INVESTIGATION OF ANTIMICROBIAL ACTIVITY AND MORPHOLOGICAL PROPERTIES OF METAL COATED TEXTILE SURFACES

Necdet Aslan[1], Kenan Şentürk[2], Tuba Şen[1] , Turgay Çoruhlu[3], İpek Vartürk[4], S. Şeker[5], S. Shahidi[6], A.M. Dobrovolskiy[7], V.V. Tsiolko[7], S.V. Matsevich[7], S.S. Keskin[8], May Korachi[6]

[1]Yeditepe University- Physics Department-Kayışdağı/Istanbul, Turkey;
[2]Beykent University- Energy Systems Engineering Department-Ayazağa/Istanbul, Turkey;
[3] Beykent University-Vocational School- Dept. of Technical Programmes-Beykent /Istanbul;
[4]Yeditepe University-Genetics and Bioengineering Department- Kayışdağı /Istanbul, Turkey;
[5]Gebze Institute of Technology, Materials Science & Engineering Dept. Gebze Istanbul, Turkey;
[6]Department of Textile, Arak Branch, Islamic Azad University, Arak, Iran;
[7]Institute of Physics NASU, Kyiv, Ukraine;
[8]Marmara University, Environmental Engineering Department, Turkey

E-mail: tsiolko@iop.kiev.ua

The results of investigation antimicrobial and surface properties of the textiles metal coated by means of magnetron or the cleaning-deposition system, which is based on sequentially arranged DC anode layer accelerator and hollow cathode, are presented. The antimicrobial properties against bacteria *E. coli* and *S. aureus* of cotton and polyester/cotton textiles coated by Cu, Ti and Ag with the use of two different systems were examined and compared.

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INTRODUCTION

In recent years the production of a textiles with antimicrobial properties caused an increasing interest from industry because of their potential to provide beneficial health effects leading to a higher quality of human life. It is connected to the fact that textile products provide a suitable environment for the growth of many microorganisms, including pathogens, which could be the source of infection transfer, unpleasant odors, color degradation and general deterioration of the textile.

Current antimicrobial products, such as triclosan, quaternary ammonium and metallic salts have disadvantages such as short active durations and high costs. Moreover, they have been known to leach out from the fabric towards the environment and diffuse into the skin of the wearers.

It is known that many metals by themselves (primarily silver and copper) also have antimicrobial properties (though the mechanisms of their antimicrobial activity are not yet known precisely [1]). Therefore, the deposition of metal films on fabrics is a promising method for creating antimicrobial coatings. Currently, the most suitable way of the antimicrobial metal films deposition on a textile is the sputtering technique. Recently, quite a number articles on this topic have been published [2-8]. Metal film deposition was carried out using a variety of devices–direct current (DC) magnetron, direct current pulsed (DCP) magnetron and high intensity power impulse (HIPI) system. SiO_2 fabrics [2], polyester textile [3, 6, 7], cotton [4, 5] were used as substrates in the studies. In [2] it was found that Cu was effective against bacteria and fungi, while Ag was effective only against bacteria, since its effect was limited against fungi. The effectiveness of other used metal (Pt, Pt/Rh and Au) was much lower. So most of the studies was devoted to the investigation of antimicrobial properties of Ag, Cu, TiO_2, Cu/TiO_2 sputtered films.

An interesting phenomenon has been described in [8]. Antimicrobial activity of Cu films, deposited by DCP magnetron was found to be significantly higher than the activity of the films produced by DC magnetron. The reason for this effect may be that the Cu ions produced by DCP with an energy up to 100 eV create Cu films with different structure compared with the films deposited by DC magnetron Cu ions with lower energy 5…15 eV.

An important point in the sputtering technique on textile is the adhesion of the deposited metal film and, correspondingly, wearability and washability of the resulting fabrics. It is known that, for obtaining high-quality coatings on substrates, efficient methods of cleaning and activation of the surface to be coated is required immediately prior to the deposition. Polarity switch in magnetron discharge for cleaning the treated surface by ion flow is generally possible only in case when the last one is conductive. Therefore, for the plasma pretreatment of substrates ignite the gas discharge or the entire volume of the chamber, or by using a special electrode between the magnetron and the substrate as the cathode [9, 10].

The aim of this study was to investigate the antimicrobial activity and morphological properties of cotton and cotton/polyester textiles with Cu, Ag and Ti film coated by DC magnetron sputtering and cleaning-

deposition system, which is based on sequentially arranged DC anode layer accelerator and hollow cathode. Using the second system we were able first to clean the sample with Ar ions with an energy of 400…600 eV, then deposit of the metal films with help of metal ions with energy about 200 eV. Selection of titanium due to the fact that although the Ti itself does not exhibit antimicrobial activity [1], in the ambient air at the surface of the Ti film TiO_2 layer is fairly quickly formed, which already has antimicrobial properties.

1. EXPERIMENTAL SET-UPS AND METHODS

The DC/RF magnetron, used during the sputtering, had no specific differences from equipment used in other researches. The dimensions of the cathode (Ag, Cu and Ti of 99.99 % purity) were 50.8 mm in diameter and 4 mm in thickness. The magnetron sputtering coating was established at 10 mTorr of Ar pressure and a DC voltage of V=400 V and I=0.3 A producing ion current density nearly 11 mA/ cm^2.

The cleaning-deposition system is based on sequentially arranged DC anode layer accelerator with permanent magnets and hollow cathode, which is coupled to accelerator cathode. The surfaces to be coated are situated inside the hollow cathode. At low gas pressure in the system, cleaning of the surfaces is performed by Ar ions accelerated in crossed magnetic field B and electric field E. Increase of working gas pressure above certain value results in discharge glow between the accelerator anode and hollow cathode, and to intense sputtering of material of the targets attached to the accelerator cathode and material of the hollow cathode . The sputtered target atoms (Ti, Cu) are ionized additionally in the hollow cathode plasma and deposited on the substrate surfaces. For deposition of Cu and Ti onto textile samples, accelerator cathode cover plates, made of copper and titanium (99.9 % purity) foil with a 50…100 μm thickness were used. The hollow cathode was made of the same materials as the ones used for the accelerator cathode cover plates. Textile samples (50x20 mm) were placed inside the hollow cathode at about 150 mm distance from the bottom plane of the accelerator electrodes during the deposition. The cleaning of the textile samples inside the vacuum chamber was carried out for 5…6 min of discharge voltage V=900 V and Ar ion current density of ~0,1 mA/cm^2. The coating was then established for 20 mins of voltage V=600…650 V and current of I= 500…600 mA.

In order to prepare the textile substrates for coating, they were pretereated by washing in water, cleaning detergent (OMO, Turkey 1 g/l) and 1 g/l of sodium carbonate compund for 15 min at 70ºC and then air dried for 45 min. The same cleaning procedure was carried out for all substrates to be coated by both magnetron sputtering and cleaning-deposition system.

The antibacterial properties of the Ag, Ti and Cu coated fabrics were qualitatively evaluated using a gram-negative bacterium *E. coli* (ATCC 25922) and gram-positive bacterium *S. aureus* (ATCC 25923) provided from the culture collection of Microbiology laboratory, Yeditepe University. Bacterial inoculum with a suitable concentration was prepared in the Tryptone soya broth (Fisher Scientific). For the antimicrobial tests the parallel streak method (AATCC-TM 147) was used. Briefly, plates of Luria-Bertani Agar (Sigma-Aldrich) were streaked with a loopful of the bacteria. The coated side of the textile strips was placed face down onto the agar and aerobically incubated (Binder, USA) for 24 h at 37^{o}C. Following this incubation the zone of inhibition was determined and the textile surface microscopically examined (Leica, Germany) to check for growth on top of the textile surface. All experiments were carried out three times and the mean values were calculated.

2. EXPERIMENTAL RESULTS AND DISCUSSION

Examples of SEM images (5 K magnification) of the coatings Cu, Ti, Ag on cotton fibers, obtained using magnetron sputtering and cleaning-deposition system are presented by in Fig. 1.

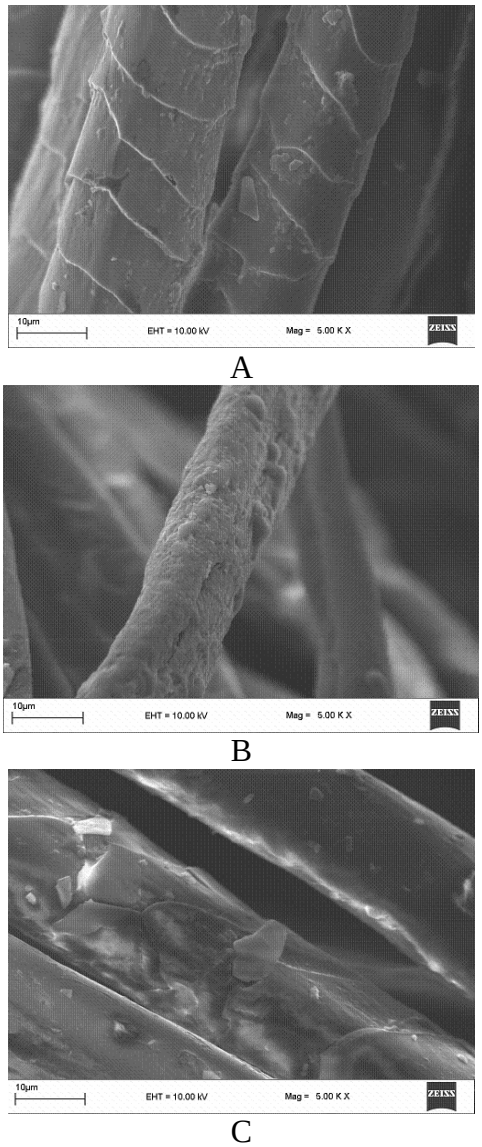

Fig. 1. The SEM pictures of cotton fibers coated by Cu, Ti, and Ag. A – Cu coatings for 15 min; B – Ti coatings for 30 min; C – Ag coatings for 8 min

When these coatings are examined, it is seen that the Cu coating creates smooth circular zones which are attached to each other while Ti coatings are more uniform but not smooth. The silver coatings are weak, but smooth and shiny. The SEM pictures (5K magnification) of Ti coating (20 minutes) on the cotton/polyester textile obtained by magnetron sputtering and cleaning-deposition systems under the same conditions are presented in Fig. 2.

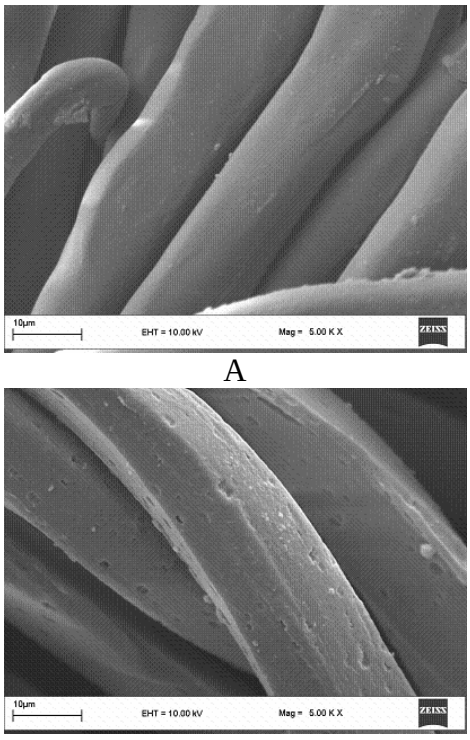

Fig. 2. The SEM pictures of cotton/polyester fibers coated by Ti. A – magnetron sputtering; B – cleaning-deposition system

As seen, cotton/polyester fibers allow more smooth surface against Ti and the magnetron sputtering coating is more uniform than cleaning-deposition system coating.

Fig. 3 shows the SEM picture (5K magnification) cross section of cotton/polyester fibers magnetron sputtering coated by Ag for 20 min coating.

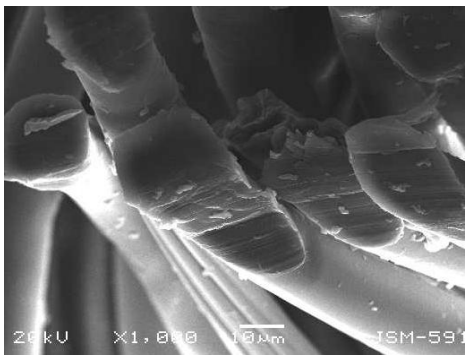

Fig. 3. The SEM pictures of the cross section of cotton/polyester fibers magnetron sputtering coated by Ag

The coating seems homogeneous and its thickness appeared to be nearly 200 nm.

The results of the antimicrobial property of Cu, Ti, Ag films on cotton textile coated by magnetron sputtering and cleaning-deposition systems against *S. aureus* and *E.coli* bacteria are shown in Table. This table was produced by measuring the thickness of inhibition zones around coated textiles.

Antimicrobial activity of the coating on cotton textile

Metal/bacteria	Inhibition zone, mm	
	S. aureus	*E. coli*
Cu	0	0.1…0.2
Ti	0	0
Ag	0.2…0.3	0.2…0.3

It has been found that in the case of Cu coating no growth of *E. coli* on the surface of the samples was observed and the value of the inhibition zone around the samples was 0.1…0.2 mm. At the same time, the antimicrobial efficiency of copper on *S. aureus* was significantly lower. Ti coating demonstrated similar antimicrobial activity as Cu one although no inhibition zones were formed. Sufficiently high activity of the titanium (comparable with the copper activity) can be connected, as we have indicated above, with the formation a TiO_2 film on the surface of Ti films. It was also found, that silver coating is more effective than others – no bacteria growth onto the substrate surface was observed and zone of inhibitions was of 0.2…0.3 cm for all studied substrates. The comparison of sputtering and hallow cathode systems revealed that nearly identical results are obtained although the coating morphologies were slightly different.

CONCLUSIONS

It was shown that cotton and cotton/polyester textiles coated by DC magnetron sputtering and hollow cathode systems produced similar antimicrobial activity. The coated Cu, Ag and Ti films by both methods can produce total elimination of the bacteria of *E. coli* and *S. Aureus* from the textile surfaces while only Cu and Ag coated fabrics produced up to 0.2 mm inhibition zone around the surfaces. These results show that all these metal coatings can be used for antimicrobial activity on the textile surfaces.

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REFERENCES

1. A.J. Varkey, M.D. Dlamini, A.B. Mansuetus, A.T. Tiruneh. Germicidal Action of Some Metals/Metal Ions in Combating *E. coli* Bacteria in Relation to Their Electro-Chemical Properties // *Journal of Water Resource and Protection*. 2013, v. 5, p. 1132-1143.

2. J. Scholza, G. Nockea, F. Hollsteinb, A. Weissbach. Investigations on fabrics coated with precious metals using the magnetron sputter technique with regard to their anti-microbial properties // *Surface & Coatings Technology*. 2005, v. 192, p. 252-256.

3. S.X. Jiang, W.F. Qinb, R.H. Guo, L. Zhang. Surface functionalization of nanostructured silver-coated polyester fabric by magnetron sputtering // *Surface & Coatings Technology*. 2010. v. 204, p. 3662-3667.

4. M.I. Mejia, G. Restrepo, J.M. Marın, et al. Magnetron-Sputtered Ag Surfaces. New Evidence for the Nature of the Ag Ions Intervening in Bacterial Inactivation // *Appl. Material & Interfaces*. 2010, v. 2, № 1, p. 230-230.

5. J. Kiwi, C. Pulgarin. Innovative self-cleaning and bactericide textiles // *Catalysis Today*. 2010, v. 151, p. 2-7.

6. S. Rtimi, O. Baghriche, R. Sanjines, et al. Photocatalysis/catalysis by innovative TiN and TiN-Ag surfaces inactivate bacteria under visible light //*Applied Catalysis B: Environmental*. 2012, v. 123,124, p. 306-315.

7. J. Kiwi, S. Rtimi, R. Sanjines, and C. Pulgarin. TiO_2 and TiO_2-Doped Films Able to Kill Bacteria by Contact:New Evidence for the Dynamics of Bacterial Inactivation in the Dark and under Light Irradiation // *Inter. J. Photoenergy*. 2014, v. 2014, p. 1-17.

8. J. Kiwi, S. Rtimi, and C. Pulgarin // *Microbial pathogens and strategies for combating them: science, technology and education*, Formatex Research Center, 2013, v. 1, p. 74-82.

9. T. Yuranova, A.G. Rincon, A. Bozzi, et al. Antibacterial textiles prepared by RF-plasma and vacuum-UV mediated deposition of silver // *J. Photochem. Photobiol. A: Chemistry*. 2003, v. 161, p. 27-34.

10. D. Depla, S. Segers, W. Leroy, et al. Smart textiles: an explorative study of the use of magnetron sputter deposition // *Textile Research Journal*. 2011, v. 81(17), p. 1808-1817.

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ИССЛЕДОВАНИЯ АНТИМИКРОБНОЙ АКТИВНОСТИ И МОРФОЛОГИЧЕСКИХ СВОЙСТВ ПОВЕРХНОСТИ ТКАНЕЙ С МЕТАЛЛИЧЕСКИМИ НАПЫЛЕНИЯМИ

Necdet Aslan, Kenan Şentürk, Tuba Şen, Turgay Çoruhlu, İpek Vartürk, S. Şeker, S. Shahidi,. А.М. Добровольский, В.В Циолко, С.В. Мацевич, S.S. Keskin, May Korachi

Представлены результаты исследования антимикробных и поверхностных свойств тканей с металлическими напылениями, созданными при помощи магнетрона или чистяще-распылительного устройства на базе последовательно расположенных ускорителя с анодным слоем и полого катода. Определены и сопоставлены.антимикробные свойства тканей из хлопка и смеси хлопок/полиэстер с напылениями из Cu, Ti и Ag, созданными с использованием двух этих устройств, против бактерий *E. coli* и *S. aureus*.

ДОСЛІДЖЕННЯ АНТИМІКРОБНОЇ АКТИВНОСТІ ТА МОРФОЛОГІЧНИХ ВЛАСТИВОСТЕЙ ПОВЕРХОНЬ ТКАНИН З МЕТАЛЕВИМ НАПИЛЕННЯМ

Necdet Aslan, Kenan Şentürk, Tuba Şen, Turgay Çoruhlu, İpek Vartürk, S. Şeker, S. Shahidi, А.М. Добровольський, В.В. Ціолко, С.В. Мацевич, S.S. Keskin, May Korachi

Представлено результати досліджень антимікробних і поверхневих властивостей тканин з металевими напиленнями, створеними за допомогою магнетрона та чистяче-розпилювального пристрою на базі послідовно розташованих прискорювача з анодним шаром та порожнистого катода. Визначені та співставлені антимікробні властивості тканин з бавовни та суміші бавовна/поліестер з напиленнями з Cu, Ti та Ag, створених за допомогою цих пристроїв, проти бактерій *E. coli* та *S. Aureus.*