ISSN: 1231-4005
e-ISSN: 2354-0133
DOI: 10.5604/12314005.1138634

SURFACE MODIFICATION OF POLYPROPYLENE NONWOVEN WITH COMPOSITE METALLIC LAYERS

Kazimierz Reszka, Ewa Dobruchowska

Koszalin University of Technology
Institute of Mechatronics, Nanotechnology and Vacuum Technique
Śniadeckich Street 2, 75-453 Koszalin, Poland
tel.: +48 94 3486621, +48 94 3486651, fax +48 94 3486652
e-mail: kazimierz.reszka@tu.koszlin.pl, ewa.doruchowska@tu.koszalin.pl

Joanna Koprowska, Błażej Wiśniewski

Textile Research Institute
Brzezinska Street 5/15, 92-103 Łódź, Poland
tel.: +48 42 6163145, fax +48 42 6792638
e-mail: koprowska@iw.lodz.pl, bwisniewski@iw.lodz.pl

Abstract

Polymer fibres have the great potential for application due to their large surface area relative to volume, incomparably large length relative to the cross-section, high strength and ease of forming the nonwovens in thermal processing. Due to the specific properties of textiles, they are applied, among others in the manufacture of filters, sensors, biomedical devices and protective clothing.

This study was aimed to evaluate the surface morphology of polypropylene nonwoven modified with metallic layers CuSn, CuZnNi, NiCuFe, deposited by the magnetron sputtering technique. There was also carried out a qualitative and quantitative analysis of deposited thin layers and their compositions were compared with compositions of targets used for magnetrons. The surface morphology was tested using the metallographic optical microscope with a CF160 optical system and the scanning electron microscope adapted to work in an environmental mode. A study of composition was based on a microanalysis using the energy dispersive X-ray radiation deriving from the excited atoms (EDS).

Keywords*: polymer fibres, polypropylene, surface, magnetron, deposition, thin layers, SEM, EDS*

1. Introduction

Technologies of manufacturing (spinning) the fibres of polymeric materials, which also include polypropylene, are known and widely used for many decades. Due to their numerous advantages, from which the most important are a small stretchability, smooth surface, tear and fire resistance, and good air permeability, they have found a wide range of applications in production of mattresses, pillows, quilts and filtration materials. As nonwoven fabrics they are used in production of medical and sanitary articles, in footwear industry and leather working; they are also used in production of lubricants and upholstery for furniture industry and the manufacture of sensors, electronics and photovoltaic devices. They are also used in production of protective and medical clothing.

Studies conducted on oriented polymers also indicate a very high potential for textile applications as structural materials due to their much better mechanical properties than constructional steel. In their production raises the importance of the gel-spinning technology, used mainly for polyethylene of very high molecular weight (UHMWPE, ultra-high molecular weight PE). However, this is complicated and expensive technology.

The electrospinning method developed in the early 20th century belongs to the most effective ones. The presence of an electric field, with choice of voltage from 5 to 55 kV between the nozzle or disk, offers ample opportunities of forming the fibres from a few to tens of nanometers. One of important factors in this formation is the selection of solvent and the rate of its evaporation during the spinning formation of a polymer solution jet induced by the electric field. Numerous modifications to the classical method of electrospinning have led to applications on an industrial scale. Among them, the high-performance technology "Nanospaider" developed by the Technical University in Liberec [1] and used by Elmarco Ltd. is worth noting. It consists in the formation of fibres from the layer formed on the surface of a rotating cylinder, partially immersed in a polymer solution.

The gained experience and the metallization technology of solid polymer products used for many years on an industrial scale gave rise to research and implementation of metallization technology also from fibres and nonwovens. This applies especially to non-woven fabrics, because of the simple technology and good mechanical properties and permeability, which are successfully increasingly used in production of protective clothing. One of the areas to increase their use is the production of heat-insulating and anti-radiation clothing particularly in the high-frequency radio waves and the production of flexible protective screens of the same properties.

2. Experimental procedure

The subject of research was non-woven polypropylene (PP) with a weight of 150 g/cm^2 manufactured under the trade name of "Termonina" by Lentex SA Lubieniec, Poland. Nonwoven fabrics were coated with metal layers by magnetron sputtering of targets consisting of metal compositions of (% by wt.) fractions given in Tab. 1. Nonwoven fabric in the form of ribbon was rewound in cycles (repeatedly) with constant linear velocity at a distance of 10 cm from target. Process conditions are presented in Tab. 2.

Tab. 1. List of targets from which the layers were deposited

No. of target/test	Fraction of target basic components [wt%]
1	**CuZnNi** (53.5–56.5% Cu, 25–30% Zn, 17–19% Ni)
2	**NiCuFe** (65% Ni, 33% Cu, 2% Fe)
3	**CuSn** (80% Cu, 20% Sn)
4	**CuZnNi** (53.5–56.5% Cu, 25–30% Zn, 17–19% Ni) / **NiCuFe** (65% Ni, 33% Cu, 2% Fe) / **CuSn** (80% Cu, 20% Sn)

The aim of this research was to produce the qualitative assessment of the layers; uniformity and consistency with the ground, based on microscopic observations made by the metallographic microscope (MM) Nikon MA-200 with CF160 optics. Images were recorded using a digital camera DS-FI1 and software NIS – Elements of Nikon. Also, the surface structure (morphology) of deposited layers by means of SEM 5500 LV, JEOL Company was determined. Observations were conducted in vacuum environment at pressure (p) equal to 2–5 x 10^{-4} Pa, and high-pressure conditions, at p = 10 Pa. The voltage accelerating the electron beam (probe) V = 20 kV was applied.

Tab. 2. Breakdown of tests and conditions of metal layers deposition of on nonwoven fabric

No. of test	Feed rate relative to target V [mm/s]	Total power supply to target P [kW]	Pressure in the chamber during the layer deposition p_{Ar} [mbar]	No. of cycles	Target-substrate distance [cm]
1	15	2.0–2.1	$1.9 \cdot 10^{-3}$	15	10
2	10	2.0–2.1	$2.2 \cdot 10^{-3}$	15	10
3	15	2.0–2.1	$2.3 \cdot 10^{-3}$	30	10
4	25	2.0–2.1	$2.3 \cdot 10^{-3}$	20	10

In the description of microscopic images, the following terms were used:
- "Weave" as the equivalent of crossing the "threads" made up of polypropylene fibres,
- "Overpress" is understood as an area located between the four "weaves" and corresponding to the site of thermal joint of unwoven fabric,
- "Thread" – the equivalent of the PP fibre set between overpresses, forming weaves (Fig. 1).

The composition of layers was also tested using the quantitative microanalysis by the method of Energy Dispersive X-ray Spectroscopy. The test results allowed the evaluation of differences between the composition of layers and the corresponding targets.

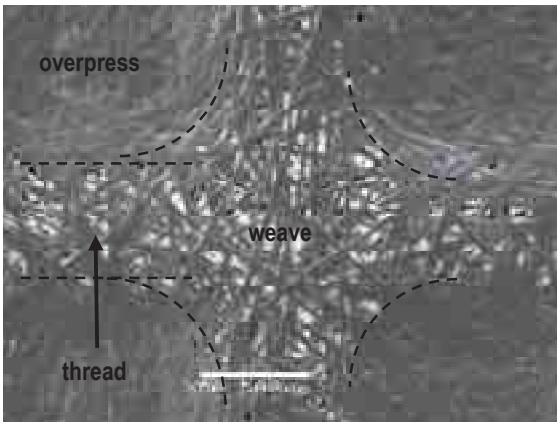


Fig. 1. SEM image, analyzed areas of polypropylene nonwoven fabric: thread, weave and overpress

3. Results

The layers were analyzed on nonwoven fabric in areas conventionally known as "overpressing", corresponding to sites of thermal joints and understood as areas lying between the four "weaves" of "threads". They were analyzed in areas of "weaves" as the equivalents of crossing spots of the polypropylene "threads" and on single "threads" made up of "fibres" (Fig. 1).

3.1. Qualitative assessment of changes proceeding in nonwoven fabric under the influence of temperature and the layers on the basis of metallographic microscopy

CuZnNi layers

Images obtained by metallographic microscopy (Fig. 2) provide a monolithic surface of the nonwoven fabric, melted under the influence of temperature, and a few holes that are residues of free spaces characteristic of the design of non-deformed "weave". A metal layer covering the molten substrate is continuous, marked by a few cracks, visible clearly in all sampling areas.

Fig. 2. MM images of 1 (CuZnNi) sample surface: a) the scale of 100μm, b) the scale of 50μm, c) the scale of 20μm

"Over-pressed" spots show a similar structure in all areas of the surface sampling. There are no visible signs of "flow" of substrate material. The deposited layer is uniform and smooth, and the visible points of discoloration may be a sign of initial chemical changes, possibly corrosive destroying of the layer.

NiCuFe layers

Images obtained by metallographic microscopy (Fig 3) illustrate the “weaves” i.e. areas of unwoven fabric between “over-pressed” spots. The fibres of this zone are highly molten and form a compact structure. One can only see a few pores, which are residua of the free spaces of nonwoven fabric produced prior to deposition of metal layers. The fibres are outlined with cracks on a metal layer, running across the fibres and extensive staining accumulated at elevations. This is probably an image of places where the metal layer was subjected to peeling or chipping.

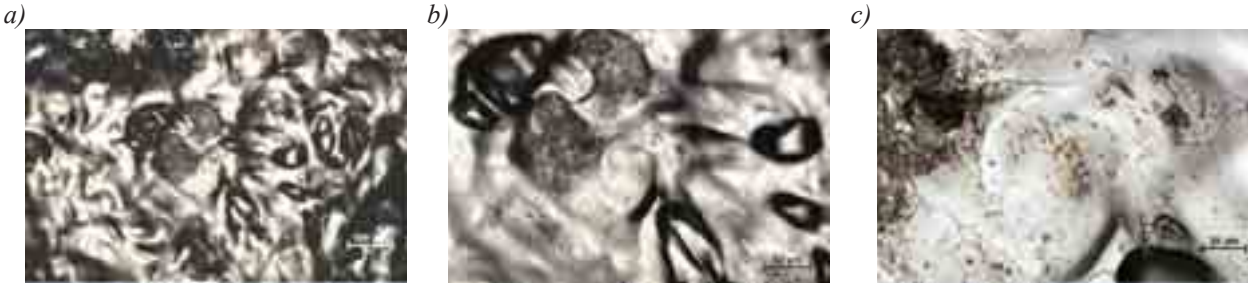


Fig. 3. MM images of 2 (NiCuFe) sample surface a) the scale of 100μm, b) the scale of 50μm, c) the scale of 20μm

CuSn films

Images obtained by metallographic microscopy (Fig. 4 a, b, c) of the areas of unwoven fabric between locations of "overpresses" and "weaves" provide a confirmation of previous observations. They show that the dominant role in evolution of unwoven fabric morphology in the deposition process, in relation to the uncoated unwoven fabric, play two effects: partial melting and binding of the surface fibres forming "threads" and scaling leading to disruption of a deposited metal layer. Compared to the previously described layers, the temperature accompanying the Cu /Sn layer deposition process resulted in less deformation of their shape.

Fig. 4. MM images of 3 (CuSn) sample surface a) the scale of 100μm, b) the scale of 50μm, c) the scale of 20μm

Three-layer system: CuZnNi / NiCuFe / CuSn

Images obtained by metallographic microscopy (Fig. 5 a, b, c) of the areas of unwoven fabric between locations of “overpresses” and “weaves” show that there was a total deformation of the fibres under the influence of temperature. The metal layer revealed cracks that run across the entire width of the fibres. There occurs local extensive scaling that exposed low-lying fibre fragments of fibres of lower deformation.

Fig. 5. MM images of 4 (three-layer system: CuZnNi / NiCuFe / CuSn) sample surface a) the scale of 100μm, b) the scale of 50μm, c) the scale of 20μm

3.2. Testing the morphology of layers using a scanning electron microscope (SEM)

CuZnNi layers

An image of "weave" (Fig. 6a) shows that there has been a fusion of fibres without the pressure. Both in the fusion zones of fibres and the preserved, non-deformed their fragments (Fig. 6b); there are cracks in a metal layer of isotropic orientation. There is also a tendency to accumulate the crack lines of layers around the holes that remained between non-melted fibres (Fig. 6c). A deposited layer despite the cracks is free of peeling and represents the shape of substrate.

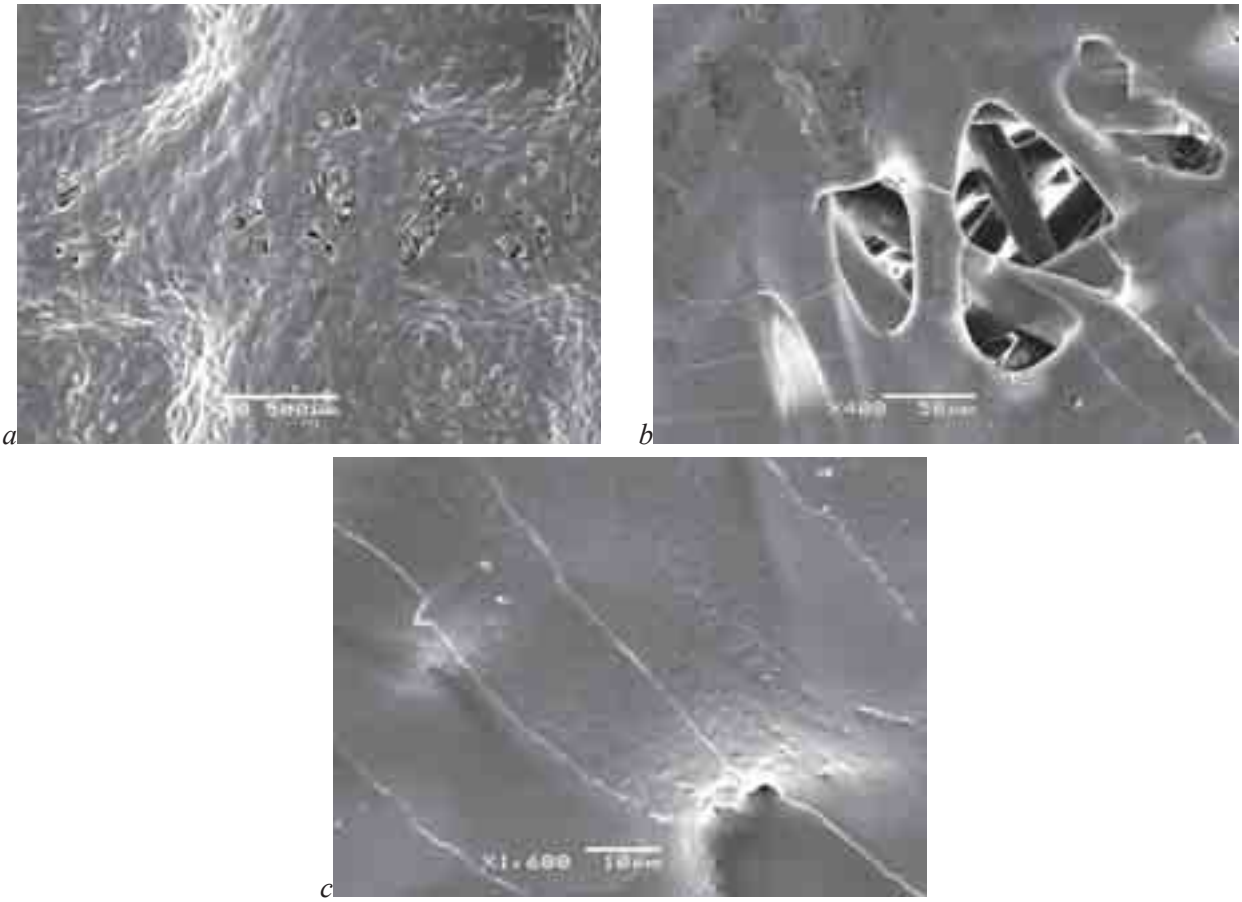


Fig. 6a, b, c. SEM images of 1 (CuZnNi) sample surfaces

NiCuFe layers

An image of "weave" (Fig. 7a) shows that, as a result of fibre melting the compact surface was produce also on "threads" forming "weave". There are only a few fragments of the surface with perforations, with survived fragments of flattened and partially melted fibres (Fig. 7b). Deeper one can see parts of fibres less deformed, which may indicate a direct impact of high pressure forces to the surface of weave and its flattening. Numerous cracks peripheral in character confirm the small flexibility of a metal layer deposited on the fibres. There are also extensive chippings. In some places, the layer morphology is similar to orange peel (Fig. 7c). Based on the protruding parts of the layer, its thickness can be determined at 0.4 - 0.6 μm.

CuSn layers

Visible fibres of "threads", forming a "weave" indicate a much smaller effect of temperature on the process of their deformation and fusion (Fig. 8a). Flattening of the fibres indicate the influence of pressure forces (Fig. 8b). Deeper parts of fibres that can be seen are less deformed, because they are not subject to the direct impact of these forces, likely as in the coated samples (NiCuFe). Fig. 8 b, c shows that in the analyzed areas the metal layer is continuous, with few inclusions. This layer is relatively

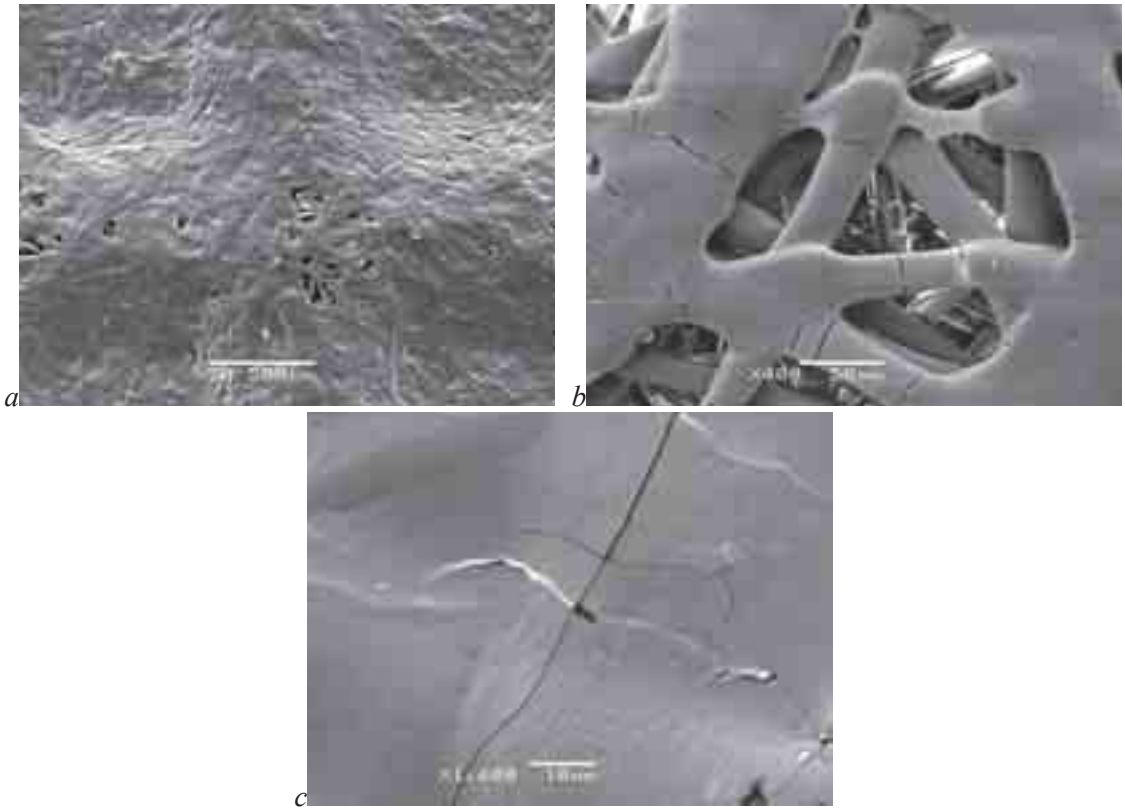


Fig. 7a, b, c. SEM images of 2 (NiCuFe) sample surfaces

little cracked; damages in the form of scaling occur only in places where fibres are overlapped and strongly flattened. Fig. 8c illustrates the junction of two fibres with traces of plastic flow and cure. The resulting crack in the layer may be due to temperature shrinkage or mechanical stress.

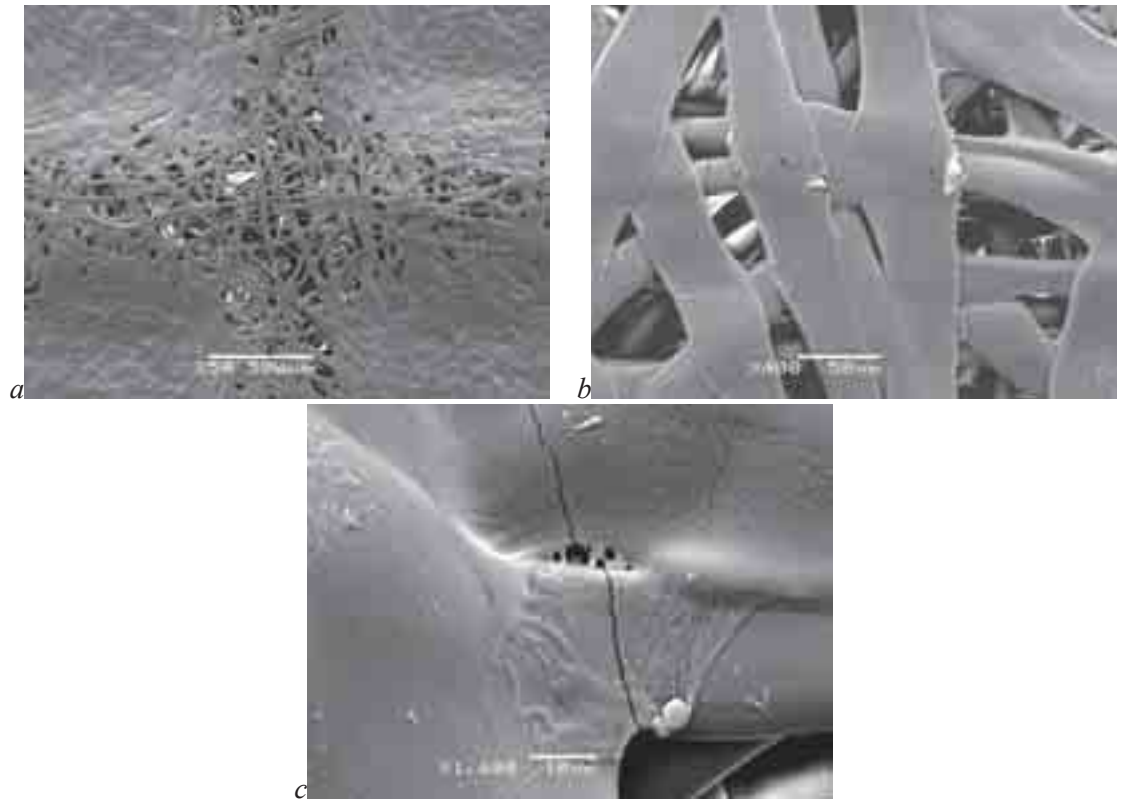


Fig. 8. a, b, c. SEM images of 3 (CuSn) sample surfaces

Three-layer system: CuZnNi / NiCuFe / CuSn

The area of "weave" - along with forming it "threads" preserves only a small part of the porous surface (Fig. 9a) with strongly deformed fragments of fibres. Deformation of the fibres as a result of prolonged exposure to heat in the remaining area has ensued to such an extent that by reason of complete fusion, their shape disappeared and they formed a compact surface structure (Fig. 9a, c). The preserved remains of fibres with a much-flattened shape also showed the impact of stress on the deformation in the process of melting. Enlarged images reveal (Fig. 9b, c) that the deposited layer has numerous cracks. Metallic cracks are linear and extend in directions transverse to fibres, presumably due to the occurrence of tensile stress. A fragment of fracture with overlapping layers (Fig. 9 c) suggests that the cause of this was sufficiently large deflection of the fibre. Sources of fibre bending should be sought in the stresses triggered by the fusion of fibres forming the top layer and the fibres lying below, which were not directly affected by temperature and pressure and preserved unchanged shapes and structure.

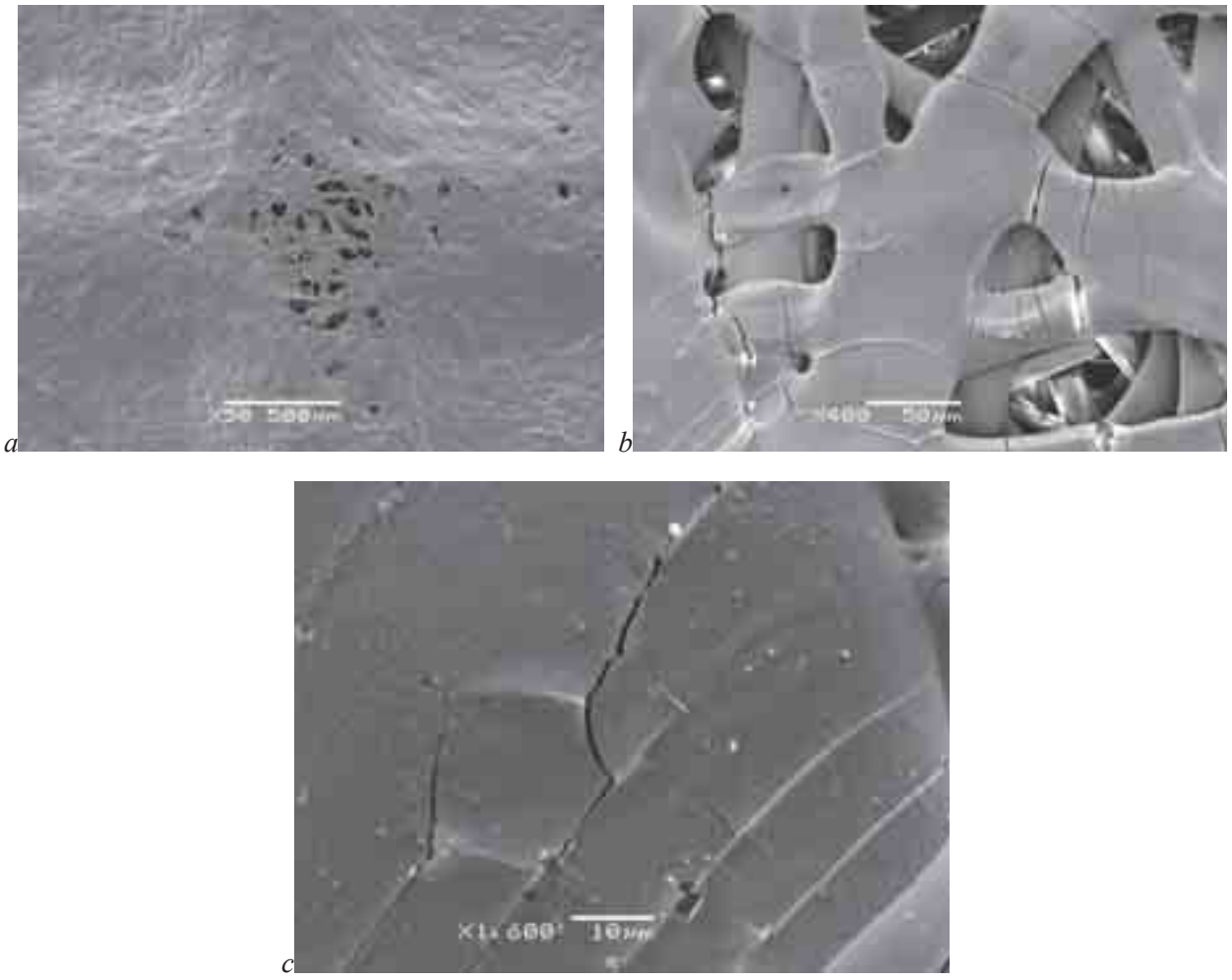
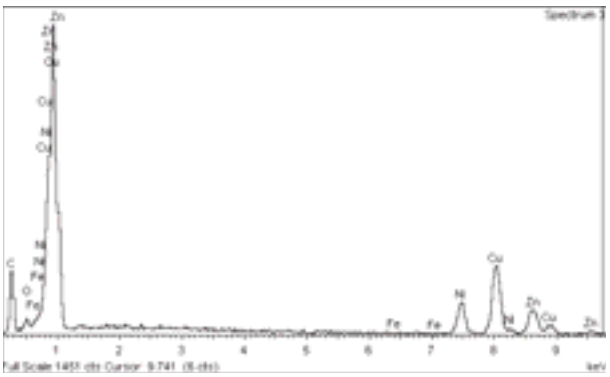
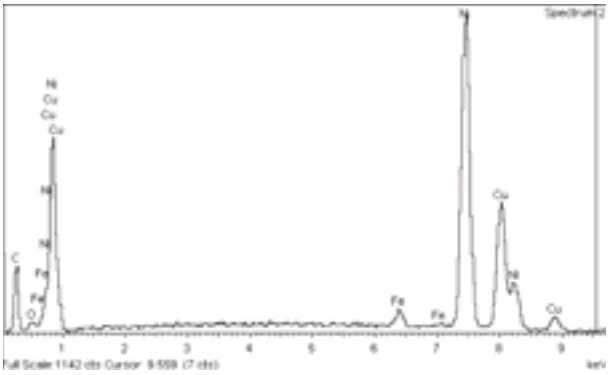
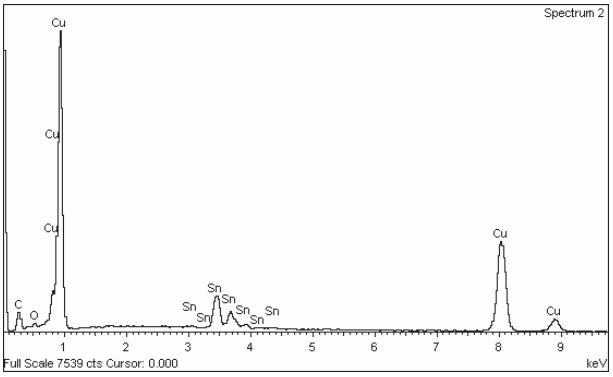
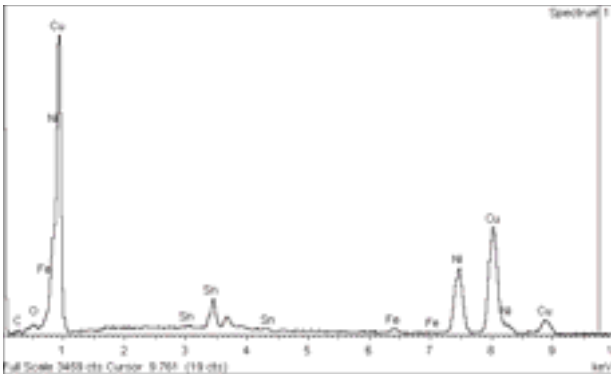


Fig. 9. a, b, c. SEM images of 4 (CuZnNi / NiCuFe / CuSn) sample surfaces

3.3. Microanalysis of layer composition

Table 3 presents the fraction of elements constituting the composition of the metal targets used for the layer deposition and elements forming the deposited layers. Fractions of elements forming the layers are the average selected from three arbitrarily selected points of measurement. Next to each set, there is a spectrogram from one of the measurement points.

Tab. 3. The elements constituting the metal targets and elements forming the deposited layers

Type of target/ layer	Target composition (wt%)	Layer composition (wt%)	Spectrogram
CuZnNi	Cu (53.5-56.5) Zn (25-30) Ni (17-19)	C(6) O(4.02) Cu(49.23) Zn(25.57) Ni(15.08) Fe(0.1)	
NiCuFe	Ni (65) Cu (33) Fe (2)	C(6) O(3.8) Ni(61.6) Cu(28.0) Fe(1.32)	
CuSn	Cu (80) Sn (20)	C(6) O(2.51) Cu(75.82) Sn(15.67)	
CuZnNi/ NiCuFe/ CuSn	(compositions as mentioned above)	C(6) O(1.7) Cu(56.0) Ni(28.0) Sn(7.6) Fe(0.7)	

It follows from these sets that the chemical composition of the analyzed area is composed mostly of carbon. It is identified for the most part, as a component of polymer substrate from which the unwoven fabric is made. There was also found the presence of small amounts of oxygen in all the analyzed layers. There was no presence of zinc in the three-layer system.

4. Conclusions

1. The main emphasis was placed on the analysis of surface structure within the "weaves". In these areas, the metal layers showed the highest heterogeneity, due to the possibility of distraction in the process of metal penetration into the unwoven fabric, across open spaces. Additionally, these are the places most sensitive to mechanical damage.
2. Application of a metallographic microscope showed its usefulness for the assessment of macroscopic changes occurring on the polypropylene fibres under the influence of temperature and on the basis of collared sites, which can be regarded as the initiation of corrosion processes. It was also possible to identify microcracks and chippings.
3. Tests of fibre morphology by SEM made it possible to evaluate the surface changes in unwoven fabric under the influence of temperature and pressure, leading to partial and sometimes total destruction of the fibres (samples 3 and 4). It was found that repeatedly led scrolling and layer deposition caused serious mechanical damage to the layers. Based on a comparison of cracks and chippings it was found that CuSn layers revealed the least damage and the most damage had three-layer system.
4. Experimental investigations on the chemical composition of analysed areas of layers have revealed a large proportion of carbon in them. Large values of signals coming from carbon are the result of very thin metal layers, sometimes order of several tens of nanometres and the emission of X-rays, which can even come with a sample depth of about 1 μm. The presence of oxygen may be due to a partially oxidized layer. As a result, the fraction of individual metal elements in the composition of the layers is smaller than in the composition of targets. One also cannot rule out smaller fractions of metal elements in the layers due to the different rates of sputtering from the surface of target and the condensation on the surface of unwoven fabric, and then the crystallization in the volume of deposited layers. The results therefore should be regarded as an indication of the proportion between the various components of the layer and the main components of targets.

References

[1] Rożek, Z., *Nanokompozyt węglowo-polimerowy na bazie nanowłókniny wytworzonej metodą Nanospaider (Carbon-polymer nanocomposite based on nonwoven nanofabric produced by Nanospaider method),* Doctoral Thesis, Technical University of Lodz, Institute of Materials Science and Engineering, 2011.