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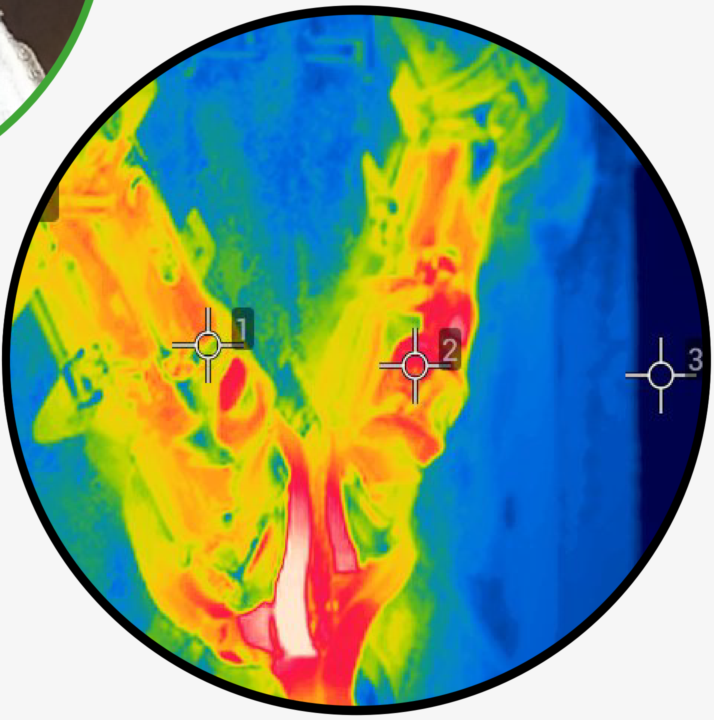

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Effect of Cavitation Phenomenon on the Quality of High-Pressure Aluminium Alloy Castings

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Abstract

This article presents an analysis of the effect of cavitation on the erosion of pressure moulds intended for the HPDC casting mould manufacturing process. Changes in the surface area of the eroded areas were investigated via photographs of castings at the beginning of the mould life as well as at 30%. The individual process variables were described and their influence verified via the cavitation potential module of the Flow3D simulation programme. The results are presented graphically with a description of the relationships and observations. The summary provides an explanation of the results and the dependencies that occurred.

Keywords:

foundry, aluminium alloys, cavitation, casting defects, simulation

1. INTRODUCTION

High-pressure casting, due to its production characteristics (high process efficiency) and advantages such as dimensional accuracy and stability, and very good surface finish, is the leading technology for casting [1, 2]. This contributes to the choice of high-pressure casting as the main casting method in the context of high-volume production. As interest in this method of casting production is increasing, so to is the complexity of projects implemented via die casting. As the main customer for die casting is the automotive industry, manufacturers are faced with the need to select increasingly demanding technology to meet market expectations. While using advanced technologies, at the same time as increasing process requirements, undesirable effects can occur, the phenomenon of which itself is not obvious and the reasons for its appearance are ambiguous [3–5].

One of the basic conditions for obtaining die castings with the required quality parameters is to minimise air occlusion and to fully control the filling phase of the mould cavity with the liquid casting alloy. Minimising the contact between liquid aluminium and air is a guarantee of high strength properties and low porosity [6, 7]. These measures are implemented in several stages. One example is Parashot technology. It is based on the time-varying speed of the piston in the first filling phase, consisting of a smooth initial movement and constant acceleration. This results in a continuous increase in metal velocity, creating an accelerating wave of aluminium [8]. Due to the varying cross-sections in the gate system, the velocity increases until close to the gate gap, where the start of phase II, the filling of the mould cavity, takes place [9, 10]. In this way, the aluminium moves in a laminar fashion and the continuity of the velocity increase results in an inability to switch to turbulent flow and increase air contact. Another translation of eliminating air contact with the liquid metal is the use of reduced pressure in the cavity [11]. This allows the better evacuation of air and gases through the vacuum created in the die cavity before and during injection of the liquid metal. As a result, foundries are increasingly retrofitting their machines with vacuum systems [8, 12]. In addition to the many advantages, the problem of premature mould erosion occurred in the case studied after the application of vacuum. After analysis, the occurrence of a cavitation problem was demonstrated. This phenomenon, not only in die-casting but also in other industries where conditions are favourable to its occurrence, is the cause of the premature erosion of tools and deterioration of their working conditions [13]. Unlike the moulds used in traditional casting, which are based on classic moulding materials, the cost of a mould in a die-casting machine represents a large percentage of the total project. The mould must be able to withstand several hundred thousand castings in an unaltered state (within the appropriate tolerance range). Therefore, the phenomenon in question is a highly unfavourable, undesirable factor that is also very difficult to predict [14]. This paper presents an attempt to find the root cause of the problem of premature mould erosion, which resulted in a costly regeneration of the tool at 30% of its declared service life.

2. RESEARCH METHOD

The aim of the study was to determine the cause of the mould failure in the selected section, based on casting analysis and simulation. The suspected cause is the effect of the cavitation phenomenon. In addition, an analysis of the influence of individual process parameters on the cavitation tendency was carried out on a selected design example. Figure 1 shows the design of the analysed casting system.

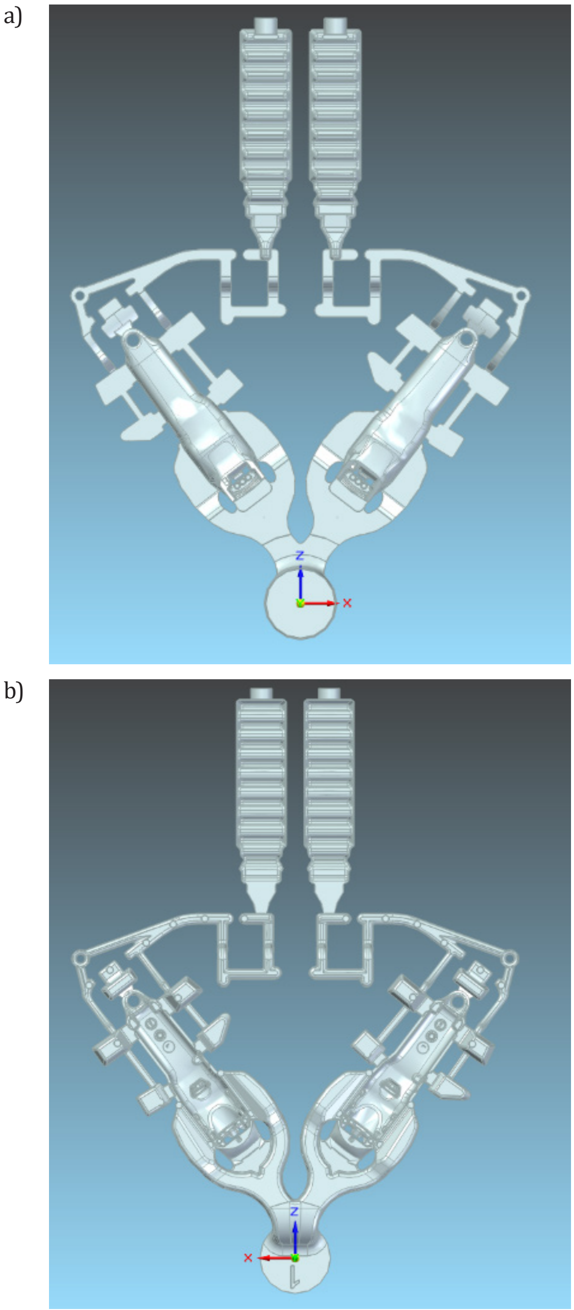

Fig. 1. Photograph of the project under analysis. View: a) from the fixed half; b) from the mobile half

A thermal imaging analysis is shown in Figure 2. It allows quality critical points in the mould to be observed.

In this project, a vacuum generator was used in the casting process to reduce the gas/air pressure in the mould cavity to facilitate the removal of gases from the mould cavity.

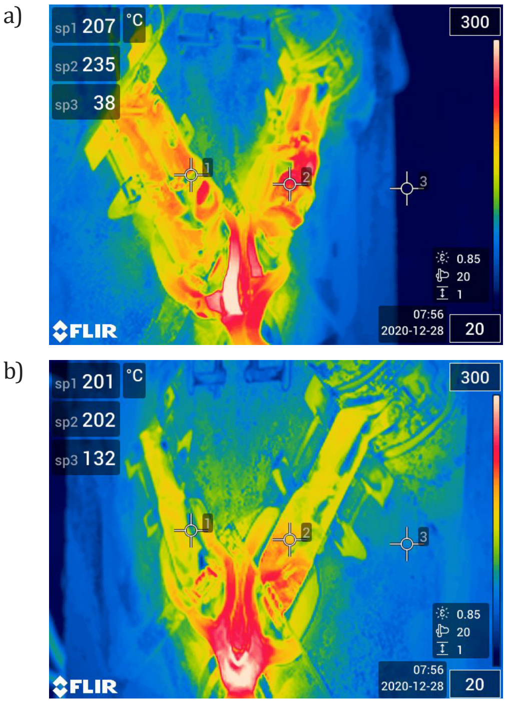

Fig. 2. Thermal images of the mould used in the study: a) fixed half; b) mobile half

3. EXPERIMENT

Due to the conditions of die casting, there are times when the metal pressure locally drops several atmospheres below the evaporation pressure during the filling of the cavity. Such events usually occur at the filling cavity where the metal flow velocities are highest. Under such conditions, the phenomenon of liquid metal cavitation occurs, which in turn contributes to mould erosion. The propensity for cavitation in die casting can be analysed by simulation using the ‘cavitation potential’ model as an element of the Flow3D-cast software [15]. This method allows the detection of areas where cavitation bubbles are likely to nucleate, rather than the area of their implosion. This means that the areas shown by the Flow3D simulation module do not define the specific locations of the flaw. They indicate areas where conditions are created that favour the onset of the cavitation phenomenon. Figure 3 shows the result of the input simulation.

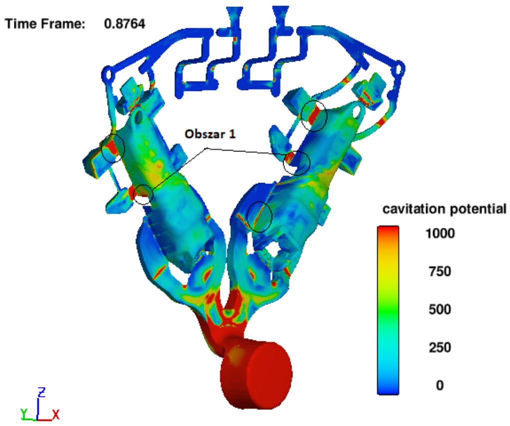

Fig. 3. The result of an input simulation

Figure 4 shows images of the mould after 300 and 29100 injections.The difference between the photos after 300 injections and those after 29,100 clearly shows an increased degree of mould degradation. The degraded areas are located at the overflow slots, in the shadow of the feed gate, on sharp edges, perpendicular to each other. This design forces a rapid change in the direction of metal flow.

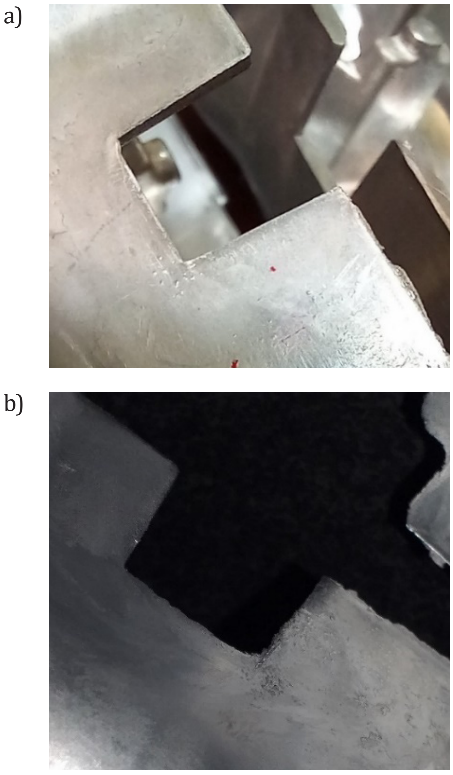

Fig. 4. Summary of visually inspected areas of the casting made at the beginning of the mould life and at 30% of the life: a) 300 injections; b) 29,100 injections

From the results of the tests and analyses carried out, it can be concluded that the defects described, which contributed to the premature wear of the mould, are the result of the phenomenon of cavitation. The differences in the areas of defect occurrence between the cavities are due to the lack of symmetry of the entire casting branch, which means that the left-hand casting is filled differently from the right-hand casting. The areas most prone to cavitation are those with sudden, rapid changes in flow direction and velocity (Fig. 5). Therefore, castings that are more developed and structurally complex (sharp edges, perpendicular planes) are more prone to cavitation.

Fig. 5. Areas of remaining castings visually inspected at beginning of mould life and 30% of mould life

By analysing the simulation results, it can be concluded that the tendency to cavitation is directly influenced by the use of vacuum. As the pressure in the cavity decreases, the tendency to cavitation increases. This is due to the existence of suitable conditions for the phenomenon. The initiation of cavitation requires a boiling process caused by a pressure differential in the cavity [12]. Due to the very high speeds used in die casting, even at atmospheric pressure, media can form in the cavity at a significantly reduced pressure. When the cavity pressure is reduced to a value of 200 mbar, the tendency to cavitation is significantly increased and the influence of cavitation media is further increased.

Through the use of simulation, mould design experience and a continuous improvement process, it is possible to compensate for unfavourable phenomena in the mould. This makes it possible to meet the highest quality requirements of demanding customers such as the automotive industry.

4. CONCLUSIONS AND SUMMARY

Problems of premature mould wear can be caused by the adverse effects of cavitation. Castings with more complex designs (with variable directions of metal flow, with sharp edges, kinks and shadows at the gaps) are subject to its adverse effects. The use of a vacuum has a direct effect on increasing the propensity for cavitation to occur and its presence is currently a necessary addition to die casting technology. Recommendations from the research presented in this article suggest that when implementing technologically challenging projects, an analysis of the potential for cavitation problems and their negative impact on the die casting mould should be carried out, for example using the ‘cavitation potential’ simulation module.

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Ecological Electroplating Baths and Their Application in the Tin-coating of Copper Wires Intended for Photovoltaic Cables

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Abstract

Copper wires are covered with various coatings for many different applications. The most popular are tin based coatings and both their thickness and quality have been standardized by means of appropriate standard specifications. Copper wires intended for photovoltaic cables are subjected to especially high requirements due to their exceptionally long operating time and extremely unfavourable working conditions. Tin coatings are applied using the electroplating method and generally a fluoroborate bath is used during the process, however, it has been proved to be a health hazard in general and harmful to the environment as a whole. The paper presents the research results of a new ecological methane-sulfonate bath which does not form hazardous waste in the process. The examples of tin coatings of various thickness and the way of obtaining them at varying electrodeposition speeds at constant current or constant speed with varying current intensity were analysed. It has been determined that the use of the new electroplating bath is not only beneficial from an ecological point of view, but also in terms of the coating quality and efficiency of the process.

Keywords:

tin-coated copper wires, photovoltaic cables, ecological electroplating baths, electrodeposition parameters

1. INTRODUCTION

The global trend regarding electrical energy obtained from renewable sources such as solar energy has resulted in the dynamic development of the photovoltaic panel manufacturing industry as well as cables and wires intended for their production. This trend is so powerful that photovoltaic capacity is expected to increase tenfold by the year 2050 [1, 2]. The work of a photovoltaic installation, and as a result its efficiency, depends on all of the components it is made of. Beside the most obvious and visible components, i.e. modules and inverter, the cabling which forms their connections is also a fundamental part of the photovoltaic panel as a whole and requires, among others, high electrical conductivity and operational reliability of cables and joints. Bearing that in mind, high quality copper is used in the manufacturing process of photovoltaic cables [3–5]. Challenging and unstable operating conditions of photovoltaic panels and copper wires and cables, especially direct contact with atmospheric air and damp, results in lower conductive properties since resistivity will increase over time [6, 7]. Therefore, in order to extend the original technical parameters and the durability of copper wires, they are covered with solder-like tin alloy. The abovementioned technical parameters are defined in the proper standards such as EN 50618 standard, describing in detail the construction of dedicated photovoltaic cables made of copper wires with a protective tin coating, estimating their operating time at 25 years. This standard also requires that the maximum temperature of the conductor intended for photovoltaic applications does not exceed 90°C, whereas it is allowed for the temperature to reach 120°C for a maximum of 20,000 hours under the condition that the ambient temperature is not higher than 90°C.

Research on the life cycle of modules, wiring, and photovoltaic cables conducted in recent years has shown that the electrical properties may diminish due to for instance ineffective soldered connection or increasing amount of corrosion [8, 9]. Both of these may be caused by the low quality of tin coating covering the copper wire. Obtaining a tin coating of copper wires is mostly possible through the electrodeposition process which requires either an alkaline or acidic galvanic bath. Alkaline baths are usually base on hydroxides, whereas acidic baths operating at pH around 4 include sulphate, chloride and fluoroborate baths. The latter is the most widely used and is made from tin (II) fluoroborate. Decreased cathode efficiency, and thus lower deposition capacity especially at low current densities, is caused by reducing the pH, particularly in sulphate baths [10, 11]. However, at higher pH coarse-crystalline and spongy coatings unfavourable for these types of solutions are formed [12, 13]. Even though fluoroborate baths are most often used due to their exceptional adhesion and high cathode efficiency, they unfortunately have numerous disadvantages such as being susceptible to corrosion caused by the oxidation of Sn^{2+} ions to Sn^{4+} ions and also adverse environmental effects caused by fluoride ions [14–17]. The modern response to harmful fluoroborate compounds is a methane sulfonic bath [18, 19]. Methane sulfonic acid exhibits an excellent solubility of metal salts in electrolytic baths, low toxicity, low corrosivity and biodegradability [20–22] and is thus perfectly in compliance with pro-ecological guidelines and environmental regulations of the European Union and G7 countries.

Selecting the proper chemical composition of the electroplating bath is just one of the factors influencing the tin-coating process. Other important factors are current density, constituting current intensity and the conductor cross-section, and also bath temperature, type, quality and chemical purity of the substrate, type of current, shape of the anode and process velocity [23–27]. The pulsed current techniques have also been a concern of the researchers [28]. All the above-mentioned factors significantly affect the quality and durability of the coating and thus directly influence the profitability of the process. The morphology of the electrodeposited coating is more important as it influences its density and as a result the efficiency of the entire photovoltaic system. The efficiency of the process is measured in terms of metres of wire manufactured per minute and the efficiency of electroplating bath are the results of Faraday's law. Obtaining an optimal, dense and even tin coating is possible due to the correlation of all of the process factors. Further processing in the wire drawing process of the tin-coated material is a significant problem regarding the need for high quality of the coating. To be more specific, a good adhesion of the tin layer to the copper wire is crucial in order to prevent tin depositing inside of the die, elements of the on-line annealing chamber or emulsion used during the process. The presented paper concerns electroplating processes using two various industrial solutions in terms of electroplating machines and baths used during each process. The main difference between these two machines regarding their design is the length of the wires being submerged in the bath, since its length is about twice as long in the modern methane-sulphonate bath (new solution) in comparison to fluoroborate bath (old solution).

2. MATERIALS AND METHODS

Copper wires of ETP grade (Electrolytic Tough Pitch) and diameter of 1.39 mm, typically used in photovoltaic systems, were selected for research purposes on the newly designed ecological electroplating baths. The paper presents the research results of a methane-sulphonate bath in comparison with the traditionally used fluoroborate bath, which is to be avoided due to it being harmful to both human health and the environment as a whole [14–17].

The thickness of the tin layer is a direct result of the recipe prepared based on Faraday's law of electrolysis, stating that the mass of the substance deposited on one of the electrodes is proportional to the current intensity and the duration of the electrolysis process. The nominal thickness of the desired coating ranged from 1 μm to 6 μm. The various thicknesses of the tin coating were obtained by differentiating the velocity of the electrodeposition at the constant electric current (approximately 70 A) or constant velocity (40 m/min) and varying current intensity. The process velocity ranged between 12.5 m/min and 80 m/min and the electric current intensity ranged between 34 and 208 A depending on the required recipe. The tin coatings were obtained using industrial electrodeposition lines.

2.1. Copper wire tin-coating technology

The tin-coating industrial process begins with copper wire being fed from the cardboard packaging to the electroplating line through the system of specifically designed rolls. The processing line guides the wire with the rotating grooved wheels through the technological process.

The wire surface was degreased in order to remove not only the remaining lubricants resulting from the wire drawing process, but also impurities and the initial distortion of the oxide layer. The electric current applied to the technological bath causes the release of hydrogen on the wire, which intensifies the process by tearing and removing impurities from the surface and consequently etching the residues of the degreasing process which prepares the wire surface for the actual tin-coating process.

The tin-coating process takes place in the working runner powered by a separate power supply. The degreasing and etching collectively take place over a 6.5 metre distance whilst turning the wire back and forth 5 times inside the bath. The anode of the tin-coating process is an especially profiled tin sheet. The whole process is conducted at an elevated temperature in order to intensify the outcome. Below the runner with the degreasing and etching bath, a special tank with the bath supply is located. After the degreasing and etching process is over, the excessive amount of bath formula is blown back into the working runner with the use of an air nozzle followed by a twofold rinsing. The rinsing is being carried out in a closed environment thanks to the installed dryer system and it is necessary as it removes both impurities and the electroplating bath itself from the surface of the wire before the further processes. The water to the primary rinsing system is supplied by overflowing the secondary system, which on the other hand is supplied with demineralized or purified water in the filtration process.

Any electrochemical or galvanic tin-coating process depends on the tin ions being transferred from the anode and deposited on the wire surface with the electroplating bath being just the process medium. In this case, an ecological methane-sulphonate bath was used. The properly deposited tin coating allows for the wire drawing process of the core material to be conducted. Whilst the tin-coating process is carried out, appropriately 75 metres of copper wire is inside the runner at a time. Tin anodes are placed in titanium boxes located along the wire path. After the tin-coating process is completed, the excessive electroplating bath is blown off which is followed by a double rinsing process. Its purpose and maintenance is analogical to those previously mentioned. The dried wire is eventually wound up and stored in circles arranged from top to bottom in octagonal octabins.

The process velocity is regulated automatically with a system of rollers and adjustable compensator depending on the tin-coating process speed. The wire feeding device is located on the first contact roller in the tinning bath, which prevents the elongation of the wire during the tin-coating process. However, its purpose is more complex than just that, as the proper thickness of the tin coating deposited on the wire surface is obtained by the appropriate velocity of the wire and therefore they are strongly linked.

Tin-coating with a methane-sulphonate bath differs from fluoroborate baths mainly in the fact that the new machines use a degreasing-etching bath in one runner, while in the old type of lines they required two separate runners. Another significant difference is the operating length of the wires immersed in the individual baths, which increases the final efficiency of the technological line drastically from 30 tons per month to 60 tons per month of tin-coated copper wire of the same diameter. The ecological tin-coating process is equipped with a filtering, closed circulation of the rinsing water, an impossibility with the fluoroborate bath due to the toxicity of the water after the rinsing of the wire. The water recycling system increases the profitability of the process, making the use of methane-sulphonate bath much cheaper in comparison to the fluoroborate baths.

Table 1 presents the list of the research materials divided by the electroplating parameters and distinguished thickness of the tin coating.

Table 1
Electroplating process parameters necessary to obtain the given thickness of the tin coating on the surface of the copper wire

Type of electroplating bath	The thickness of the tin coating (as requested)	Process speed	Electric current intensity
	µm	m/min	A
Fluoroborate bath	1	40.0	34
	2	40.0	69
	3	40.0	104
	4	40.0	138
	5	40.0	173
	6	40.0	208
	1	80.0	70
	2	40.0	70
	3	27.5	70
	4	20.0	70
	5	15.0	70
	6	12.5	70
Methane-sulphonate bath	1	40.0	44
	2	40.0	87
	3	40.0	131
	4	40.0	174
	5	40.0	218
	6	40.0	262
	1	80.0	69
	2	40.0	69
	3	27.5	71
	4	20.0	69
	5	15.0	65
	6	12.5	65

2.2. SEM observations and EDX microanalysis

In order to determine the morphology, homogeneity, and uniformity of the electroplated tin coating on the surface of the copper wire, the samples were subjected to structural scanning electron microscope (SEM) observations (Hitachi Ltd., Tokyo, Japan). The microscope used for the analysis is equipped with energy-dispersive X-ray spectroscopy microanalyzer (EDX) model Noran 986B-1SPS (Hitachi Ltd., Tokyo, Japan). The EDX detector made the identification of the elemental composition of the tin coating on the wire surface and across the longitudinal section possible as well as research on sludge which is a post-production waste in order to confirm the ecological aspect of methane-sulphonate electroplating bath.

2.3. Coulometric analysis

The thickness of the tin coating deposited on the surface of the copper wire was determined with a COULOSCOPE CMS2 laboratory coulometer (Fisher, Sindelfingen, Germany). The coulometric analysis consists in removing (dissolving) a metallic coating of the defined surface area. The dissolving is conducted with the use of an electrolyte solution of appropriately selected composition (a water solution of an acid mixture) and electric current. The applied current intensity depends on the mass of the metal. The analysis is automatically terminated by the sudden voltage peak after the last scraps of coating have been etched. This analysis may function as an additional assessment method and reference to the SEM images.

2.4. Electrical conductivity measurements

Research on the electrical conductivity of the wires was conducted using a model 2304 Thomson bridge resistomat (Burster, Gernsbach, Germany). The Thomson bridge method uses resistors with low resistance values as four terminals, i.e. two current terminals (current leads) are used to deliver current and two potential terminals (voltage leads) are used to determine the voltage drop in the resistance occurring between them. The measurements were conducted at constant ambient temperature of 20°C at an air-conditioned laboratory. For the test purposes, regarding the high chemical purity of the test material, the temperature coefficient α_R was assumed to be 0.004 1/K and the gauge length of the samples was set to 1,000 mm. Denotations of the electrical properties used in this research paper are as follows:

R_{20} – electrical resistance at 20°C;
ρ_{20} – electrical resistivity;
γ_{20} – electrical conductivity.

3. RESULTS AND DISCUSSION

The new methane-sulphonate bath is deemed ecological since the chemical composition assessment of post-production sludge classifies it as non-hazardous waste containing mostly of Sn (65%) and S (30%) and other elements with no significant values as opposed to fluoroborate baths which have been classified as hazardous. The utilization cost of the latter is about 1,000 USD per megagram of sludge whereas the cost of utilizing the sludge from the methane-sulphonate bath (ecological bath) is about ten times lower. The post-production sludge from the new solution (methane-sulphonate bath) has been tested for its elemental composition in the microarea using high resolution and high magnification microscope images using a scanning electron microscope with an EDX analyzer, which further proved that the sludge contains mostly environmentally save Sn, as shown in Figure 1.

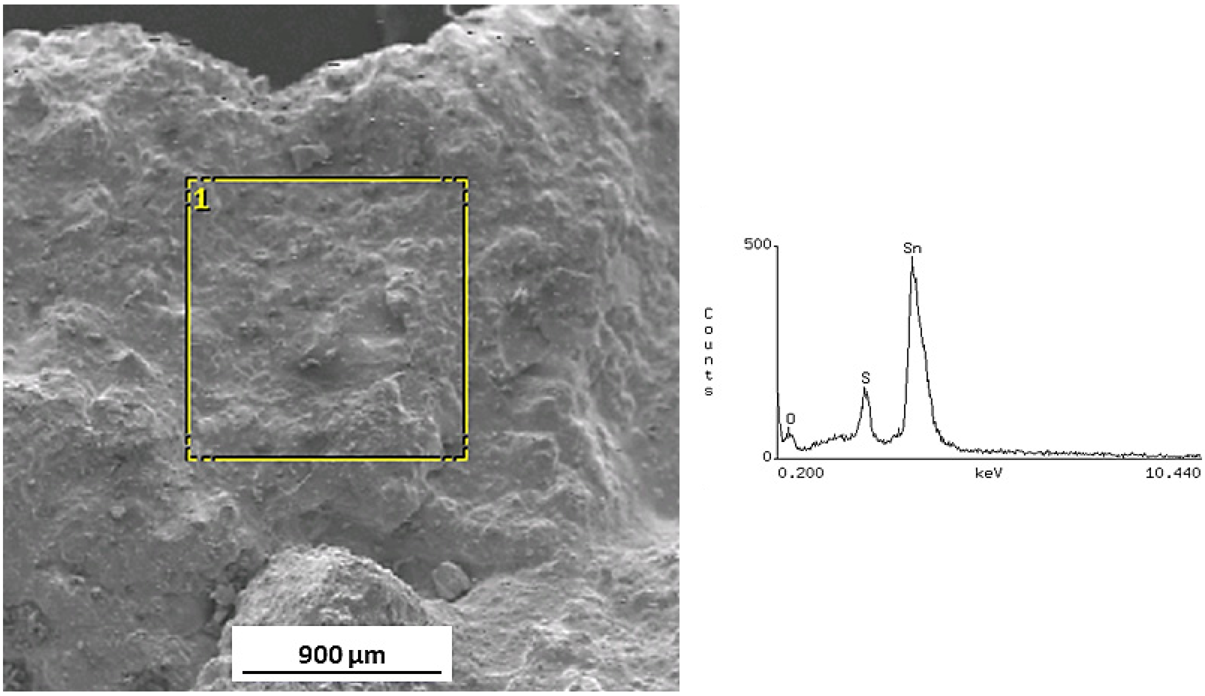

Fig. 1. EDX analysis and X-ray spectra of the post-production sludge from a methane-sulphonate bath with the measurement area marked

After the ecological aspect of the methane-sulphonate bath was confirmed, the analogical method of assessment as above was used with the final product of electroplating process. The obtained wires were subjected to the analysis of their elemental composition in the micro-area using high resolution and high magnification microscopic images. As predicted, the EDX analysis of the wires provided at Figure 2 proved that the coating, both at the surface and at the longitudinal section, exhibits the presence of tin, while the wire matrix shows only copper. At the surface, single crystals of tin formed during the process are visible, especially at high magnifications. These results recurred regardless of the electroplating bath used and the parameters of the electrodeposition process. Additionally, the chemical composition of tin anode used in the electrodeposition process is provided in Table 2.

The assessment of the coating quality and the proper deposition of the tin layer was conducted based on the SEM images. Figures 3 and 4 present images of the tested copper wires (surface and longitudinal section of the wire), distinguishing the type of electroplating bath and divided according to the process conditions – constant process speed or constant applied electric current.

The images of the copper wires obtained using a fluoroborate bath exhibit a macrocrystalline structure of various growth direction of the tin coating. As the thickness of the layer increases, the more visible is the direction of tin growth and the tin ions accrue epitaxially. Their growth depends on the mutual relations between the substrate (Cu) and deposited material (Sn), as well as the energy at the phase boundary and process parameters. At a constant low process speed, numerous gaps are visible, which may consequently cause the faster oxidation of the copper wire through the direct contact with the external environment. The samples obtained at a constant electric current value are characterized by higher tin coating quality, however, the process velocity is extremely low, and thus disadvantageous due to the low efficiency and profitability of the manufacturing process.

The tin coating deposited in the methane-sulphonate bath is characterized by high adhesion and ease of tin deposition (even, centric layer). Even though the coating may seem porous, no areas were observed without a layer of tin, which indicates higher tightness. Properly conducted tin coating process allowed for the obtaining of a smooth, satin surface favouring further plastic working i.e. wire drawing process. Therefore, the assessment of adhesion was not only conducted based on the analysis of the longitudinal sections of final products (tin-coated wires) particularly contact surface of tin with copper and the occurrence of spots not covered with tin, but also the macroscopic assessment of copper/tin adhesion such as the amount of Sn in the post-production sludge at the bottom of electroplating tank or the amount of tin pulp in the drawing machine.

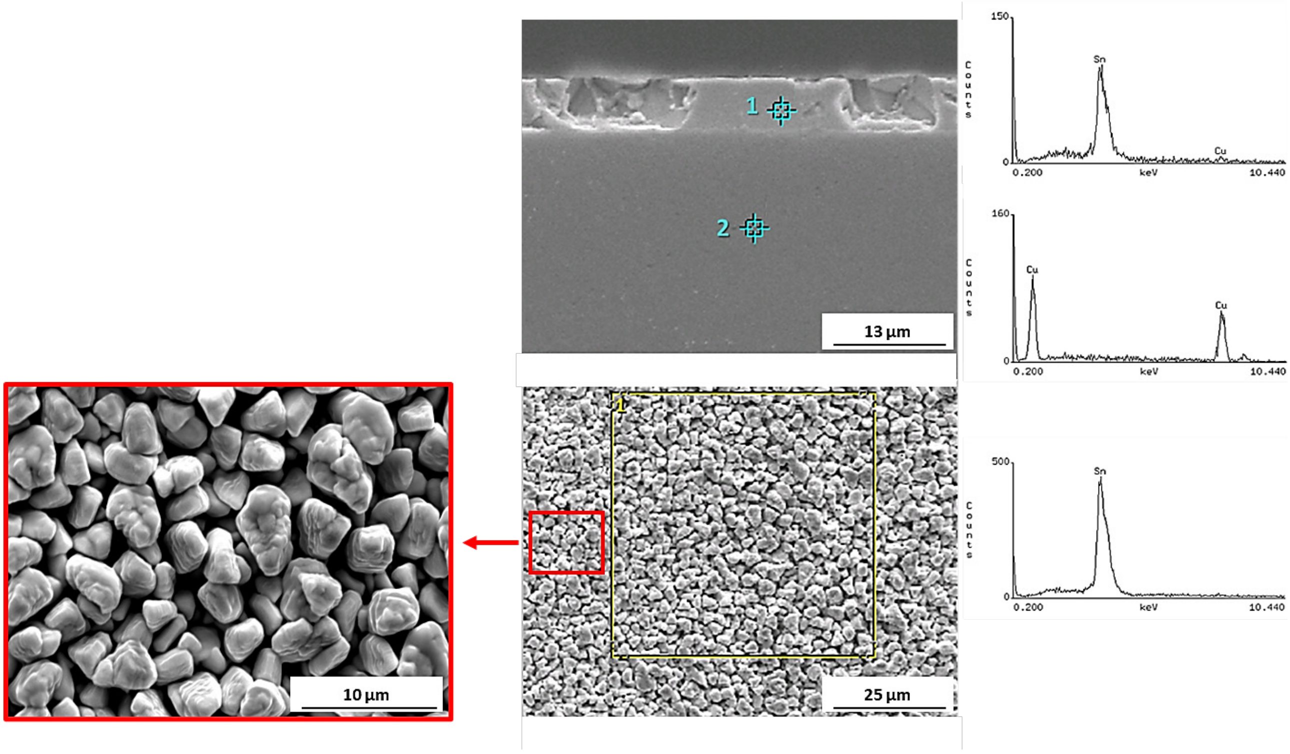

Fig. 2. EDX analysis and X-ray spectra of the copper wire with marked measurement areas and points

Table 2
Chemical composition of tin anode used in electrodeposition process

Pb [ppm]	Bi [ppm]	Sb [ppm]	Cu [ppm]	Zn [ppm]	Ag [ppm]	Al [ppm]	As [ppm]	Cd [ppm]	Fe [ppm]	In [ppm]	Ni [ppm]	Sn [%]
10	17	13	5	1	14	6	15	1	14	1	1	99.9903

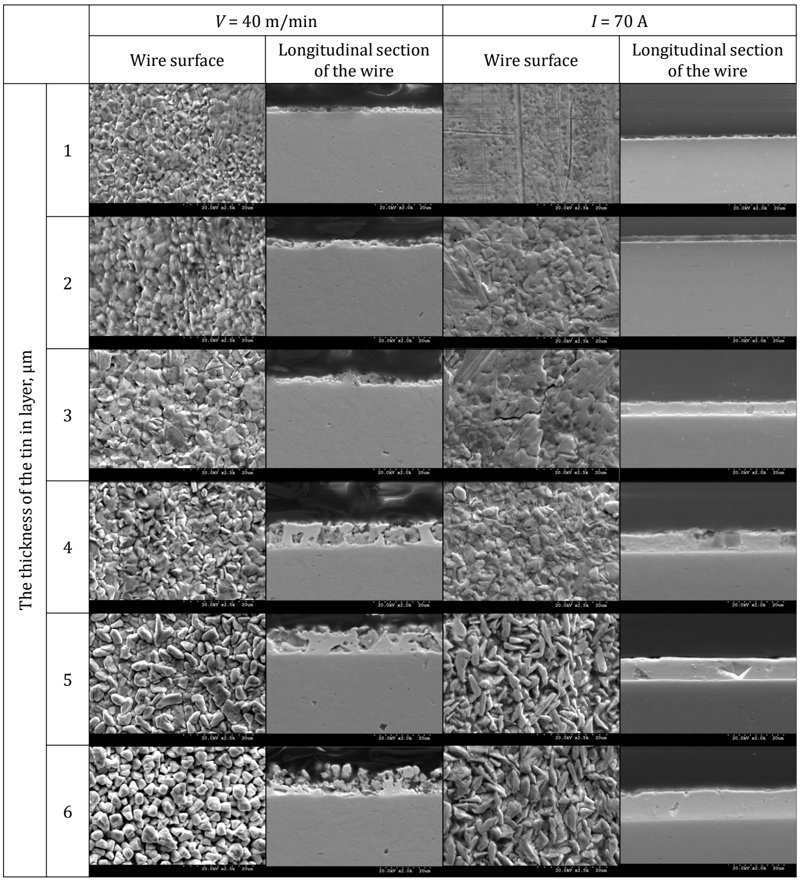

Fig. 3. Morphology of the tin coating obtained in the electroplating process using fluoroborate bath; magnification ×2500 (wire surface) and ×2000 (longitudinal section)

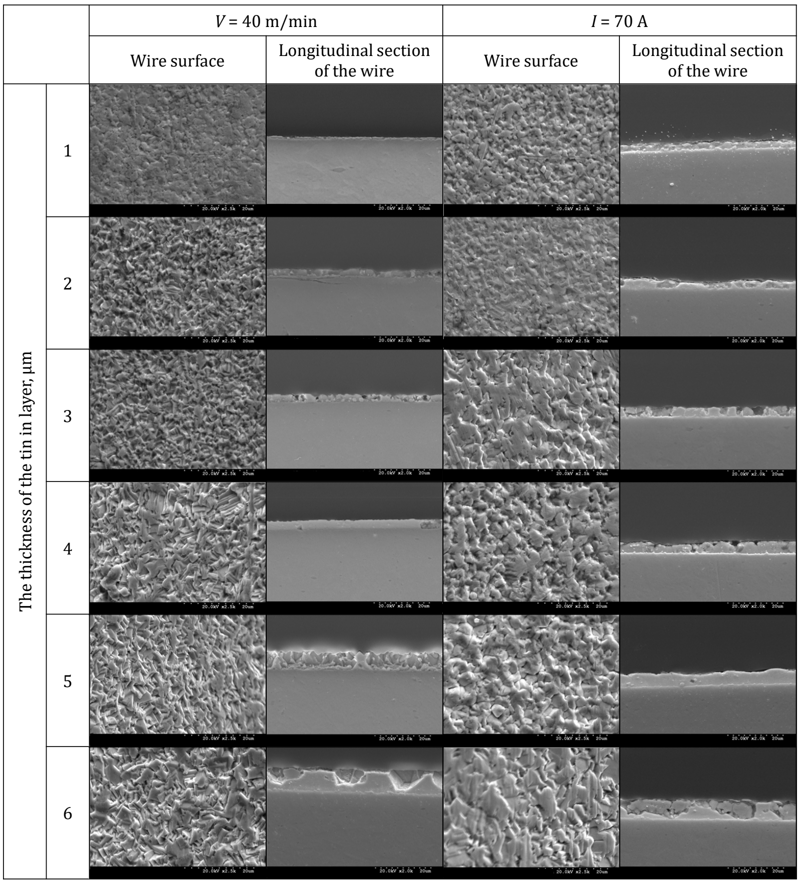

Fig. 4. Morphology of the tin coating obtained in the electroplating process using methane-sulphonate bath; magnification ×2500 (wire surface) and ×2000 (longitudinal section)

Regarding the fluoroborate bath (old solution) there was a significant amount of tin pulp on various elements of the drawing machine and on the filters, whereas such phenomena did not occur when wire were obtained using methanesulphonate bath (new solution). Based on this, it may be concluded that the copper/tin adhesion is better when the ecological bath is being used. Another practical observation concerning fluoroborate bath (old solution) is that in certain unfavourable relations between deposition speed and current density, hexavalent tin, which is brittle (non-plastic) may be deposited on the copper surface and during wire drawing process it separates from the surface proving low copper/tin adhesion. Table 3 presents collectively the data on the thickness of the tin coating on the surface of copper wire measured with coulometer and the electrical properties of the samples.

Table 3
The thickness of the tin coating, process parameters and electrical properties of the copper wires

Type of electroplating bath	The thickness of the tin coating (as requested)	The thickness of the tin coating (coulometric analysis)	Process speed	Electric current intensity	R_{20}	ρ_{20}	γ_{20}
	µm	µm	m/min	A	mΩ	nΩm	MS/m
Initial wire	–	–	–	–	11.225	17.03	58.71
Fluoroborate bath	1	1.4	40.0	34	11.269	17.11	58.45
	2	2.1	40.0	69	11.244	17.12	58.41
	3	3.2	40.0	104	11.248	17.11	58.45
	4	3.9	40.0	138	11.219	17.14	58.35
	5	4.9	40.0	173	2.244	17.24	58.00
	6	6.1	40.0	208	1.686	17.28	57.86
	1	0.9	80.0	69	2.276	17.08	58.56
	2	1.9	40.0	69	11.353	17.11	58.44
	3	3.7	27.5	71	11.346	17.15	58.31
	4	4.4	20.0	69	11.346	17.19	58.17
	5	6.2	15.0	65	11.324	17.19	58.17
	6	7.8	12.5	65	11.323	17.31	57.76
Methane-sulphonate bath	1	0.9	40.0	34	2.286	17.13	58.39
	2	1.9	40.0	69	11.482	17.17	58.23
	3	2.7	40.0	104	11.471	17.18	58.20
	4	3.8	40.0	138	11.472	17.21	58.11
	5	4.9	40.0	173	11.470	17.24	58.01
	6	6	40.0	208	11.481	17.30	57.81
	1	1.5	80.0	69	11.470	17.12	58.40
	2	2	40.0	69	11.463	17.16	58.27
	3	3	27.5	71	11.444	17.16	58.28
	4	4.1	20.0	69	11.436	17.20	58.12
	5	5.3	15.0	65	11.451	17.27	57.91
	6	6	12.5	65	11.447	17.27	57.90

The measurements of the thickness of the tin coating using the coulometric method showed slight differences when compared to the estimated values according to the recipe selected with the process parameters. Most of the measured values exhibit higher than assumed thickness, especially in terms of wires manufactured using a fluoroborate bath. The higher the coating thickness, the less convergent were the results, which is in compliance with the SEM observations, were numerous gaps and spongy structure were observed when traditional fluoroborate bath was used. In terms of the ecological parameters, the layer thickness in the methane-sulphonate bath only differs in a few cases from the assumed levels in the recipe and it was usually slightly lower than requested. Altogether it proves that the coating has a compact and even structure, much more advantageous in terms of further processing and corrosion protection. Figures 5 and 6 present the influence of the applied process parameters and the type of the electroplating bath on tin coating thickness.

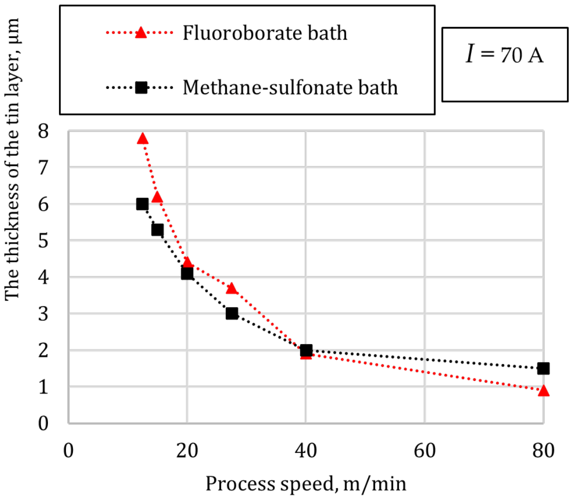

Fig. 5. The thickness of the deposited tin coating depending on the electroplating bath and process speed

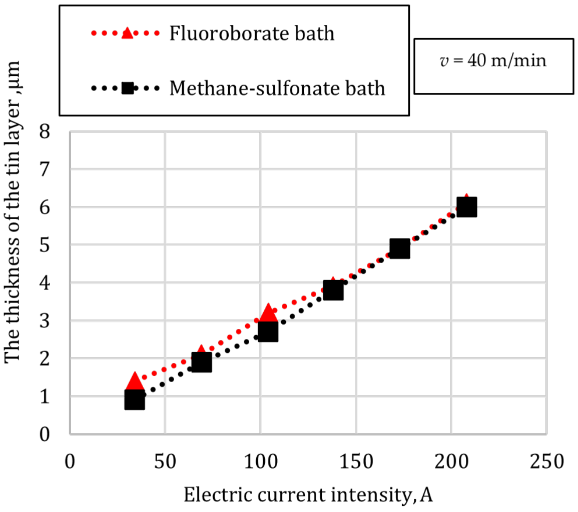

Fig. 6. The thickness of the deposited tin coating depending on the electroplating bath and electric current intensity

Therefore, the tin-coating thickness measurements for the same process speed and the same current values (Fig. 5) prove that methane-sulphonate bath is half as efficient as a fluoroborate bath in terms of the electroplating process (as the designs of electroplating machines were described in Section 1, the wire in the former is twice as long than in the latter, meaning the wire needs to be submerged in the electroplating bath for double the time in order to obtain the same thickness of tin-coating).

It was observed that the fluoroborate bath is more efficient than the methane-sulphonate bath at low process speed, however, the ecological bath becomes more effective as the process is sped up. When the process speed was constant and the electric current intensity was high, both baths had similar characteristics. The conducted research is crucial to the energy industry, as tin-coated copper wires are used in many branches of technology, for instance photovoltaics, which is why the manufacturers aim at increasing process speed and thus greater efficiency.

Copper wires used in photovoltaic cables must be characterized by high electrical conductivity. The ability to transfer electrical energy depends on many factors, i.e. the type of metal matrix and its structural condition, the amount and concentration of impurities, the amount and type of defects and last but not least the temperature, which significantly influences the free path of electrons. The quality of the tin coating is also essential in order to prevent the oxidation of the copper core as the electrically active cross-section of the oxidized copper wire will be lower, consequently lowering the output of the whole photovoltaic system. Figure 7 presents the research results of the electrical properties of the tin-coated copper wires with various coating thicknesses (coulometric measurement) and manufactured using different electroplating baths.

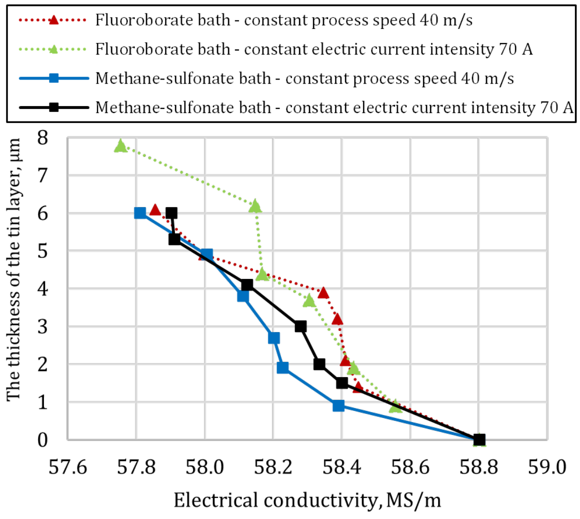

Fig. 7. Electrical conductivity of the copper wires with various tin coating thicknesses

When analysing the results of the electrical properties measurements, a clear decrease in electrical conductivity is noticeable as the thickness of the tin layer increases. The electrically active cross-section increases by the amount of tin layer thickness. The electrical conductivity of pure tin is approximately 8.7 MS/m, which is why the electrical conductivity of the tin-coated wire decreases. This is why wires with a photovoltaic designation should have as large a copper core as possible, compliant with the proper standard, ensuring high electrical conductivity and the appropriate thickness of the tin layer. The balance needs to be maintain in order to provide adequate anti-corrosion protection with only a slight reduction of electrical conductivity, which is why it is more advantageous to choose a wire with the thinnest possible coating, but evenly deposited and of high quality. The conducted research proved that there is no significant difference in terms of electrical conductivity between the type of electroplating bath used during the manufacturing process in the coating thickness range of between 1 μm and 6 μm. During the wire drawing process, a correctly deposited tin layer will become thinner in proportion to the root of the wire elongation factor. For instance, a copper wire with a diameter of 0.14 mm obtained from a tin-coated copper wire with a diameter of 1.4 mm should have an average coating thickness of 10% of its initial value.

4. CONCLUSIONS

Based on the results concerning the use of new ecological electroplating baths for copper wires designed for photovoltaic applications, the following conclusions were made:

- When comparing the two industrial electroplating lines with the characteristics described in the introduction to the paper, it should be stated that at the same process speeds and at the same current values, the mass (thickness of tin coating) for wires of the same diameter will be the same, despite the fact that cathode densities are different in relation to the quotient of the length of the wires. On the other hand, a change in the process speed or current value will affect the thickness of the coating.
- The coating obtained with a fluoroborate bath exhibits a macrocrystalline structure of various growth direction of the tin coating with numerous gaps, while the coating obtained with a methane-sulphonate bath on the other hand is characterized with high adhesion, uniformity, and centricity.
- The coating obtained with a fluoroborate bath is more effective at low process speeds, while at a higher velocity it is the other way around and the methane-sulphonate bath is more efficient.
- By measuring the electrical conductivity of the tin-coated wires the thickness and quality of the tin coating may be effectively assessed.
- Due to the increasing awareness of the environmental and health risks among both manufacturers and consumers, the use of a traditional fluoroborate bath may be replaced by a new ecological methane-sulphonate bath as it is not harmful to either the operator or the environment and is easy to dispose of.
- The beneficial use of a new ecological bath was demonstrated by positive results in terms of surface quality and process efficiency tests at high process speeds.

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