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RESEARCH

Advanced Military Materials made by Metal Particle Coating Techniques

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ABSTRACT

Different fields of industry, such as electronics, textiles, biomedicine, ceramics etc use nanofilms made of various materials (polymers, metals ceramics etc) for improving the properties of substrates. Various methods like chemical vapour deposition, chemical deposition, sol-gel method and magnetron sputtering., are used to cover materials, including textile materials.

Conductive textiles are materials that can conduct electricity. There are known different methods to obtain this functionality of textiles: embedding metal yarns into the textile structure by weaving or knitting technology, metallic thin film deposition on the surface (EB-PVD and Sputtering), 3D printing technology etc.

In our research, a primary haemostasis device was designed and developed, which consists of a tourniquet-type system that automatically activates when bleeding in the limbs is detected to stop the bleeding. The tourniquet is automatically tightened until no more oscillations in blood pressure measured by the pressure sensor connected to the pneumatic cuff are detected.

The pressure sensor consists of a conductive textile structure, that was achieved by thin film deposition of Cu particles with a hybrid PVD (Physical Vapor Deposition) system, type Torr-Model No: 5X300EB-45KW. A Cu target with 99.999% purity with a diameter of 2 inches and a thickness of 3 mm was used for deposition. The technological flow of EB-PVD deposition and working parameters for achieving Cu coating were established.

The thickness of the deposited layer on textiles was 5µm. The values of electrical conductivity (S/m) obtained on 1 inch of textile surface, were 34.426,67 S/m (V1-treated with ITOBINDER-AG-Acrylate) and 6.179,15 S/m (V2- treated with PERMUTEX-EX-RU-13-737-Urethane). On a 10- cm textile surface, the electrical conductivity was 84.005,38 S/m (V1) and 7.961,02 S/m (V2). SEM analysis of the coated surfaces and semi-quantitative EDS chemical point analysis were performed.

KEYWORDS

Advanced, textiles, thin film, sputtering, conductivity

INTRODUCTION

Being a soldier is a dangerous job. Today, in a World with a lot of "trouble", the lives of the soldiers who are involved in terrestrial actions are permanently in danger, because, all the time they can be killed, injured (e.g. legs blown off) and suffering of mental illness (e.g. after seeing their friends are killed), **Fig. 1**.

Fig. 1. Main risk for soldiers [**1**].

The risks associated with military service include actual war-fighting, training with weapons and explosives, operating with armoured vehicles or deployment to climatic extremes [**2**]. The published data highlights the rapid growth of the military personal protective equipment market globally at a CAGR of around 7.8% until 2028 and for body armour at over 19.8%, due in particular to the increased demand for ballistic and hostile environment protective equipment [**3**]. For example, in conflicts such as the one in Syria, over 10 years, more than 300,000 lives have been lost, and in the one in Russia and Ukraine, which started in 2022, there is a death rate of about 100-200 soldiers per day [**4,5**].

Off-the-shelf plate carriers (SPCS) are tested from 2009, bythe (**Fig. 2**) for issuing to troops deploying to Afghanistan as a lighter and more comfortable alternative to the IOTV (Improved Outer Tactical Vest) [**6**].

(a)
(b)

Fig. 2. (a) IOTV (b) Soldier Plate Carrier System (SPCS) [**6**].

But the main constraint of the current technique consists in the fact that ballistic protection equipment is designed and made for the protection of the upper part of the human body excluding the upper/lower limbs which remain exposed to external stress factors (shooting, cutting, etc.) and which can lead to the death of the combatant due to large blood losses over long periods.

Blood is the only liquid tissue in the human body that consists of the liquid phase - plasma and the solid phase - figurative elements. The blood circulates continuously through the vascular system, the driving force of the movement being the cardiac pump. The total amount of blood in the body that fully occupies the cardiovascular apparatus (capillaries, arteries, veins, cardiac cavities) constitutes the total blood volume. It constitutes 5-7.5% of body weight or 65-76.7 mL/kg/body. In an adult weighing 70 kg, the total blood volume is 4.5-5.0 L, of which 2/3 circulates through the vascular system, and 1/3 is stored in the spleen, liver and other organs. Stored blood is a dynamic reserve that can be mobilised in case of need. The reserve is required in case of massive haemorrhages and other pathological conditions. Blood is a viscous liquid, its total viscosity being 4-6 poises at 38°C. Blood is distributed to body tissues through blood vessels. Arteries represent the distribution of blood vessels, through which the blood circulates from the heart to the organs and are composed of the three types of tunica (externa, media, and intima), and basement membrane (**Fig. 3a**). The veins carry blood from the organs to the heart. They are consistsing of tunica externa, tunica media and tunica intima (**Fig. 3b**).

(a)
(b)

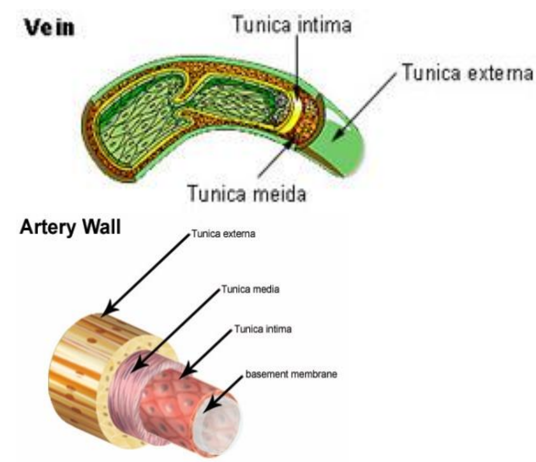


Fig. 3. a) The structure of the arteries b) the structure of the veins.

Arterial pressure in the larger vessels is formed of several distinct components: systolic and diastolic pressure, pulse pressure and mean arterial pressure (**Fig. 4**) being recorded as a ratio of two numbers (120/80 adult normal blood pressure).

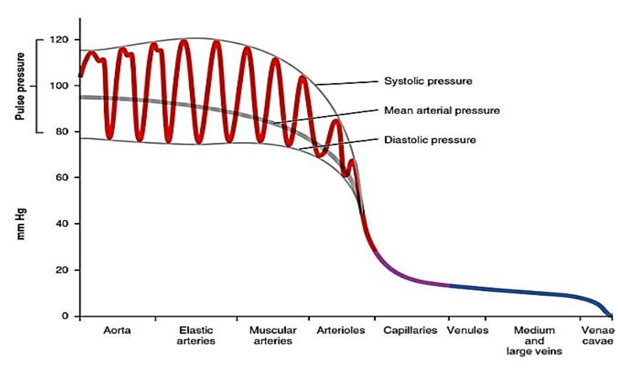


Fig. 4. Blood pressure components.

In military operations, 12% of all injuries are associated with significant vascular injuries requiring treatment. Among the vascular injuries, 80% involve the vessels of the limbs, 10% the vessels of the cervical region and 10% those of the abdomen and chest, despite the use of bulletproof vests. From the moment of trauma with vascular damage, control of haemorrhage remains the number one priority to ensure survival until the patient can be transferred to a specialized hospital unit [**7**]. It is well known that arterial haemorrhages are the most dangerous, because the blood "spurts" rhythmically and with a high flow rate, which quickly leads to significant blood loss, and ultimately the person's death [**8**].

In accordance with Oxford Languages, haemorrhage can be defined as "a loss of blood from a ruptured blood vessel". This condition ranges from mild to life-threatening.

Considering their severity The American College of Surgeons Division of Advanced Trauma Life Supportdefined four levels of haemorrhage (level I-IV). A class IV haemorrhage occurs when more than 40% of the patient's circulating blood volume is lost. In this case, after a gunshot wound or blunt trauma affecting a major artery , blood pressure cannot be maintained due to the lower volume of the circulating fluid and the patient may become unconscious. The time until permanent muscle damage occurs (tissue necrosis) is 2 hours and until the muscle damage is complete: 6 hours. From the moment of trauma with vascular damage, bleeding control remains the number one priority to ensure survival until the patient is transferred to a specialized hospital unit [**7**].

In the event of a shooting or knife injury, to stop the bleeding, we must induce the haemostasis process. Haemostasis is the mechanism that stops bleeding from a blood vessel. It is a process that involves several interconnected steps (**Fig. 5**).

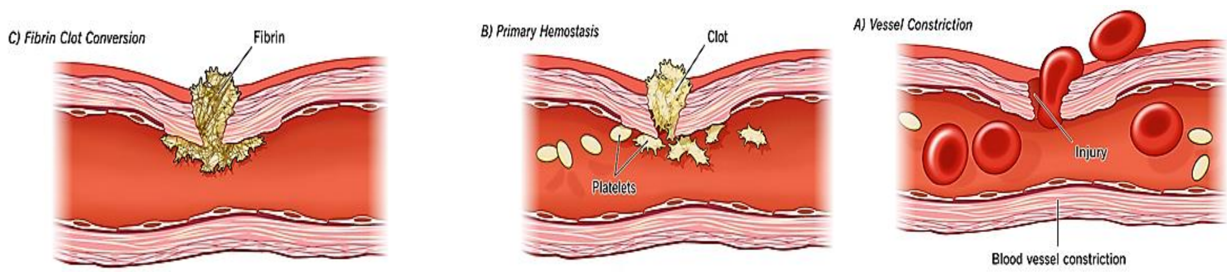


Fig. 5. The mechanism of haemostasis [7].

The research project proposes to obtain intelligent protective equipment with a primary haemostasis system, which ensures the survival of combatants at least 3 hours after aggression. The stoppage of mixed bleeding is achieved by an automatic system incorporated in the protective equipment which is automatically triggered as a result of the interruption of the electrical circuit in a conductive elastic fabric by the occurrence of an event such as a gunshot wound, stabbing or cutting of the limbs, which is the medical translation of the existence of a haemorrhage (**Fig. 6**) The electric circuit is provided by conductive textile structures made by covering with conductive metal by EB-PVD technology.

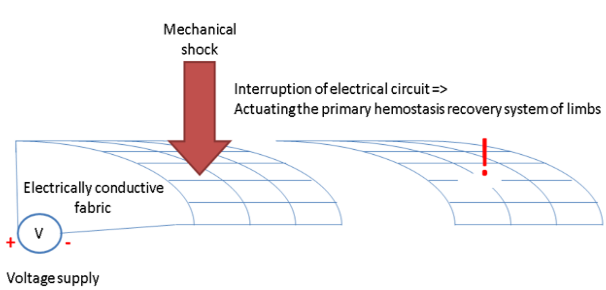


Fig. 6. Working principle of the device.

Nowadays, the fabrication of electronics, ceramics, biomaterials, etc iinvolves using of nanofilms, to enhance their functional characteristics [**9**]. Fabrics coated with nanofilms are usually prepared through chemical vapour deposition [**10**], chemical deposition [**11**], sol-gel [**12**] method and magnetron sputtering [**13**]. Electron-beam Physical vapour deposition (EB-PVD) is a well-known technology that is widely used as crreate conductive textiles. This technique involves the use of a high-energy electron beam , while a metal is deposited on the surface of the substrate in the molecular form under high vacuum conditions (**Fig. 6**). Two electrodes connected to a high-voltage power supply and a vacuum chamber constitute the PVD reactors.

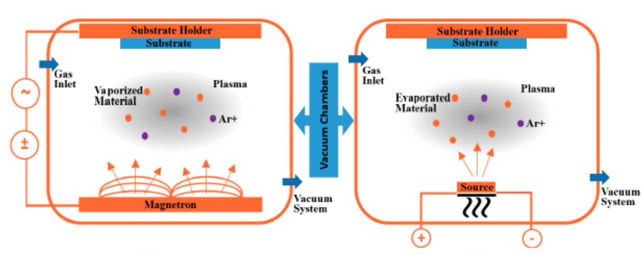


Fig. 7. Schematic drawing of conventional PVD processes [15]

The EB-PVD process can be applied to almost all materials, and allows obtaining layers of different thicknesses and with various physical and chemical properties. Among the so many advantages of this technique, there are the following: high purity, efficiency and ecological nature of the process; the possibility of using substrates mainly in the form of gases and pure metals instead of expensive; the possibility to produce both non-stoichiometric and non-equilibrium coating materials with different properties.

MATERIALS AND METHODS

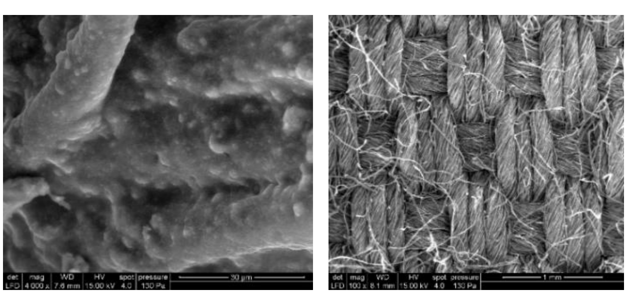
Textile structures

Textile substrates made of 100% Cotton were treated with ITOBINDER-AG-Acrylate (V1): 70g/l, followed by drying at 120^0C for 120s and condensation at 150^0C and PERMUTEX-EX-RU-13-737-Urethane (V2): 70 g/l, drying at 120^0C for 120s and condensation at 140^0C for 60s (**Table 1**).

Table 1.

Technological phase	Chemical auxiliary	Concentration [g/l]	Working parameters	
			t [^{0}C]	T [min]
Alkaline boiling	KEMAPON PC/LF	2g/l	98	90
	Seghion MC200	1,5 g/l		
	Sodium hydroxyde	8 ml/l		
	Trisodium phosphate	3g/l		
	Sodium carbonate	3g/l		
Washing	95^0C, for 15 min			
Washing	70^0C, for 15 min			
Washing	50^0C, for 15 min			
Washing	30^0C, for 10 min			
Acidulation	Acetic acid	1ml/l	30	15
Rinsing	Cold			15
Squeezing	Padding			
Drying	Room temperature			
Impregnation I	ITOBINDER AG-Acrylate	70	-	-
	Drying	-	120	2
	Condensation	-	150	2
Or				
Impregnation II	PERMUTEX EX-RU-13-737-Urethane	70		
	Drying	-	120	2
	Condensation	-	140	1

The treatment of the textile supports with chemical auxiliaries was necessary to orient the movement of the metal particles. In previous experiments, it was found that the metal particles tend to penetrate between the fibres and do not form a continuous film on the surface of the substrates. Thus, obtaining an electrical signal was not ensured. By treating the textile substrates, this inconvenience was eliminated. (**Fig. 8**)



(a) (b)

Fig. 8. SEM images a) before b) after treatment.

Equipment

Electron beam deposition installation Torr-Model No: 5X300EB-45KW was used. The system is designed to combine several layers, having 4 guns with electron emission, with a power of 10 kW/ton. Each gun is equipped with a carousel system with 4 "pockets", in which 4 crucibles with a volume of 75 cm^3 each can be placed, thus allowing an almost continuous evaporation of up to 16 different materials from all 4 guns. The installation has the possibility of deposition on rotating 3D plates or cylinders with a maximum length of 350 mm; simultaneous or multilayer deposition of thin films; heating of the substrates during deposition; melting and deposition of grains of metals and alloys (W, Ni, Co, Cr, Al, Y), dielectric materials (Al_20_3, $Si0_2$, $Zr0_2$, etc.) and compounds [**14**]

The textile materials used as the substrate were fixed on the support of the deposition installation (**Fig. 9**).

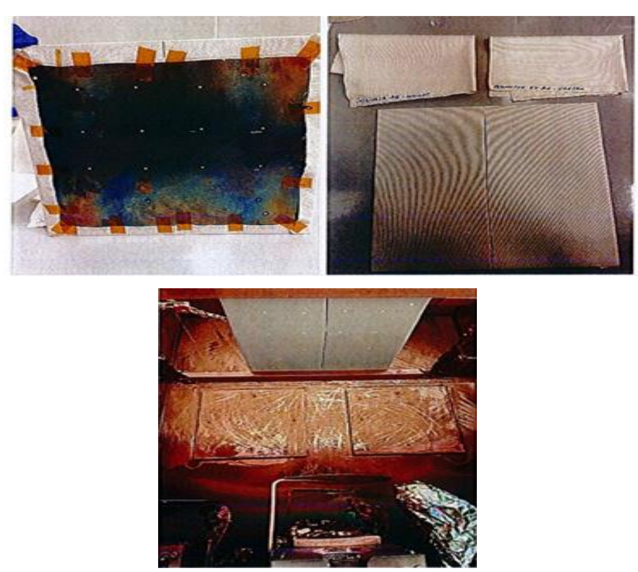


Fig. 9. Fixing textile materials on supports.

The preparation phases of the evaporation system are shown in **Fig. 10.**

For the EB-PVD deposition of copper on textile materials, a crucible was loaded with Cu material of 99.99% purity.

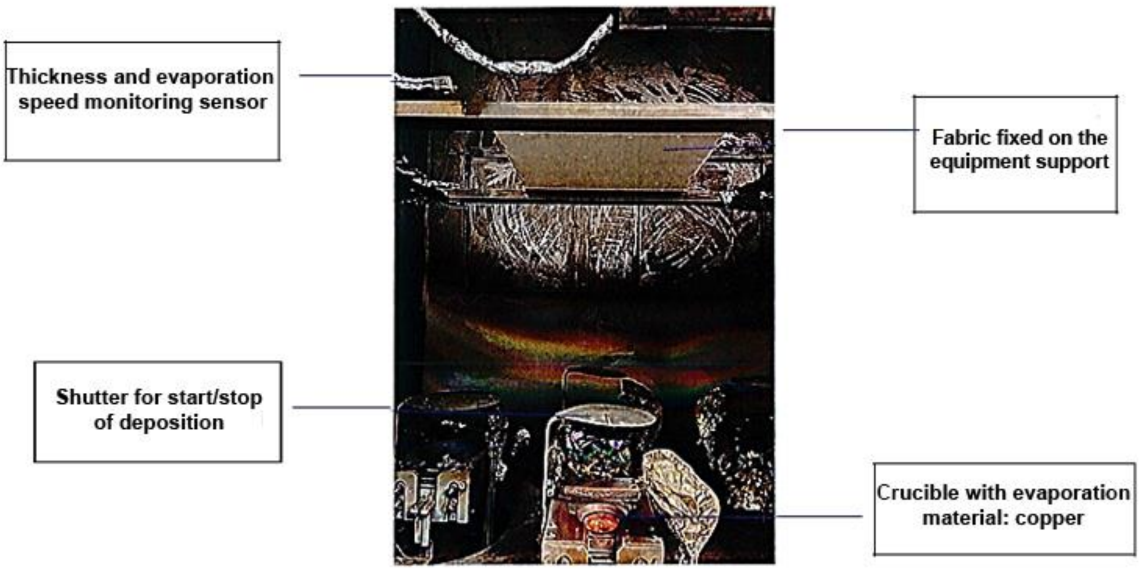


Fig. 10. EB-PVD system ready for evaporation.

The technological flow of EB-PVD deposition for achieving Cu coating included the phases shown in **Fig. 11**.

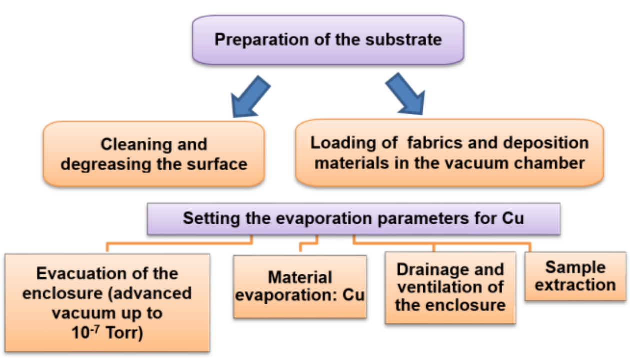


Fig. 11. Technological flow of EB-PVD deposition.

The working parameters are presented in the **Table 2**: starting vacuum (Torr) - 10^5, working vacuum (Torr) - $2x10^5$, deposition speed (Å/s) - 3, maximum power e-beam gun: 10 kW.

After completing thedeposition process, the sample was removed from the deposition chamber (**Fig. 12**).

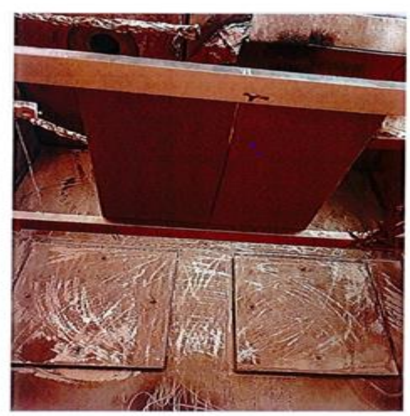


Fig. 12. EB-PVD system after the evaporation process

Samples V1 and V2 were studied on the surface and in sections by scanning electron microscopy in Low Vacuum mode, using the backscattered secondary electron (ABS) detector and the energy dispersive spectroscopy (EDS) detector.

Table 2

TORR electron flow deposition equipment, Model No: 5X300EB-45KW							
Substrate	Materials and number of crucibles, capacity 75 cc used for evaporation	Starting vacuum (Torr)	Working vacuum (Torr)	Deposition speed (Å/s)	Estimated thickness (μm)	Maximum e-gun power:	The distance between the crucible and the substrate
Impregnated textile materials	1 Cu crucible	10^5	$2x10^5$	3	5-6 μm	10KW	0.8 m

The electrical resistivity (Ω) was determined on one inch and 10 cm of textile surface, using the BX PRECISION 889B Bench LRC/ESR METER and the electrical conductivity was calculated (1).

The measurement scheme (**Fig. 13**) and the calculation formulas (1) for conductivity are presented below:

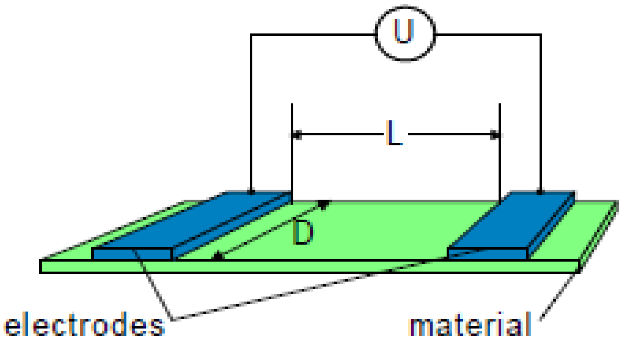


Fig. 13. Scheme of measurement of electrical surface resistance.

$$\rho = \frac{U}{I} \cdot \frac{D \cdot g}{L} = R \cdot \frac{D \cdot g}{L} \qquad (1)$$

where: electrode width (D) = 0.01 m, L1-0.0254 m, L2-0.1 m, thickness (g)-0.00062 m

RESULTS AND DISCUSSIONS

Table 3 shows the physical-mechanical characteristics of the 100% cotton textile structures before and after treatment.

Table 3

Characteristic/ Variant		UM	Variants			
			Plain 100% cotton woven structure	100% cotton woven structure cleaned/ washed	100% cotton woven structure - treated with ITOBINDER	100% cotton woven structure - treated with PERMUTEX
Mass		g/m^2	207,62	197,92	199,15	199,7
Yarn density	U	No. of yarns/ 10 cm	610	610	620	620
	B		360	360	360	360
Breaking force	U	N	1311,15	1290,31	1219.61	1142,43
	B		539.97	527,13	558,56	614,43
Elongation at break	U		11,40	12,21	19,15	19,95
	B		6,69	7,12	8,32	8,97
Thickness		mm	0,57	0,49	0,53	0,55
Pattern weave		-	plain	plain	plain	plain
Water vapor permeability		%	29,9	30,9	33,0	31,6
Air permeability		$l/m^2/s$	215,5	85,52	79,77	80,09
Losding degree		%	-	-	0,77	1,95

The physical-mechanical characteristics of the textile structures made of 100% cotton, cleaned/washed and treated with chemical auxiliaries ITOBINDER AG and PERMUTEX EX-RU-13-737 vary within 3-15% compared to the physical-mechanical characteristics of the raw fabric.

Samples V1 and V2 were studied on the surface and in sections by SEM analysys.

The study of sample V1 revealed a fibrous structure, on the surface of which a fine coating layer was deposited (**Fig. 14**). The coverage has a columnar appearance and is uniform and continuous over the sample surface.

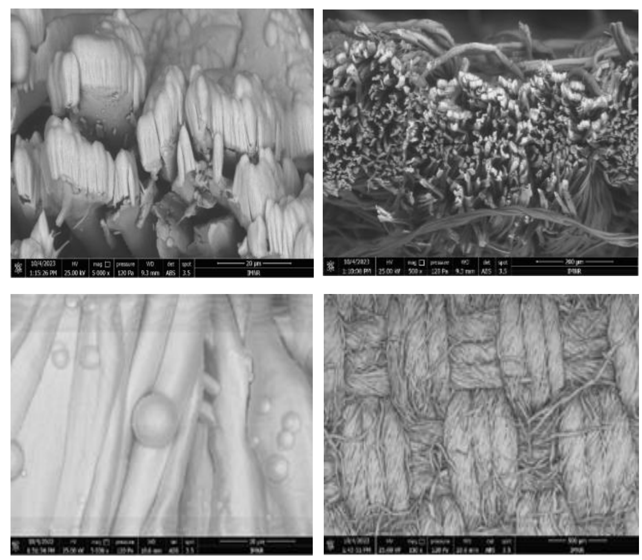


Fig. 14. SEM image of V1 sample: a) surface b) section.

The study of the V2 sample revealed a fibrous structure, on the surface of which a fine coating layer was deposited. The coating has a columnar appearance (**Fig. 15**) and is uniform and continuous on the sample's surface.

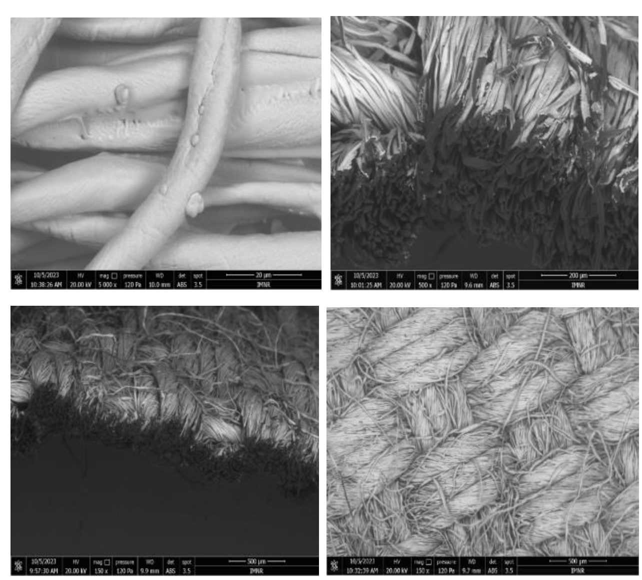


Fig. 15. SEM image of V2 sample: a) surface b) section.

The EDS semi-quantitative chemical analysis of samples V1 and V2 highlighted the presence of the element Cu with the atomic and mass percentages shown in **Fig. 16**.

The thickness of the deposited layer is 5µm for both variants. The electrical resistivity (Ω) was determined on one inch and 10 cm of textile surface, using the BX PRECISION 889B Bench LRC/ESR METER and the electrical conductivity was calculated.

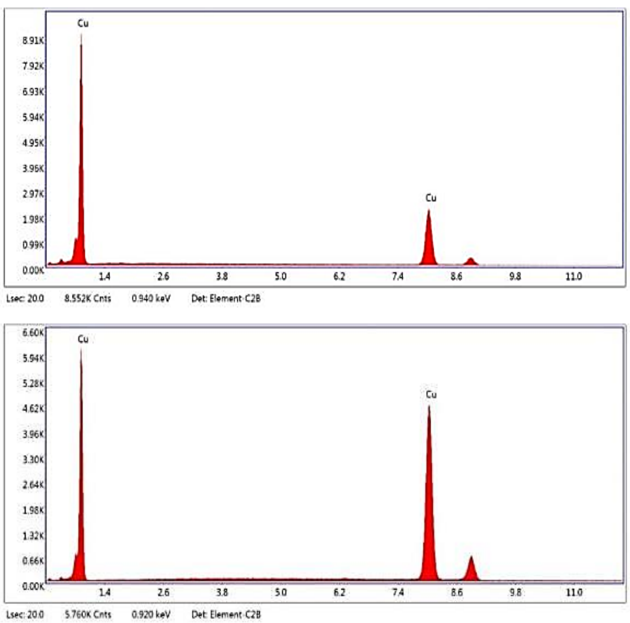


Fig. 16. The results of the EDS analysis of sample a) V1 b) V2.

The values of electrical conductivity (S/m) obtained on 1 inch of textile surface, were 34.426,67 S/m (V1-treated with ITOBINDER-AG-Acrylate) and 6.179,15 S/m (V2-treated with PERMUTEX-EX-RU-13-737-Urethane). On a 10-inch, textile surface, the electrical conductivity was 84.005,38 S/m (V1) and 7.961,02 S/m (V2).

CONCLUSIONS

- Electron beam deposition installation Torr-Model No: 5X300EB-45KW was used. The system is designed to be able to combine several layers, having 4 guns with electron emission, with a power of 10 kW/ton. Each gun is equipped with a carousel system with 4 "pockets", in which 4 crucibles with a volume of 75 cm^3 each can be placed, thus allowing an almost continuous evaporation of up to 16 different materials from all 4 guns.
- The technological flow of EB-PVD deposition and working parameters for achieving Cu coating were established.
- The coverage has a columnar appearance that is uniform and continuous over the sample surface.
- The best electrical conductivity values were obtained for textile structures treated with ITOBINDER AG-Acryl which were between 34,426 S/m (1 INCH) and 84005.38 S/m (10 inch).
- In the next period, experiments will be carried out to create conductive textile substrates by applying the EB-PVD method on Ag.

ACKNOWLEDGEMENTS

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REFERENCES

1. Independent guide to the British army. How dangerous is a soldier’s job? https://beforeyousignup.info/joining/risks/
2. Bricknell MC, Amoroso PJ, Yore MM. What is the risk associated with being a qualified military parachutist? Occup Med (Lond). **1999** Apr; 49(3), 139-45. DOI: 10.1093/occmed/49.3.139. PMID: 10451594.
3. Qian-ran Hu, Xing-yu Shen, Xin-ming Qian, Guang-yan Huang, Meng-qi Yuan, The personal protective equipment (PPE) based on individual combat: A systematic review and trend analysis, *Defence Technology*, Volume 28, **2023**, Pages 195-221, ISSN 2214-9147, https://doi.org/10.1016/j.dt.2022.12.007.
4. Mizrahi, T., & Yallouz, J. (**2022**). Internet Performance in the 2022 Conflict in Ukraine: An Asymmetric Analysis. *ArXiv,* abs/2205.08912.
5. CAI Yi. Typical Individual Combat Scenarios and Night Vision Goggles[J]. *Infrared Technology,* **2022**, 44(4): 315
6. Ghai RS, Chen K, Baddour N. Modelling Thermal Conductivity of Porous Thermal Barrier Coatings. *Coatings.* **2019**, 9(2), 101. https://doi.org/10.3390/coatings9020101[6] https://www.armorexpress.com/product/spc-soldier-plate-carrier/
7. B. Tuncali, G. Kokten, F. Altinel, Z. Kayhan, Efficacy of arterial occlusion pressure estimation-based tourniquet pressure settings in upper limb surgery, *Journal of Orthopaedic Science,* **2021** 10.1016/j.jos.2021.06.011
8. U.S. Army Institute of Surgical Research, TCCC Guidelines for Medical Personnel. **2020**, www.usaisr.amedd.army.mil/pdfs/TCCCGuidelinesforMedicalPersonnel170131Final.pdf.
9. M. Asad, N. Saba, A.M. Asiri, Preparation and characterization of nanocomposite films from oil palm pulp nanocellulose/poly (Vinyl alcohol) by casting method, *Carbohydrate Polymers,* **2018**, 191, 103-111.
10. S.V. Lomov, S. Wicks, L.Gorbatikh, Compressibility of nanofibre-grafted alumina fabric and yarns: Aligned carbon nanotube forests, *Composites Science and Technology,* **2014**, 90, 57–66.
11. Y. Lu, Electroless copper plating on 3-mercaptopropyltriethoxysilane modified PET fabric challenged by ultrasonic washing, *Applied Surface Science*, **2009**, 255, 8430–8434.
12. C. Pan, L. Shen, S. Shang, Preparation of superhydrophobic and UV blocking cotton fabric via sol–gel method and self-assembly, *Applied Surface Science,* **2012**, 259, 110-117.
13. J.Y. Liu, K.B. Cheng J.F. Hwang, Study on the electrical and surface properties of polyester, polypropylene, and polyamide 6 using pen-type RF plasma treatment, *Journal of Industrial Textiles,* **2011**, 41, 123–141.
14. https://www.grandviewresearch.com/industry-analysis/military-personal-protective-equipment-market#
15. https://imnr.ro/wp/en/projects/modernised-eb-pvd-system-for-development-and-assesment-of-thermal-barrier-coatings-for-aeronautic-applications-acronym-aero-coat/
16. Choolaei M, Vostakola MF, Horri BA. Recent Advances and Challenges in Thin-Film Fabrication Techniques for Low-Temperature Solid Oxide Fuel Cells. *Crystals.* **2023**, 13(7), 1008. https://doi.org/10.3390/cryst13071008