TiO$_x$ THIN FILMS AP DBD DEPOSITION ON POLYAMIDE ROPE

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In our study we investigated the process of atmospheric dielectric barrier discharge (ADBD) application for deposition of titanium oxide thin film on polyamide ropes to improve their abrasion resistance and hydrophobicity. Exploration focused on optimisation of the deposition process. Surface morphology was studied by the SEM. The rope fiber abrasion tests were performed, too. The samples covered with TiO$_x$ thin film proved to be more abrasion resistant. their surface stayed relatively steady in comparison with unmodified samples after the abrasion test.
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1. INTRODUCTION

In the recent years, much attention has been paid to thin film deposition process under atmospheric pressure. There are some indisputable advantages of atmospheric deposition methods over vacuum processing [1, 2]. Furthermore atmospheric non-thermal plasma sources are already used successfully in many fields, such as biomedicine, food or surface treatment, ozone generation, and surface modification [3, 4].

This paper describes practical application of TiO$_x$ thin films deposited by ADBD PE-CVD process on polymeric substrate – polyamide (PA) ropes for strengthening their abrasion resistance and hydrophobicity. Research focused on achievement of film homogeneity and good film adhesion to individual polyamide fibres of the rope. Tested types of ropes are usually used by mountaineers.

2. EXPERIMENTAL

Experiments were carried out in a Plexiglas reactor with dimensions (90x79x41) mm^3. AP DBD CVD system consists of the reactor, gas input and AC power supply. The discharge was ignited between two brass electrodes (45x8x18) mm^3 and (40x17x18) mm^3 which were placed within the reactor. Bigger grounded electrode was covered by a glass plate ((70x46x1) mm^3). The electrode configuration is shown on Fig. 1. The inter-electrode distance was adjustable 10 mm. Fuller description of set-up is described in [5].

To be able to place the rope properly into the reactor during experiments, two holes (D ~ 10 mm) symmetrically placed in the walls of the reactor had to be bored. The axis passing through centres of the holes was parallel with upper planes of electrodes and perpendicular to the longitudinal axis of symmetry of electrodes. It also passed through the centre of the inter-electrode region (see Fig. 1). Several thin films “areas” 7 cm long and 1 cm wide, each separated by 4 cm long unmodified region were deposited one after another on every tested rope. Each thin film “area” deposition time was 10 min.

Titanium (IV) isopropoxide (TTIP) 97% purity (producer: Alfa Aesar) was chosen as a precursor for TiO$_x$ thin film deposition because it is ecologically benign and harmless to humans or the environment.

TTIP vapour was mixed with Ar (gas flow rate 1 slm) in the evaporator and transported into the HV electrode cavity where it was mixed with oxygen (gas flow rate 2.5 slm). The gas mixture was blown into discharge space through the hole (diameter 3 mm) in the high voltage electrode perpendicularly to the sample. Gas streams were monitored using mass flow meters. Experiments were performed with 30˚C of TTIP evaporation temperature. Argon and oxygen were purchased in the Air Products Company, CZ.

Film deposition was performed with discharge power about 350 mW (at 15…15.5 kV, 50 Hz). The maximum value of the current was about 1 mA. AP DBD during deposition sustained in the filamentary mode only. Experiments were performed in air at room conditions (pressure about 756 Torr, humidity (40…45) %, and room temperature 22…24˚C).

Scanning electron microscopy (SEM) was used for surface exploration of ropes. SEM was performed with electron microscope JEOL JSM–7401F. SEM test samples formed shredded pieces of ropes with deposited thin film; each sample contained about 1 cm^2 of the film.

Fig. 1. Electrode configuration in the AP DBD setup

We performed also test of individual fibres. The fibres were deep-frozen (at approx. (-170) °C), cut with scalpel and then SEM examined. Studies focused on the shape of uppermost cutting plane and its edges. Results will be discussed in next part of this paper.

The home-build equipment for abrasion resistance test was engineered in compliance with the Germany standard TL 4020–0030 relevant to climbing and other ropes. Scheme of the abrasion resistance test installation is presented in Fig. 2.

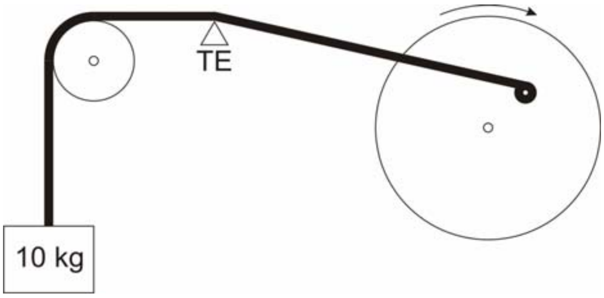

Fig. 2. Scheme of the abrasion resistance test installation (TE – test edge)[6]

Its principle is as follows: one end of the test sample-piece of rope is eccentrically fixed to the disk. The disk had been rotated by motor. The other end of the rope was stretched over the test edge (TE) and roller and was tensed by 10 kg weight. Short sample was lengthened by cord.

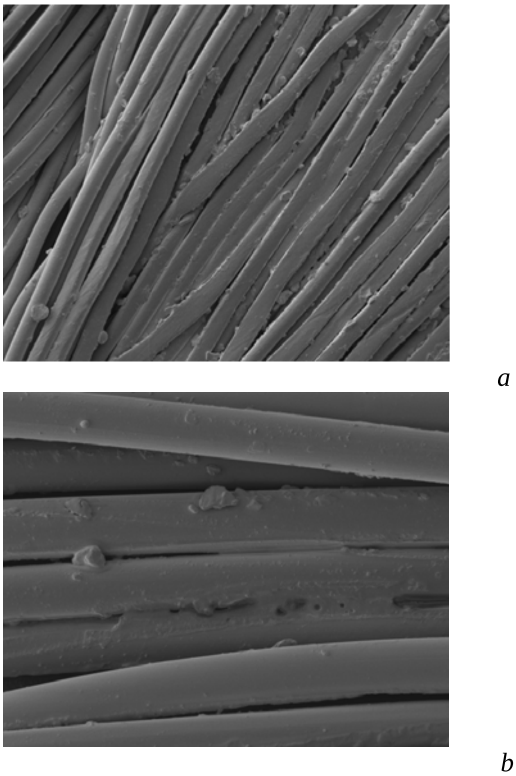

Fig. 3. SEM image of PA fibers with TiO$_x$ film: Magnification: a) 150× b) 500×

Tested rope was set in motion over the test edge by rotating disc and the rope surface had been abraded. Abraded part length of the rope was approx. 6 cm. The angle of rope slope to the motor was in the range from 12° to 39° and depended on fastening position. The test edge was covered by hard chrome-nickel abrasive coating with roughness R$_a$=250. Motor frequency was 50 turns/min. Standard number of 1000 system cycles was taken for test, i.e. 20 minutes time duration.

3. RESULTS AND DISCUSSION

The surface analysis of thin TiO$_x$ films deposited on polyamide ropes/fibres was performed with SEM. Evidently the thin film deposited in AP DBD was relatively homogeneous, but with slight sticking of individual fibers. Besides the continuous film, also some small dust-like particles were observed on the modified surface. Their existence was probably related with formation of dust particles in the discharge region. No delamination of the film was observed, its adhesion was good. Nevertheless, Fig. 3, a, b demonstrate moderate deformation of rope braid, which developed during deposition (sample stretching).

In addition to the surface analysis tests, the rope fiber breaking test was performed, too. Specifically, film detachment after fracture of individual fibers was tested.

Some of fibers were unplaited from the rope, frozen to (-170) °C and cutting by scalpel. Electron microscopy image of the cutting plane is shown in Fig. 4.

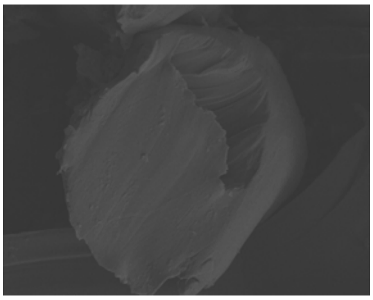

Fig. 4. PA fiber cutting plane (magnification 2000×)

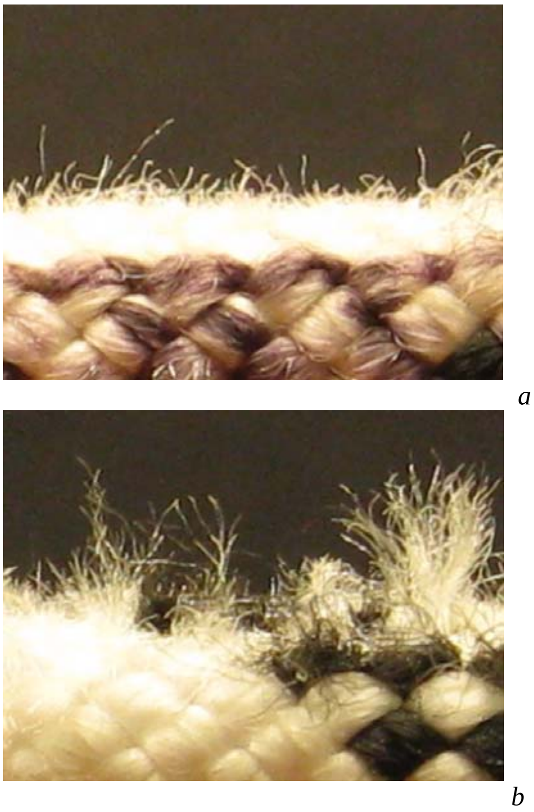

Fig. 5. Enlarged photos of the rope sample: a) thin TiO$_x$ film covered, b) unmodified

Unfortunately this method was not sufficient for fiber plane surface studies because of fiber thickness (~ 10 µm). Fibers were too flexible even at low temperatures.

Nevertheless the thin film shelling was not observed. Its absence indicates sufficient film adhesion to the fiber. However scalpel cutting deformation caused this test to be unreliable.

Abrasion resistance tests were carried out at PA ropes with and without TiO_x film deposition. Test results are presented in Fig. 5. Undeposited samples were more susceptible to the mechanical impacts and their surface was more defaceable and less abrasion resistant. Samples covered with TiO_x proved to be more abrasion resistant; their surface seemed to be less harmed after the abrasion test.

Results of experiments indicate that AP DBD thin film deposition on the polyamide rope might be applied for of polymeric mountaineer equipment quality enhancement, although further optimisation of the deposition process and reactor improvement would be unavoidable.

CONCLUSIONS

Titanium dioxide (TiO_x) thin films were deposited on the polyamide ropes/fibres by AP DBD PE-CVD method. Deposited samples proved to be more resistant to the abrasion, their surface stayed relatively steady after the abrasion test. These tests were performed on the laboratory scale only.

ACKNOWLEDGEMENTS

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НАНЕСЕНИЕ ТОНКИХ ПЛЕНОК TiO_x С ИСПОЛЬЗОВАНИЕМ АТМОСФЕРНОГО ДИЭЛЕКТРИЧЕСКОГО БАРЬЕРНОГО РАЗРЯДА НА ПОЛИАМИДНЫЕ ТРОСЫ

Ю. Кленько, Я. Пихал

Мы изучали применение атмосферного диэлектрического барьерного разряда (ADBD) для осаждения тонкой пленки оксида титана на полиамидный (PA) трос. Тонкие пленки TiO_x на PA-подложках были получены после оптимизации условий процесса. Исследовалось, в основном, влияние плазменного процесса нанесения тонкой пленки на улучшение поверхностных свойств PA-троса. Морфология поверхности изучалась с помощью SEM. Также был проведен тест на сопротивление к износу образцов волокна с пленкой и без. Образцы, покрытые TiO_x, после проведения теста на износ показали большую устойчивость, их поверхности оставались относительно неповрежденными по сравнению с образцами без пленки.

НАНЕСЕННЯ ТОНКИХ ПЛІВОК TiOx З ВИКОРИСТАННЯМ АТМОСФЕРНОГО ДІЕЛЕКТРИЧНОГО БАР’ЄРНОГО РОЗРЯДУ НА ПОЛІАМІДОВІ ТРОСИ

Ю. Кленько, Я. Піхал

Ми вивчали застосування атмосферного діелектричного бар'єрного розряду (ADBD) для осадження тонкої плівки оксиду титану на поліамідний (PA) трос. Тонкі плівки TiO_x на PA-підкладках було отримано після оптимізації умов процесу. Досліджувався, в основному, вплив плазмового процесу нанесення тонкої плівки на покращення поверхневих властивостей PA-троса. Морфологія поверхні вивчалася за допомогою SEM. Також було проведено тест на опір до стирання зразків волокна з плівкою і без. Зразки, вкриті TiO_x, після проведення тесту на стирання показали більшу стійкість, їх поверхні залишалися відносно непошкодженими в порівнянні зі зразками без плівки.