INCREASED PRODUCTION OF TIO2 NANOFIBRES FOR USE IN ADVANCED APPLICATIONS

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Abstract

Recent attention has focussed on the production of electricity from renewable energy sources, whereby protecting the environment. In this context, nanofibres that have improved properties compared to conventional materials are widely used. Titanium oxide nanofibres are mainly used for many applications, which are characterized by their crystalline structure. Nanofibres are produced based on the principle of electrospinning with subsequent calcination of the spinning material. This paper describes method leads to improve efficiency of inorganic nanofibers production. In the end will be described final structure of fibers, which could leads to improve photocatalytic activity.

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Keywords: calcination, nanofibers, photocatalysis, structure, titanium dioxide.

1. INTRODUCTION

Inorganic nanofibres can be used in many industries and applications. In comparison with other currently used materials the application of inorganic nanofibres in products improves their functionality, performance and provides an overall increase the added value of these products, which in the near future will cause a revolution in their use. Some of the most important properties of inorganic nanofibres include their large surface area in relation to their volume (up to hundreds of m^2 per gram of material), very high porosity and permeability, as well as chemical and mechanical properties, due to which they can be further modified for use in a wide range industrial applications. The highest levels of productivity of nanofibre structures can be obtained by the principle of electrospinning from a free surface using a roller. This can be achieved using a special device called a NanospiderTM [1]. The functionality of the electrospinning process depends on many parameters which can have an effect the electrostatic field around the spinning electrode and the collector. Numeric simulations of the electrical field can be used to analyze the distribution of electrical potential and intensity values. Greater intensity, resulting in an increase in the efficiency of the spinning, can be achieved by modifying elements affecting the electrostatic field. An increase in the production of fibres can also be affected by the shape of the collector, which must fulfil the function of a continuous production process. Therefore, a mechanism is required which can remove a layer of fibres from the collector. The fibres are removed from the area of the experimental laboratory to outside the spinning chamber by an extraction system. The spun layer finally undergoes a calcination process. This separates the organic ingredients and the final product is obtained in the form of a crystalline nanofibrous structure.

2. PRODUCTION DEVICE

Devices for the production of inorganic nanofibres consist of several parts depending on the type of spinning solution and the required treatment of the spinning material. In this case, the spinning solution is titanium tetrabutoxide. For these inorganic nanofibres it is necessary to have a technology for manufacturing the nanofibre layers in the first part of the line. After completion of the spinning the material is transported into the calcining unit. This forms the second part of the line, where any organic components will be incinerated and pure titanium dioxide fibres with a crystalline structure will be obtained on the output from the line. The first part of the line uses a NanospiderTM which spins from the free surface of a roller. The spinning process takes place in the empty space inside the device. The nonconductive construction is equipped with two high-voltage sources, supplying up to 100 kV to the spinning area. In the centre of the chamber is a polymer container (hereinafter referred to as a bath), which the polymer solution is poured into. A rotating spinning electrode which is partially submerged in the polymer is located in the bath. This electrode is most commonly in the shape of a solid cylinder depending on the type of spinning polymer. The polymer solution is fed along the rotating electrode into the area with an electrostatic field. Taylor cones begin to form from the polymer layer due to the action of electrostatic forces on the surface of the spinning electrode. A thin stream of polymer solution is released from their peaks, which is attracted to the collector located at a defined distance above the spinning electrode, as shown in [2]. A nanofibrous layer is obtained on the collector through the gradual evaporation and subsequent splitting of the stream. A schematic diagram of the principle of the functioning of the Nanospider is shown in **Fig. 1**.

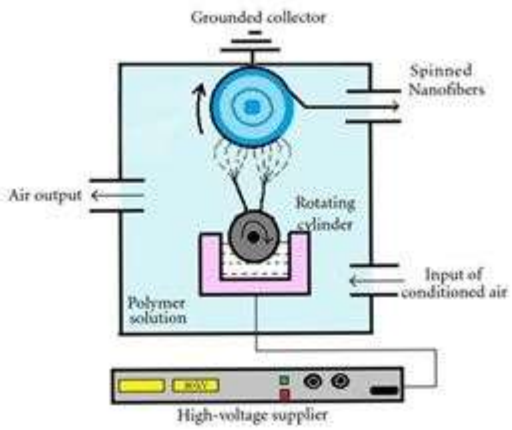

Fig. 1 Diagram of the electrospinning process

In order to create conditions for continuous operation and increase the efficiency of the spinning it was necessary to develop a special collector. The main condition is that the surface of the collector is always clean for the spinning process; otherwise it will not produce the desired nanofibre layer. Previous experiments show that a higher density of fibres on the collector decreases the electric field in its surroundings. This leads to the attraction of a smaller amount of fibres and loss of performance. For a continual process it is crucial to maintain the efficiency of the spinning at a maximum. Ideally, the fibres should fall steadily onto the clean surface of the collector. This condition can be satisfied using a rotary element which has its axis parallel to the rotation axis of the electrode. The velocity of the rotary element is lower than that of the electrode. During the first revolution spinning takes place on one half of the electrode, while the fibres are removed from the surface of the other half. At the start of the second revolution the clean surface of the electrode is located inside the spinning area. The question remains as to which rotating element should be used. Its surface must meet the conditions required for the spinning process and at the same time there must be a way for the fibres to be removed. Given that the main condition is to start the electrostatic spinning process a collector with a surface in the form of rotating brushes was chosen. This creates a number of points on its surface representing the tips of wires, around which the intensity of the voltage greatly increases. We can say that the thinner the points, the more fibres are created during the process. All of the wires must be grounded in order for them to function as a collector. The brush is rotated at a speed of one revolution every five minutes to a speed of one revolution every ten minutes. The rotating brush functioning as a collector during the spinning process is shown in **Fig. 2**.

Fig. 2 View of the machine during the electrospinning process with the bath and brush used as a collector

To maintain a continual process it is necessary to remove the accumulated fibres from the surface the brush. It is therefore necessary to integrate a device into the system with mechanical or pneumatic elements on the opposite side of the brush to where the spinning takes place. The removed fibres are then led outside the machine.The second part of the line for the production of inorganic nanofibres must be a calcination system. Calcination separates the fibres from the plastic carrier, which is incinerated. Titanium dioxide is a more stable form of titanium in nature. Therefore, it is necessary to use high temperatures of around 600 ° C in order to incinerate the carrier [3]. An appropriate calcination system takes the form of a continuous furnace. The system consists of three zones for preheating the material, calcination and subsequent cooling. The material is transported through the furnace using a continuous conveyer belt with a linear motion at a speed of approximately 2 m/h. A diagram of the continuous furnace with the temperature profile is shown in **Fig. 3**.

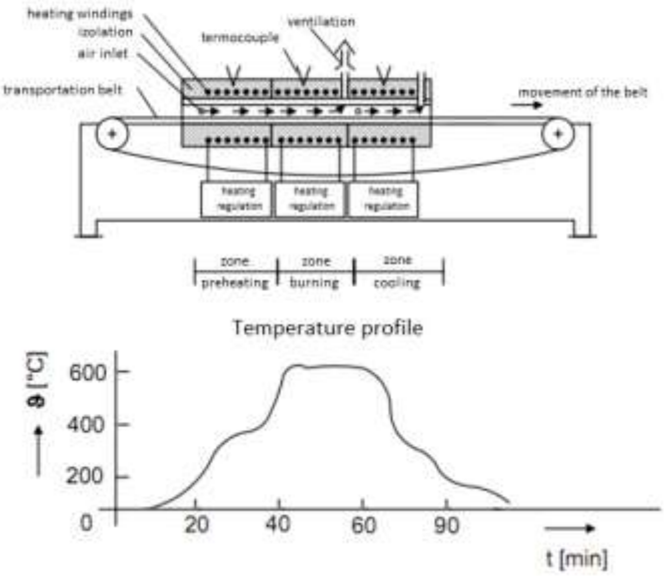

Fig. 3 Diagram of a continuous calcination system with temperature profile

3. OPTIMIZATION AND EXPERIMENT

3.1. Optimization of the el. field

Increasing the efficiency of production of nanofibres by electrospinning or increasing the proportion of nanofibres from the rotation electrode is a complex problem. It depends on the distance of the electrode, the voltage (50 to 100 kV is used), the properties of the polymer solution and also on the ambient temperature and humidity. These parameters influence the potential and the intensity of the electrostatic field. The electrostatic field is also likely to be influenced by other parameters that can be found in the construction of the bath. These include the geometrical arrangement of the structure and the construction materials used. The size of the changes in the field around the bath is given by the relative permittivity, which is represented by the proportion of the permittivity of the material and the permittivity of vacuum [4]. The following materials were selected for the model simulations based on permittivity: wood, glass, plastic, metal (with TiBC surface treatment). The selected materials have excellent dimensional stability and resistance to the solvents contained in the polymer solution.

3.2. Model simulation of the intensity of the el. field

It is very difficult to describe the potential distribution and intensity of the electric field in the electro spinning process and they are practically immeasurable. Model simulations assessing the use of the aforementioned baths were performed to compare the intensity of the electrostatic fields. These provide significant comparative values on how the geometry and relative permittivity affect the resulting intensity of the electrostatic field. When assembling the model the same arrangements with the same boundary and initial conditions are used for all of the baths. The results of the model simulations with an input voltage of 60 KV on the spinning electrode show the distribution of intensity of the electrostatic field for each bath. The distribution of potential in the individual baths is similar but not identical. This confirms that the design affects the spatial distribution of the input potential. The value of the potential subsequently affects the intensity of the electrostatic fields of the compared structures. The intensity values in the surroundings of each bath are shown in **Table 1**. The intensity was expressed in units of statvolt/cm (~~NB~~Note: 1 statvolt = 299.8 volts).

Table 1 Intensity values of electrostatic fields in the surroundings of each bath

Bath material	Intensity value in the surroundings [statvolt/cm]
Metal	295,9
Plastic	320,2
Wood	326,7
Glass	526,2

3.3. Experiment

During testing, a total of 16 measurements were taken at four positions with a brush collector. After each spinning process, which lasted 10 minutes, the mass of the spun structures was measured for the given bath. A comparison of the performance of the individual baths is characterized using the parametric graph in **Fig. 4**, where the highest value of the mass of the nanofibrous structure was obtained from the glass bath, followed the wooden bath, then the plastic and metal baths. The graph shows that the results of the performance of individual baths correspond to the values of the electric field in the simulations.

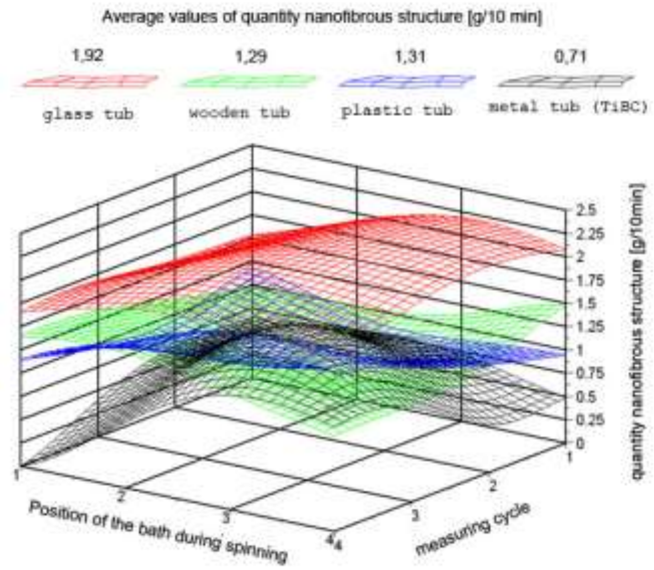

Fig. 4 Results of the experiments of spinning in individual baths

4. CALCINATION, RESULTING STRUCTURE OF THE PRODUCT

The most common forms of titanium dioxide are the minerals rutile and anatase. While rutile (titanium dioxide pigment) has been produced commercially for many years, materials based on anatase have only recently come to the forefront due to the extraordinary properties of this crystalline form. Anatase has many interesting features, the most well-known being its photocatalytic activity and photocatalytic induced superhydrophilicity. Photocatalytic activity leads to the degradation of organic structures (organic pollutants and microorganisms) on the surface of TiO_2 by radiation with a wavelength of below 390 nm. This effect means that TiO_2 based materials can be applied to the treatment of water and air, for self-cleaning and antibacterial layers.After calcination the sample was milled in a bead mill with agate balls in order to disperse clusters of fibres and to analyse phase composition, specific surface area by BET and to measure photoactivity. After dispersing the fibres in the mill the nanofibrous morphology of the sample was examined using SEM, as shown in **Fig. 5**. It was found that the nanofibrous morphology was retained but the fibres were shorter due to the milling.

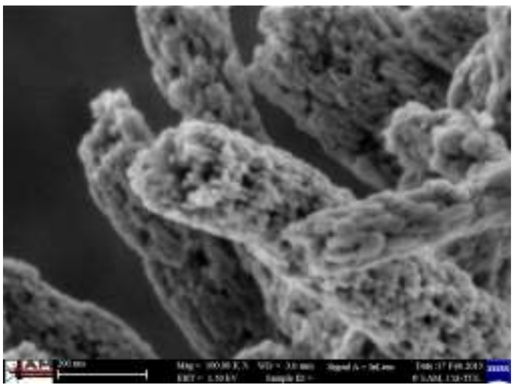

Fig. 5 Electron microscope image of the resulting nanofibrous structure of TiO_2

The phase composition of the calcined precursor was confirmed by X-ray powder diffraction. It was determined that the sample contained a pure anatase phase of TiO2 and the size of primary crystallites was 12 nm.The specific surface of the calcined precursor was analysed by adsorption-desorption of nitrogen at a temperature of 77 K and the size of the specific surface was calculated using BET isotherms (Fig. 3). It was determined that the BET specific surface of the TiO2 nanofibres is in the range of 174 to 235 m2/g with a pore size of 1.5 nm. The photoactivity of the TiO2 nanofibres was measured by using the photodegradation of Orange II dye with UV-Vis photometric indication of the dye concentration at a wavelength of 480 nm. The dye suspension with the TiO2 fibres was pumped through a photoreactor (a tube with a coaxially mounted UV fluorescent lamp) and a spectrophotometer. Three types of UV fluorescent lamp were used with wavelengths of 254 nm, 365 nm and 400 nm. The results were compared with a commercial nanopowder P25 from the company Degussa. The results were expressed using kinetic constants of the degradation of the dye (a 1st order reaction was considered). It was determined that TiO2 nanofibres showed higher photoactivity at all wavelengths than P25. The photoactivity decreased with increasing UV wavelengths. The results are shown in **Table 2**.

Table 2 Results of the photoactivity of TiO2 nanofibres compared to P25

Sample	254 nm	365 nm	400 nm
TiO_2 precursor	0,4444	0,1258	0,0054
P25	0,2851	0,1272	0,0022

5. CONCLUSION

This article describes the production of inorganic nanofibers titanium oxide using method of elctrospinning. Component optimization of the process can change electrostatic field during the spinning process. This considerably increases the efficiency of nanofibers production. Simulations and experiments have shown that how high is the intensity of the field, the higher is productivity of fibers. Spun material is burned in the calcining system which is represented as a continuous furnace. By this method the nanofibres are produced on the basis of anatase. The best known characteristic of this form of titanium oxide is photocatalytic activity, which allows degradation of organic structures on the surface of TiO2.

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REFERENCES

[1] JIRSÁK O. et al. (2005), CZ Patent, CZ294274 (B6), A, Method of nanofibers production from polymer solution using electrostatic spinning and a device for carrying out the Metod, WO 2005024101.

[2] LUKAS D. et al. Physical principles of electrospinning (Electrospinning as a nano-scale technology of the twenty-first century), Textile Progress, Vol.41, No.2, 2009, pp. 59-140, ISSN 0040-5167.

[3] HE F., MA F., LI J., LI T., LI G. Effect of Calcination Temperature on the Structural Properties and Photocatalytic Activities of Solvothermal Synthesized TiO2 Hollow Nanoparticles. In: Ceramics International, 2014. pp. 6441-6446. Volume 40, Issue 5.

[4] PETRŮ M., NOVÁK O., LEPŠÍK P. Increase of the efficiency of the production lines for the spinning of inorganic nanofibers by the electrostatic field intensity optimization. MM Science Journal, No. 4, 2012, pp. 382-385.