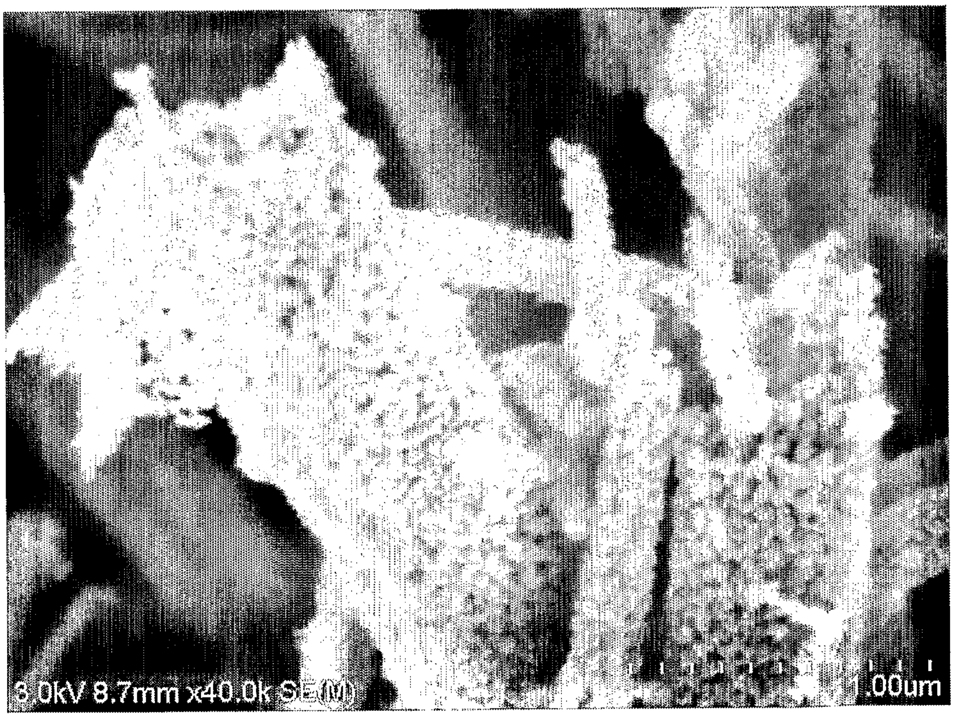

Fig. 5c

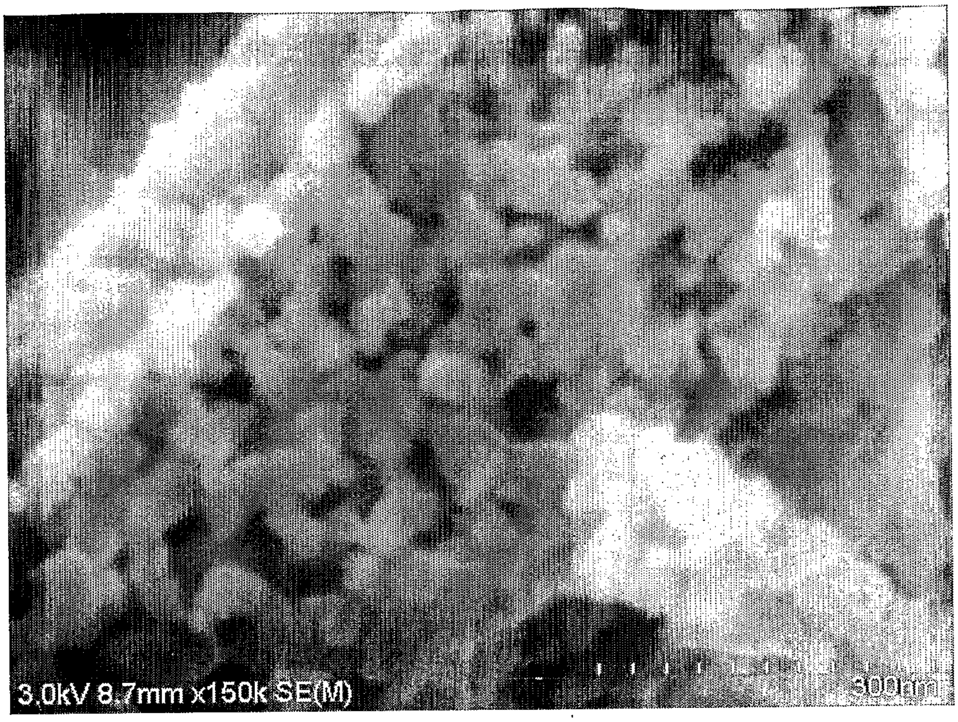

Fig. 5d

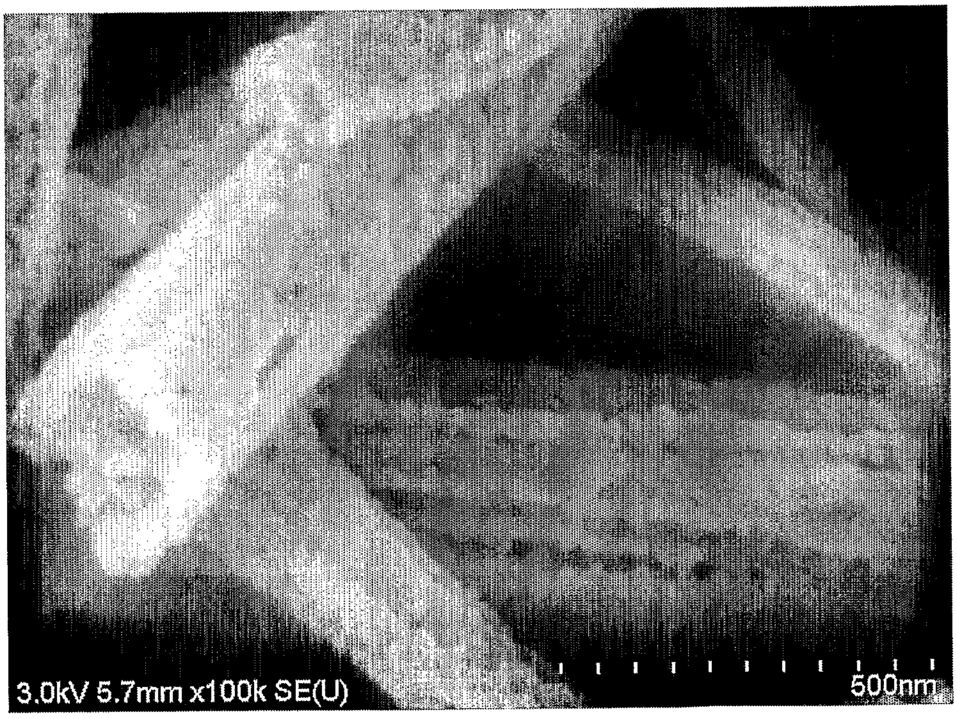

Fig. 6

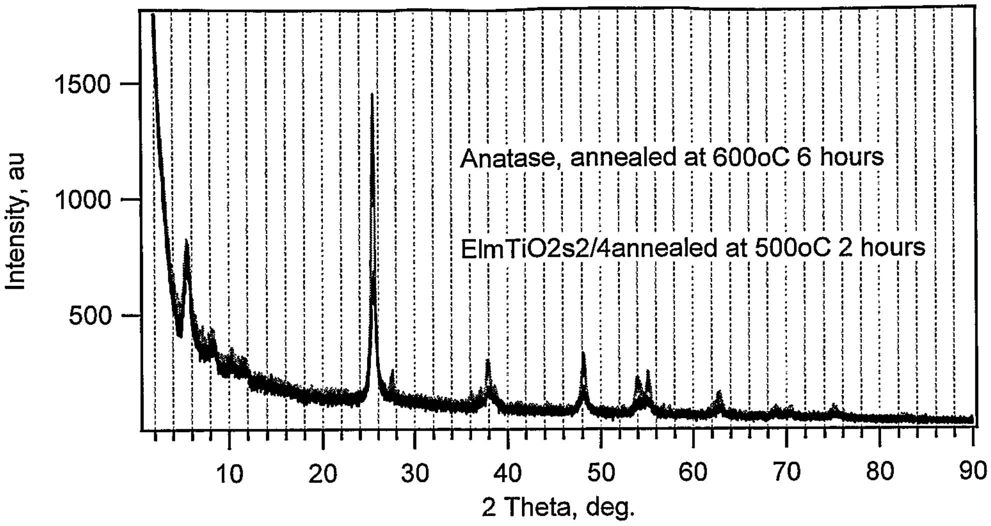
1500
1000
500
Intensity, au
Anatase, annealed at 600oC 6 hours
ElmTiO2s2/4annealed at 500oC 2 hours
10
20
30
40
50
60
70
80
90
2 Theta, deg.

Fig. 7