

Investigations on the Oxidation of Zn-coated Steel Cables

G. Pinto

Assistant Professor
School of Engineering, Polytechnic of Porto
Portugal

F. J. G. Silva

Affiliation-Professor
School of Engineering, Polytechnic of Porto
Portugal

A. Baptista

Assistant Professor
School of Engineering, Polytechnic of Porto
Portugal

R. D. S. G. Campilho

Affiliation-Professor
School of Engineering, Polytechnic of Porto
Portugal

F. Viana

Student
School of Engineering, Polytechnic of Porto
Portugal

The automotive component industry has been constantly being studying to improve its performance. Bowden cables are present in opening doors, moving windows and others. In braided cables formed by galvanized wires with Zn steel exposed to the usual environmental conditions, the generation of ZnO appears, a phenomenon known as "white corrosion". The investigation consisted of mitigating the causes of the ZnO formation. Scanning electron microscopy (SEM) and Electron Probe Micro-Analyzer (EPMA) technology, allowed to detect that the generation of ZnO was induced by the presence of nucleating elements of ZnO on the surface of the steel cable before galvanizing with Zn. The S, Cl and O became visible in the interface between coating and substrate. This allowed concluding, under the coating, there were harmful products capable of triggering the ZnO nucleation reaction. So, the storage and cleaning of the steel wire before galvanizing is essential to prevent the ZnO formation.

Keywords: Zn-coated steel cables Automotive; White corrosion; Zinc oxide.

1. INTRODUCTION

Today, the world economy is largely influenced by the automotive industry. This sector has its own dynamics, with an enormous capacity to invest in innovation. The reliability of motor vehicles is directly linked to the stipulated traffic rules, but it also depends on the quality presented by them. Indeed, quality is one of the main pillars of the automotive industry, given that it seriously affects the image of any brand face to the competitors. Thus, control and quality are respected and seen as important to make automotive technology credible. In this sector, the lack of quality can mean the loss of human lives, which can damage the image of the car manufacturers. This concern with quality extends to the entire supply chain in the entire sector.

Due to the competitiveness of the automotive sector, quality has become a major ally in Meeting the high sector standards required. This study takes into account the problem detected in Bowden cables, right after the acquisition of new cars at the beginning of their use. The identified problem relates to the generation of ZnO in steel-coated wire and the aim is to mitigate and find the problem cause. It is intended to analyze the main causes of corrosion detected in the seat control cables after a short period afterwards its manufacturing process. In the first approach will be made using Scanning Electron Microscopy (SEM) and X-Ray Micro-analysis by Energy Dispersive Spectro-

scopy (EDS) to detect unexpected products or elements inside the Zn-coated steel cable. Normally, these cables are inserted into the release command of the tilting tab on the rear seat of a car. For the correct operation of the release mechanism for tilting the rear seat, 240 N load are the maximum allowed by the customer. The problem arose when it was verified that the force required for its activation measured in lab using a precision dynamometer became 300 N, thus generating the alert for the necessary corrective measures to be taken. This study is part of the investigation for the root-causes of this problem. Initially, a search was made and it was found that there was white corrosion on the steel cables, causing an increase in friction and, consequently, an increase in driving force, which exceeded the maximum value specified by the customer.

This paper is divided into five sections. The first section begins with this brief introduction to the work. The next one, is done the literature review to support the practical work developed. In next section, it was described and explained the approach of methodology used. In Section 4, it was described the results obtained and made a critical analysis of them. At the end, it was presented the outlines the main conclusions, highlighting the main contributions of this work.

2. LITERATURE REVIEW

The automotive industry involves many areas, namely in the improvement of manufacturing processes [1,2], in the reduction of production costs [3], in the optimization of processes, namely in the application of Lean tools for the elimination of waste [4,5], improving quality [6-8], increasing equipment availability [9,10], among others. Recently, Smart Manufacturing

Received: December 2020, Accepted: April 2021

Correspondence to: Gustavo Pinto, Assistant Professor,
School of Engineering, Polytechnic of Porto,
Porto, Portugal

E-mail: gflp@isep.ipp.pt

doi:10.5937/fme2103587P

© Faculty of Mechanical Engineering, Belgrade. Allrightsreserved

FME Transactions (2021) 49, 587-597 587

and Industry 4.0 have gained extreme importance in the automotive industry [11].

The automobile components industry is regulated by demanding standards and by very frequent audits by OEMs, to strictly comply with previously established procedures. However, when problems arise, due to a defective component, OEMs need to repair complete batches of vehicles manufactured, so that it can be replaced and the conditions initially established for the vehicle are restored.

Bowden cables are components responsible for transmitting certain mechanical actions even through complicated structures, [12]. For example, a door opening or the movement of the window glass in a vehicle, use this type of components. This type of components must have high quality levels, equally demanding. The combination of low prices and the high-quality need has promoted a series of studies aimed at improving productivity, without affecting quality levels.

Bowden cables need a wide list of processes to get to the final product. Moreira et al. [12] developed a new concept for the manufacture of this product, which avoids intermediate stocks and aggregates operations in the same equipment, reducing the load in the preparation of work and making production control simpler. Thus, any quality problem can be easily detected, allowing to stop the process and avoid adding value to the components that will have to go to scrap. This concept can be easily integrated into the industry 4.0 philosophy, linking it to other engaging equipment and the production management system. Martins et al. [13] also worked on the development of a new equipment concept for the manufacture of automotive Bowden cables. This new concept allowed them to improve the product and productivity, reducing cycle times by 25%. Santos et al. [14] devoted their attention to how Bowden cables are transported over equipment in some integrated operations. It focused on reducing the configuration times between the different cable references and the drastic reduction of the stopping time of this equipment. In order for Bowden cables to promote the actions for which they were designed, they must be equipped with terminals at the ends: a terminal near the end where the force is promoted by the driver or passenger of the vehicle, and another terminal where it is necessary to produce the effect of that force. Although these terminals have only a few cubic millimeters of metal, usually Zamak (Zinc-Aluminium-Magnesium-Kupfer), the pores have been detected. To eliminate this problem, Pinto et al. [15,16] carried out studies on the injection process of these terminals and on the design of the mold using simulation and analytical methods, verifying that improvements in mold design must be made, although the adjustment of parameters in high pressure die casting also has to be adjusted. Other studies have been carried out around the casting of high pressure die, mainly with a view to eliminating quality problems in manufactured products [17,18], or reducing the typical wear of molds [19].

The Bowden cables can cross damp areas in vehicles, so there are associated risks of corrosion and the most models are filled with grease in the part

covered by the outer spiral. The filling process of this grease also presented some problems, which were properly studied by Ribeiro et al. [20]. Indeed, significant waste of that grease was recorded in the reservoirs used for its storage immediately before injection. Silva et al, studied the possible creation of a new logistics system and made the process more flexible, and the main gains were obtained in terms of saving grease, through a new and optimize design of the system for extracting the mass from the reservoirs and injecting of mass into the cables. The environment won too because the grease waste decreased [21]. Zinc oxide (ZnO) is a semiconductor, not stoichiometric, which due to these characteristics has aroused a wide interest in the scientific community that is reflected in a large number of articles on the subject. The formation of ZnO has been studied by several authors [22-25], but with very different purposes. For a better understanding of its formation and growth, Ü. Özgür et al. [26], carry out a very comprehensive analysis about the ZnO, where they not only performed an in-depth discussion of the growth aspects but also deepened optical properties, p-type doping and some device fabrication aspects. However, no specific literature has been found about the Zn oxidation on steel surfaces.

This study intends to mitigate the problems of the ZnO generation in steel coated wire-ropes used in Bowden cables.

3. METHODOLOGY

The expected maximum value is established by the automotive industry, while the load value of 300 N was obtained based in a sample of 250 Bowden cables through laboratory tests using high-precision dynamometers (PCE-FM 500N). To carry out these analyses, a FEI Quanta 400FEG scanning electron microscope (SEM) provided with an EDAX Genesis X-ray spectroscope (EDS) was used. At the began, a careful analysis of the Zn-coated steel cable was done to identify areas affected by corrosion. Trying to quantify the area affected by Zn corrosion on the Zn-coated steel wires, 100 specimens were taken and analyzed in an area of about 20 μm^2 by SEM and the pictures obtained were treated using the ImageJ software®, allowing to understand that the area affected by the corrosion ranges from 12% to 38% of the checked area. Subsequently, also the areas among wires of the cable were investigated in order to find possible contaminants. After the first round of analyses, and because the findings are not in line with the initial expectations, a CAMECA model SX-50 Electron Probe Micro-Analysis (EPMA) was used to identify specific compositions in certain areas of interest, namely in the interface between the steel wire and the Zn coating.

In those analyses, samples were bonded to a holder system through a carbon/graphite tape. Secondary Electrons (SE) were predominantly used and the magnifications were standardized taking into account the goals: low magnification for global views mentioned in the work as "Area" and medium magnification for details referred to in the work as "Zone". To find some

products found on the cables, it was also investigated the internal polymer tube. In these analyses it was used three new cables and three others manufactured three weeks ago were used. In figure 1 it is possible to see the four samples taken from each cable cut in different sections. In total, there are twelve “area” samples analyzed in the three new cables and another twelve in the 3 cables manufactured three weeks ago. In total, in the twenty-four samples, ninety zones were analyzed. Due to the lack of existing studies, this work was done on a practical analysis based on empirical principles based on the results obtained.

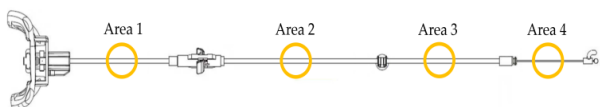


Figure 1. Different samples location taken from each of the cables.

Table 1 shows the identification of the analyzed samples. For example, the new cable 1 (CN1), in area 3 (A3) and in zone 2 (Z2) was cataloged with the reference CN1A3Z2.

Table 1. Cable 1 samples collected for analysis.

Cable (New) 1 (CN1)													
A1			A2				A3			A4			
Z1	Z2	Z3	Z1	Z2	Z3	Z4	Z1	Z2	Z3	Z4	Z1	Z2	Z3

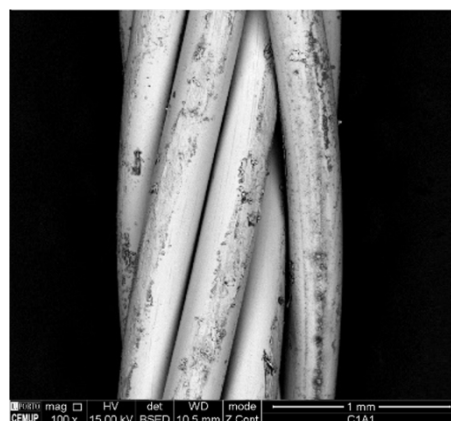
After the samples were properly cut and organized in a proper box, free from contaminants, the samples were connected to a support system that allowed their coupling to the inner base of the electron microscope sample holder, using a carbon/graphite tape. The secondary electron system (SE) was used, and the magnifications were standardized for each analysis type: low magnification for global views and medium magnification for obtaining details. The beam potential was 15 kV for all the analyzes performed. This beam potential helps to obtain a better accuracy of the chemical composition of the first layer found by the beam, despite it is also able to detect elements of the substrate, such as Iron and Carbon. However, a reduction of the potential of the beam could hidden the detection of some components on the surface of the wire and could lead to less accurate analyses. Micro-analyzes were carried out to identify zones to find some anomalies. Other investigations were also carried out to identify some flaws in the preparation process at the same cables (cleaning process), or lack of coating adherence to the steel wire (substrate) due to lack of cleaning, which will be described later.

4. RESULTS

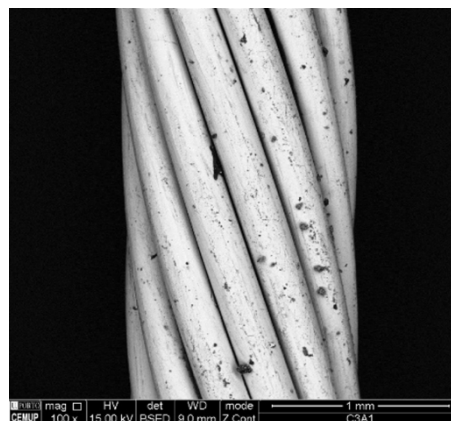
This chapter presents the results supported by the analysed samples, allowing the understanding of the phenomena presented in specific areas. Figure 2 shows an example of two samples from area 1 of the cables, with reference to the genesis of ZnO and its evolution, the type of particles and fluids.

After the observations made by SEM, and analyzing the three cables in area 1, it was possible to observe that:

- No corrosion was detected in area 1.
- In areas not affected by corrosion, the presence of these trails allows claiming that this fact cannot be considered as one of the causes of the corrosion.
- The presence of some dark stains on and between the wires, which will be shown in detail later, revealed a strong C peak, detecting or not the presence of K. It was also studied the composition of the internal polymer tube to understand if these stains could be originated by cable friction on the polymer or if it was another product. No correlations were found between the stains and the polymer tube. Possibly these stains would be leftover lubricants from the wire, which can result from the manufacturing or assembly process of the Bowden cables, where the wires are conducted by some pulleys subjected to lubrication before being cut.



(a)



(b)

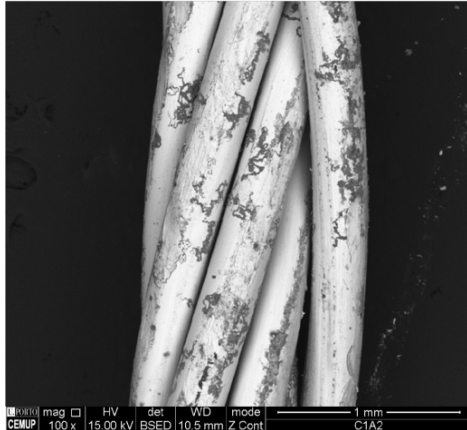
Figure 2. Two new cables in area 1, (a) CN1A1 and (b) CN3A1.

Using SEM in area 2, on the three new cables, it was possible to conclude the following:

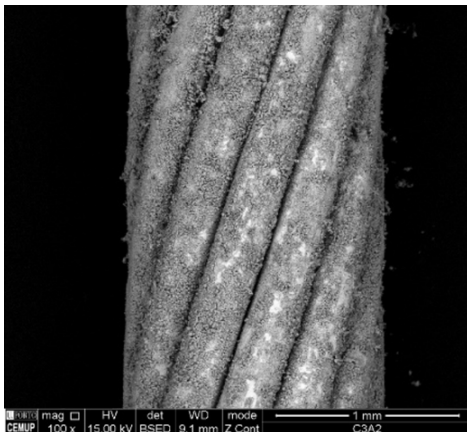
- The studied samples behaviour, from the same area, but from different cables, were very different.
- The presence of lubricant in the samples, in this area, was zero or extremely low. This confirms that lubricant found in area 1 provides accidentally from contact with the mechanical devices allocated to the manufacturing and assembly operations of these cables.
- Cable 2 showed some small ZnO aggregates. Cable 3 showed a uniform layer of fine ZnO formation, which easily leaves the wires as white

powder. This subject about powder will be depicted and dissected ahead.

- The adhesion of some small clusters of ZnO was very poor. It was possible to see the weak contact of the Zn surface layer with the substrate, particularly in cable 3, see figure 3.
- The ZnO appeared around all the wires. This phenomenon did not appear just on the external cable area. Thus, this suggests that ZnO formation is not induced by contact with any external body, being a problem induced by the environment where the single wires or the metallic cable are inserted during the cable manufacturing process.

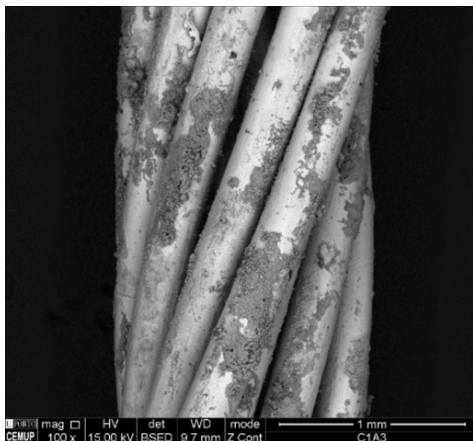


(a)

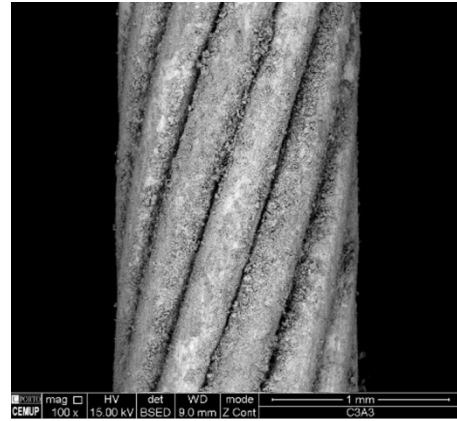


(b)

Figure 3. Two new cables in area 2, CN1A2 (a) and CN3A2 (b).



(a)

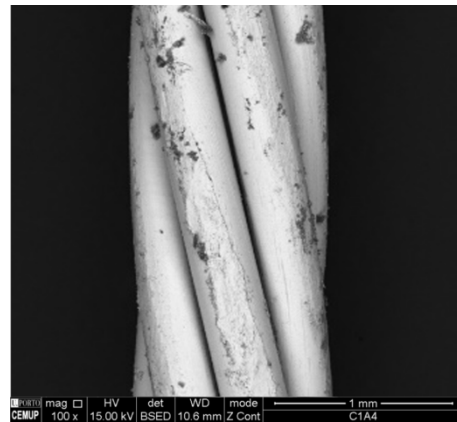


(b)

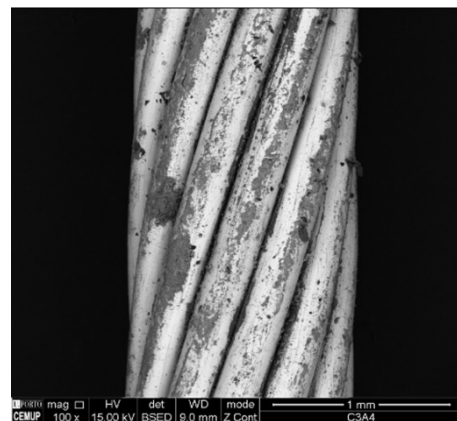
Figure 4. Two new cables in area 3, CN1A3 (a), CN3A3 (b).

After the observations of the area 3 of the cables, figure 4, it was possible to observe that:

- Taking into account the previous analysis performed on area 2, it was possible to conclude that in the area 3, just the cable 1 presented an increase in terms of ZnO formation.
- Cable 3 presented behaviour extremely similar between area 3 and area 2.
- Just cable 1 showed a consistent increase in the ZnO formation from area 1 to area 3, revealing a possible way of beginning ZnO formation.
- In a few cables, some aggregates of ZnO seemed stand-alone. These aggregates can be easily extracted when in contact with a carbon tape.



(a)



(b)

Figure 5. Two new cables in area 4, CN1A4 (a) and CN3A4 (b).

Considering the observation of area 4, as can be seen in figure 5, it was possible to conclude that in this area, the results were like in area 1, and much better than areas 2 and 3.

After analysing the four areas, it is possible to verify that the results obtained are different.

Based on the generic analysis presented, an in-depth analysis was planned and carried out to better understand some details in certain areas, for example, the appearance and evolution of ZnO, as well as other particles or fluids present.

4.1 Dark areas and tracks

The presence of dark areas over the wire coating deserved further study. Thus, it was observed and defined the dark areas most suitable to perform the micro-analyses. It will be noted that the concentration of these dark areas, considering the four areas in analysis, is a little bit more pronounced in area 1, as can be seen in figure 6.

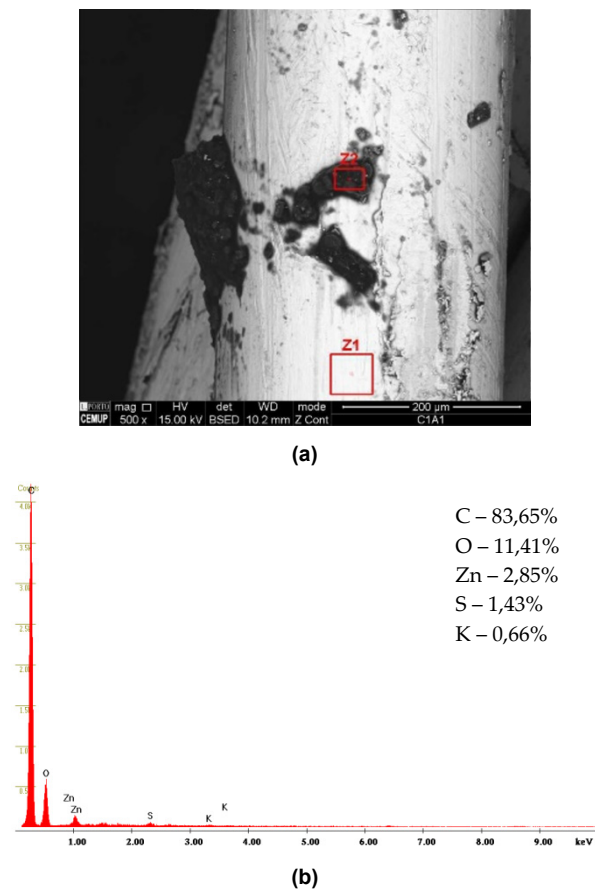


Figure 6. Dark areas on CN1A1 (a); and Zone 2 micro-analysis (b).

The areas highlighted, with Z1 and Z2 marked in figure 6 correspond to microanalyses carried out with a beam potential of 15 kV. Zone 1 corresponds to the wire coating (Zn), figure 6(a), and Zone 2 can be some lubricant or polymer substance, due to the strong peak of C, figure 6(b). Regarding the shape of the dark area, the most likely is that cable had contacted with the exterior polymeric tube and some fragments of the tube have adhered to the steel coated cable, because lubricant stains present a less defined shape. Observing

figure 7, it is possible to analyze the same cable in area 2, where it is possible to observe that:

- There were two different kinds of grooves on the wire surface: the vertical and the inclined grooves. The first one, perfectly organized, generated by the wire drawing process, and the other one, randomly distributed, which cause some surface cracks.
- In these surface cracks, no ZnO formation took place or nearby them, even though the coating has been affected. Thus, ZnO formation did not seem to be related to wire protection due to Zn coating lack.
- The randomly distributed grooves and deformations did not seem to be generated by the wire drawing process, having been formed due to high stress.
- It was found that the ZnO formation took place as an external body, easily detachable under the powder form.

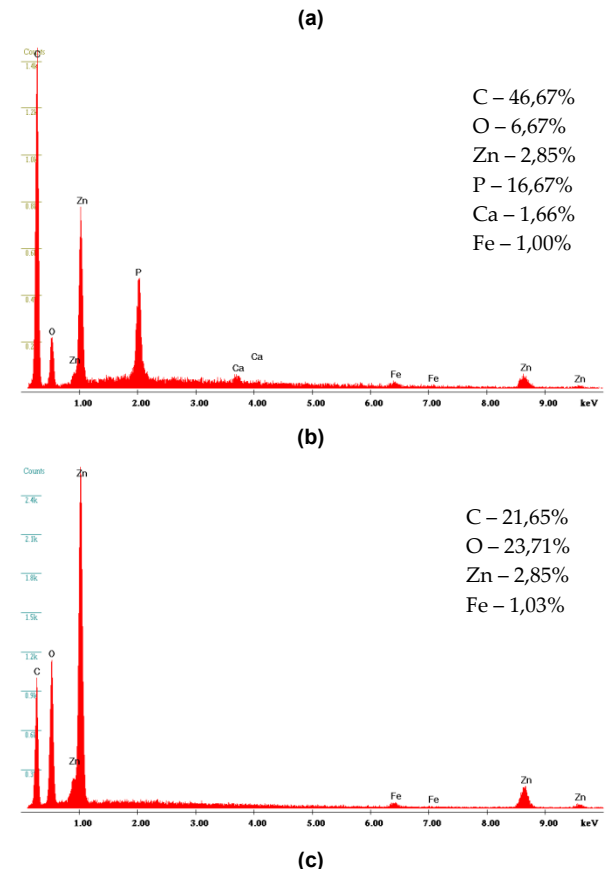
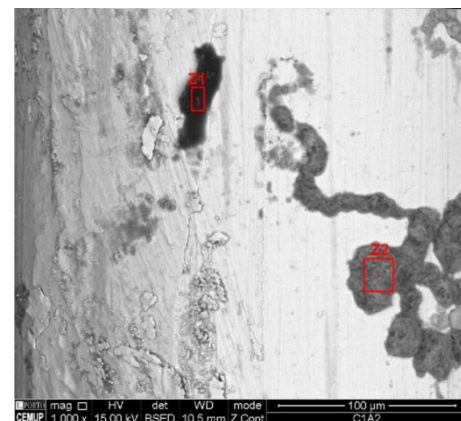


Figure 7. Different morphologies on CN1A2 (a) and micro-analysis zone 1 (b) and zone 2 (c).

Zone 1, figure 7b, showed the substances or C-rich and P products, strange to the wires, and in the zone 2, figure 7c, showed the presence of ZnO with an unexpected peak of C. To understand the behaviour of the dark substances in and out the trail along the cable, a fourth zone was studied, as can be seen in figure 8.

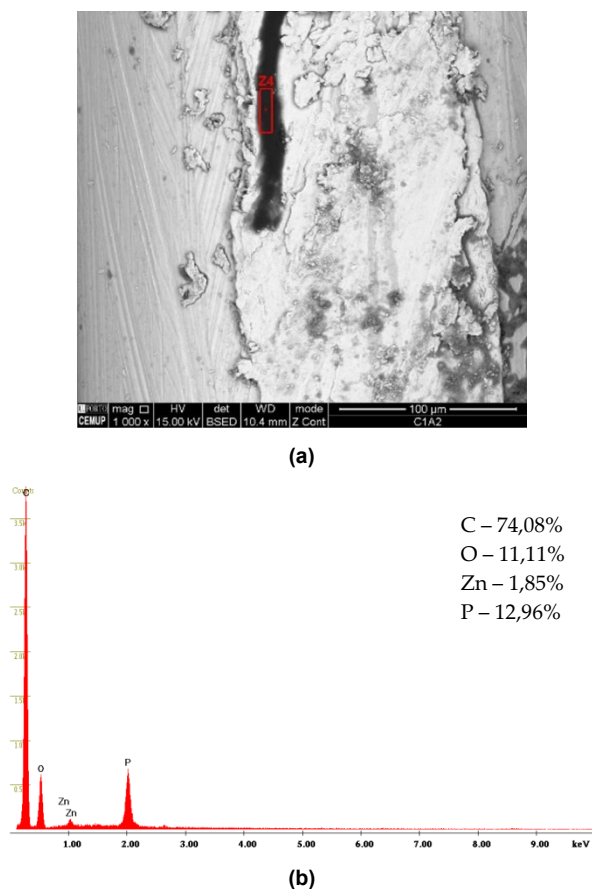


Figure 8. Dark substance analysis on the trail, in CN1A2 (a), and Micro-analysis (b).

After this analysis, some conclusions can be drawn:

- It was detected the presence of some strange substances over the wire coating, independently of the area considered.
- Micro-analysis performed allows concluding that these substances had the origin of the internal polymer tube used in this kind of pipe or from lubricant got during the cable manufacturing or assembly process. After the first analysis, the two hypotheses remained open because just C was detected. However, the second analysis led to observe that also P can be found. Hence, two situations can occur: the dark substances provided from different situations or products.
- Because dark substances and ZnO coexist in the same area, it can be stated that (1) they did not contribute to the ZnO formation because there were not corroded Bowden cables also with these dark stains on its surface, (2) they did not inhibit the ZnO formation because in many cases, they were cohabiting on the Zinc-coated surface.
- Considering the left side of the figure 7(a), it can be observed some grooves, which may have as source one of the following mechanical processes: (a) Wire drawing or (b) Matting process. In the

first one, the grooves were made by the section reduction, being covered by the Zn coating at the end; The other one, the coated wires, were subjected to contact with the driving holes which let the wires flow to the head responsible by the cable matting process. In this case, as can be seen in figure 7(a), the grooves were originated by the wire drawing process, because the coating seemed to accomplish adequately the substrate (wire).

4.2 ZnO formation and evolution

The presence of ZnO was more intense on cables 1 and 3. The figure 9 shows the first stage of ZnO formation (cable 1, area 3) generalized over the Zn coating.

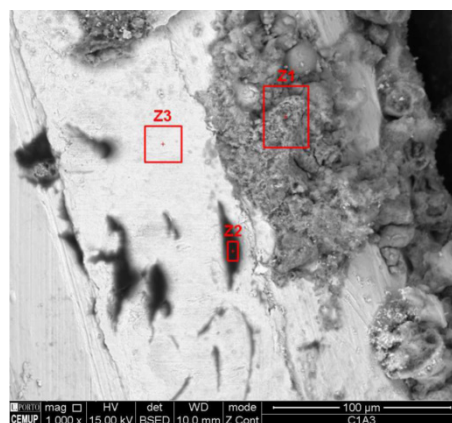


Figure 9. ZnO formation on CN1A3.

It was found that the evolution of the ZnO layer does not seem to follow any pattern, leaving some spaces to detach itself from the formation of ZnO at this stage. It was also found that there were several stages due to the different grain sizes, figure 10. After these observations, it is possible to conclude that the ZnO growth occurs around the particles themselves. In the analysis carried out, it was observed that: (a) the protection given by the zinc coating is effective because no trace of iron was found, (b) ZnO showed a continuous growth around the small crystal, but the larger these particles were, the weaker were these connections to the wire coating, (c) although the thickness of the Zn layer was not measured, the level of iron detected shows that the thickness of this layer is thick. For Fe detection, a 15 kV electron beam potential was used through the Zn layer.

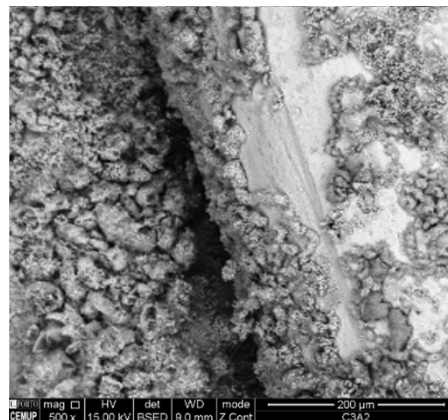
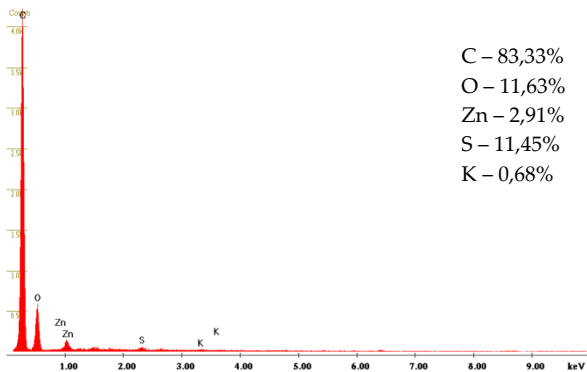


Figure 10. ZnO formation generalized stage CN3A2.

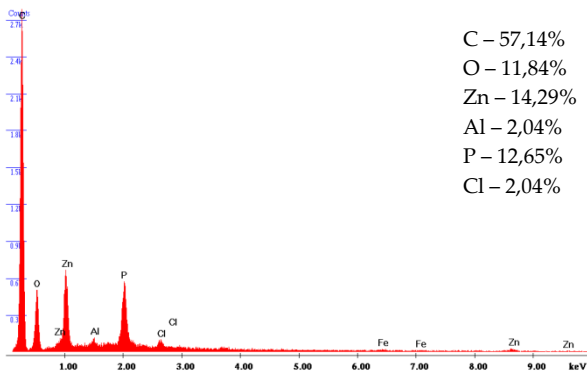
4.3 Analysis of the C presence and other elements on the wires surface

Figures 11 and 12 show the presence of C, however, C was not always linked to phosphorus and other elements in very small amounts. As can be seen in figure 11(a), P was not detectable in the sample from area 1, however, in the remaining samples it was detected.

The spectra, in figure 12, allowed to understand that there are different types of dark particles (spots) in the same area, some of them containing P and others only C or C and other small contents of other elements, such as Ca and / or Cl. In cables 1 and 3, area 1 did not have any P content, allowing to conclude that in this area it seems to be preserved from the P content. In the remaining areas they appear to contain different types of dark particles, coming from the inner polymer tube or the lubricant used during cable production.

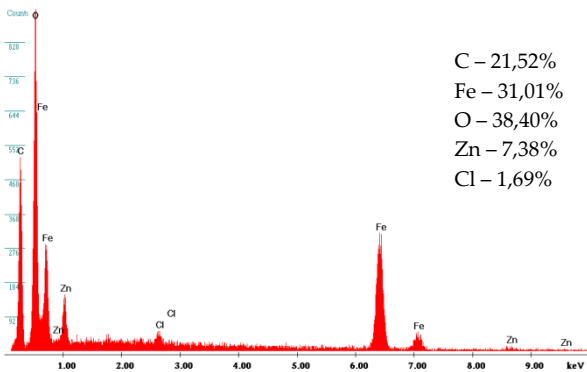


(a)

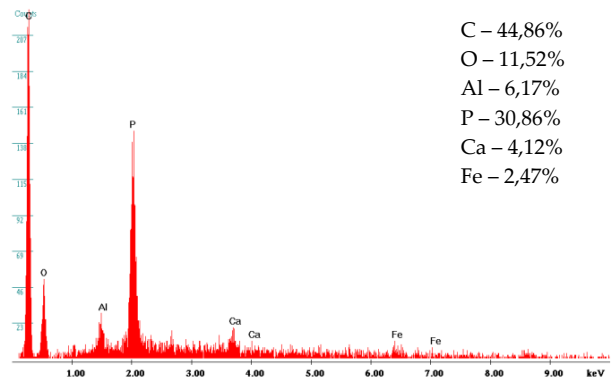


(b)

Figure 11. Analyses of different areas containing C from the cable 1.



(a)

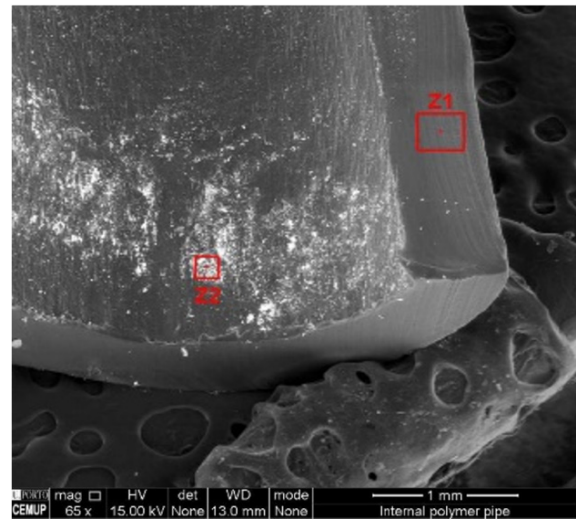


(b)

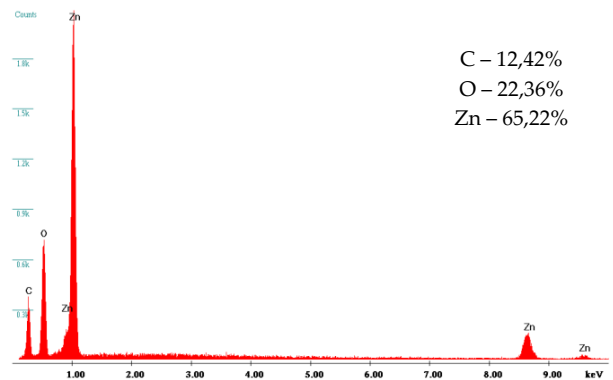
Figure 12. Analyses of different areas containing C from the cable 3.

4.4 Internal polymer tube

In figure 13, it can be seen a cable sample. To verify the cable influence with the polymer tube, an analysis was made. Small particles, with a lighter colour, were detected internally. To detect the type of particles, a microanalysis was carried out to discover its composition. Most of the particles found were ZnO, the wall of the tube contained only C and the hypothesis of the polymer to contain P or other content was discarded.



(a)



(b)

Figure 13. Internal polymer tube (a) and Micro-analysis (b).

4.5 Zinc - Steel interface analysis using Electron Probe Microanalysis

The use of Microanalysis by Electron Probe (EPMA) served to support the verification of possible foreign contents between the steel wire and the Zn coating, through a deep analysis of the cross-section, because any analysis made by the exterior of the wires do not allow to conclude how the ZnO is nucleated, showing evidence of its origin. Here, it was possible to obtain a generic spectrum through EPMA made to a set of samples referring to the cable area. This analysis allowed to obtain information about the elements present in the samples. As can be seen in figure 14, it is possible to state that Zn and O are almost always together, although when the intensity of O is more pronounced than that of Zn. It was also found that the presence of S was notorious, and its presence was clearly related to the incidence of O. Although the presence of Cl is quite reduced and dispersed at the coating/substrate interface, this amount should not be negligible. Cl has clear influence on the formation of ZnO [27].

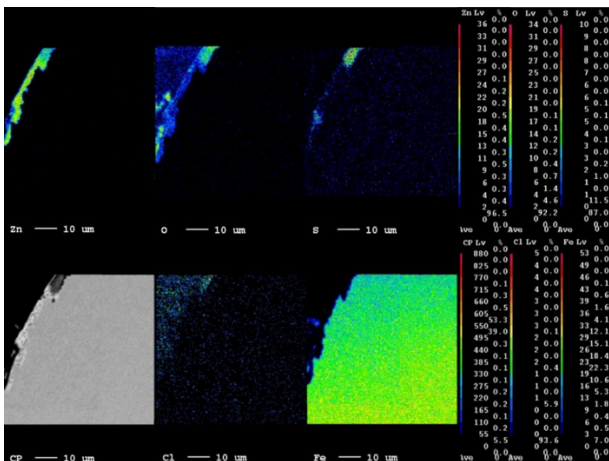


Figure 14. Spectra of the detected elements.

To understand whether these elements were on the outer face of the coating or on the coating/substrate interface, new analyzes were performed following a line (see figure 15) that runs through the coating, from the external resin used in the assembly process to the substrate.

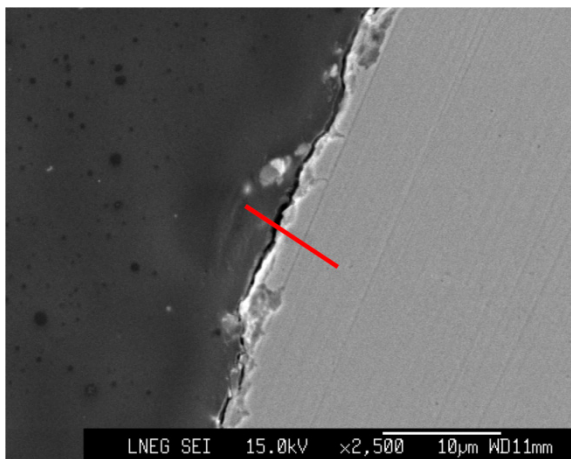


Figure 15. Sample subjected to EPMA analysis following a line.

The results can be seen in figure 16, where four channels were used in order to divide the intensity and location of each element present along the line, considering that the left side of the images is the external resin and the right side the substrate of steel. Each channel was linked to a specific element: pink to O, cyan to Cl, green to S and red to Zn. Cl and O were present in the external resin (assembly process). After that, Zn became visible (coating layer) and S, Cl and O were again visible at the interface between coating and substrate. This ensures that, under the coating, there were harmful products capable of triggering the ZnO formation.

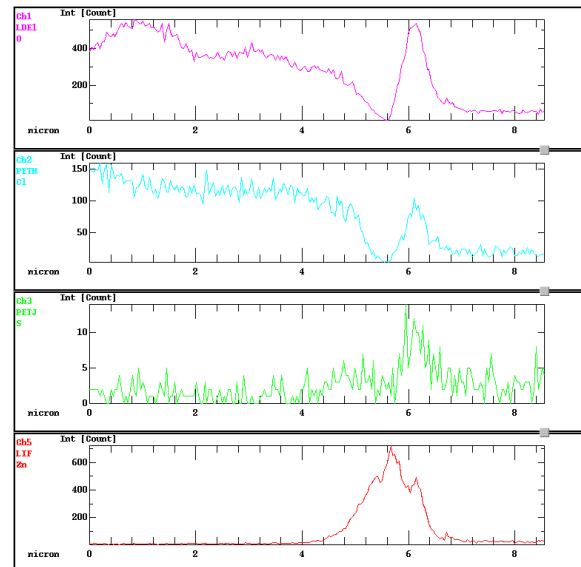


Figure 16. EPMA analyses, following a line from the outer resin to the steel substrate of figure 15.

The spectrum presented below (figure 17) makes it possible to clearly analyse the phenomenon described above. The highest peak of the green line (Sulphur) is to the right of the red peak, corresponding to the Zn coating, meaning that the Sulphur is present between the coating and the steel substrate, which leads to the perception that it is present on the surface of the wire steel, that is, before the Zn coating process.

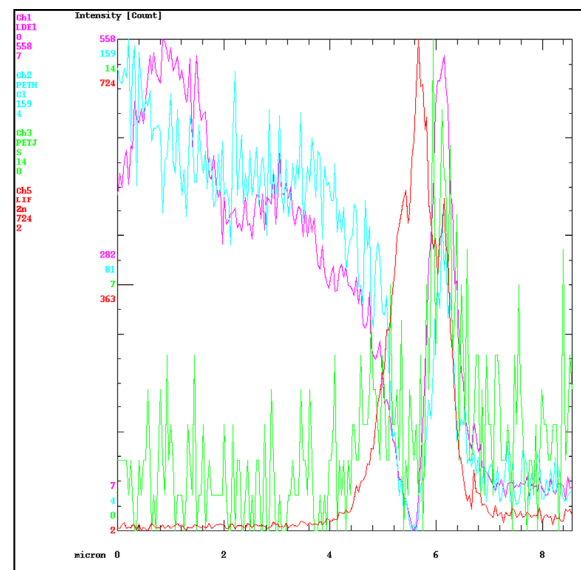


Figure 17. EPMA analysis following a line from the outside to the steel substrate - composite spectrum.

4.6 Results discussion

This work was performed intending to identify the main factors that generate the formation of ZnO. There are some ideas resulting from this study that should be made clear:

- The presence of lubricant in the cables just manufactured is clearly superior to that of the other cables previously analysed;
- The presence of foreign particles on the surface of the cables is an undoubted fact. These particles are usually connected to the steel wires through a layer of lubricant and have a very different composition from case to case;
- Some of these particles are rich in Al, Mg, Si and K, having added O. Their origin is unknown, and their presence is unexpected. However, it could result from the contact of the cable with the polymeric tube that protects the cables, or due to the manufacturing and assembly process of the cables;
- Other particles detected are particularly rich in Zn, Cl, O and C. If Zn is understandable, the appearance of O, C and Cl is strange in this group;
- Ca appears randomly in the samples, but sometimes in appreciable quantities. This may result from the manipulation that the cables may have been subjected to prior to delivery for analysis;
- In this second phase of the study, the clear presence of ZnO was not detected, with well-developed aggregates, as was found in the previous study in samples with more than three weeks of manufacture;
- The presence of the aforementioned particles may be linked to the formation of ZnO, acting as a catalyst/precursor, since the presence of some of these elements (S and Cl) to act as catalysts in the formation of Zinc Oxide is known;
- However, no clear relationship can be established at this time, between the presence of these elements and the formation of ZnO, since there is no direct relationship between the existence of particles with those constituents and the systematic presence of ZnO;
- The presence of these particles must be determined, being caused by carelessness in one or more of the following phases: (a) zinc plating process for steel cables, (b) cable manufacturing process, (c) storage at the producer and transportation to the customer, (d) storage on the client, (e) lubricant bath and (f) future manufacturing process (plastic injection, Zamak injection).
- The presence of Aluminium in areas 1 and 4 is predictable and permissible, due to the Zamak injection and due to the Zamak accessory mounted on the end of the cable, which has free movement over it in area 4. However, the presence of Al it occurs exactly outside these areas, that is, mainly in areas 2 and 3. This situation must be analyzed in terms of the production process;
- The lubricant protection must be carefully checked and filtered to ensure that it is not a vehicle for transporting particles to the cables when they are immersed. In addition, there are some conditions in which oil-in-water solutions can act as a precursor to ZnO formation. In this way, the lubricant used must be controlled;
- EPMA analyzes allow the detection of harmful elements, such as sulfur and chlorine located at the coating/substrate interface. This fact allows us to realize that these elements are in the steel wire before the coating process, which may be due to one or more of the following reasons: (a) steel wire storage procedure is being carried out in an inappropriate area, where pollutants and harmful elements can be deposited on the steel wire. However, in this situation, the concentration of pollutants would be more pronounced on the outer thread of each roll, (b) cleaning process that is being carried out after the cleaning process wire drawing/drawing and/or the lubricants used in this process, which may contain harmful products that contaminate the surface of the wire. In this case, the nucleation of zinc oxide would be much more uniform, so this hypothesis will probably be excluded, (c) cleaning process used, prior to the coating process, is not effective enough to remove elements harmful to the wire, (d) undue products are being used in the cleaning process, which is not conveniently removed in subsequent operations, (e) products such as Sulphur or chlorine are potential elements that can accelerate the nucleation and development of zinc oxide (ZnO), especially when the metallic cable is heated during the Zamak injection process.

5. CONCLUSIONS

The present study, which carried out in-depth analyses on two steel cables groups, freshly manufactured cables and cables with three weeks of manufacture, had the objective to analyse the zinc oxide formation in the cables. The results left no doubt as to the main cause of the problem was the cleaning the cables badly before zinc plating. There are no bibliographic sources that conclusively state that the elements found between the steel wire and the coating are catalysts par excellence for zinc oxide, but some references cited throughout the report, mention that Chlorine and Sulphur, with the help of a little heat, promote the formation of zinc oxide, which then proliferates on the zinc layer surface. If the formation of ZnO was premature, it could say that the origin would be associated with the solution to which the cable is immersed (oil). This could contribute to the establishment of ZnO. However, the formation of ZnO does not occur at the beginning of the process, therefore, this hypothesis was discarded. In this work the existence of unexpected elements (Cl, S, Al, Ca...) was verified at the interface between steel and Zn. These elements were at the base of the beginning of the ZnO nucleation and growth. The presence of P on the dark particles was not consistent, revealing that there are different kinds of particles over

the wires, some of them containing just C and another one presenting a strong peak of C accomplished by relatively low P peaks and, in some cases, the presence of Ca and Cl was also detected, although in very small quantities. However, the presence of the stains, containing just C, cannot be directly correlated with the ZnO formation, because they stand alone, over the wires, without any signal of ZnO nucleation over or nearby them. The presence of elements like Cl in the interface between the steel wire and the Zn coating revealed a dangerous situation regarding the nucleation of ZnO, as referred in the literature [27 -29]. Thus, some lacks in the steel wire cleaning conditions played a crucial role in the ZnO formation on the surface of the Zn-coated steel wire.

Author Contributions: Conceptualization, F.J.G.S., G.P.; methodology, F.J.G.S.; validation, F.J.G.S., G.P. and A.B.; formal analysis, F.J.G.S., G.P. and A.B.; investigation, F.V.; resources, F.J.G.S.; data curation, F.V.; supervision: F.J.G.S. and R.D.S.G.C.; writing—original draft preparation, G.P. and A.B.; writing—review and editing, F.J.G.S. and R.D.S.G.C.; visualization, G.P., A.B. and F.V.; supervision, F.J.G.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research received no external funding.

Acknowledgments: The Authors would like to thank to Mr. Rui Rocha from CEMUP due to is proactive collaboration in seeking the best images through SEM equipment. The strong cooperation of FicoCables company is also deeply acknowledge. Moreover, the support of CETRIB (Prof. Jorge Seabra) is also strongly appreciated.

Conflicts of Interest: The authors declare no conflict of interest.

REFERENCES

- [1] Figueiredo, D.; F. J. G.; Campilho, R. D. S. G.; Silva, A.; Pimentel, C.; Matias, J. C. O.: A new concept of automated manufacturing process for wire rope terminals, *Procedia Manufacturing*, Vol.51, pp. 431-437, 2020.
- [2] Antonioli, I.; Guariente, P.; Pereira, T.; Ferreira, L.P.; Silva, F.J.G.: Standardization and optimization of an automotive components production line, *Procedia Manufacturing*, 2017, Vol. 13, pp. 1120–27, 2017.
- [3] Rosa, C.; Silva, F.J.G.; Ferreira, L.P.: Improving the quality and productivity of steel wire-rope assembly lines for the automotive industry, *Procedia Manufacturing*, 2017, Vol. 11, pp. 1035-42, 2017.
- [4] Rosa, C.; Silva, F.J.G.; Ferreira, L.P.; Pereira, T.; Gouveia, R.M.: Establishing standard methodologies to improve the production rate of assembly lines used for low added-value products, *Procedia Manufacturing*, 2018, Vol. 17, pp. 555-62, 2018.
- [5] Dias, P.; Silva, F.J.G.; Campilho, R.D.S.G.; Ferreira, L.P.; Santos, T.: Analysis and improvement of an assembly line in the automotive industry, *Procedia Manufacturing*, 2019, Vol. 38, pp. 1444–52, 2019.
- [6] Costa, T.; Silva, F.J.G.; Ferreira, L.P.: Improve the extrusion process in tire production using Six Sigma methodology, *Procedia Manufacturing*, 2017, Vol. 13, pp. 1104-11, 2017.
- [7] Costa, M.J.R.; Gouveia, R.M.; Silva, F.J.G.; Campilho, R.D.S.G.: How to solve quality problems by advanced fully-automated manufacturing systems, *The International Journal of Advanced Manufacturing Technology*, Vol. 94(9-12), pp. 3041-3063, 2018.
- [8] Barbosa, B.; Pereira, M.T.; Silva, F.J.G.; Campilho, R.D.S.G.: Solving quality problems in tyre production preparation process: a practical approach, *Procedia Manufacturing*, 2017, Vol. 11, pp. 1239–46, 2017.
- [9] Araújo, W.; Silva, F.J.G.; Campilho, R.: Manufacturing cushions and suspension mats for vehicle seats: a novel cell concept, *The International Journal of Advanced Manufacturing Technology*, Vol. 90(5-8), pp. 1539-1545, 2017.
- [10] Santos, R.F.L.; Silva, F.J.G.; Gouveia, R.M.; Campilho, R.D.S.G.; Pereira, M.T.; Ferreira, L.P.: The improvement of an APEX machine involved in the tire manufacturing process, *Procedia Manufacturing*, Columbus, OH, USA, Vol. 17, pp. 571-78, 2018.
- [11] Pinto, B.; Silva, F.J.G.; Costa, T.; Campilho, R.D.S.G.; Pereira, T.: A Strategic Model to take the First Step Towards Industry 4.0 in SMEs, *Procedia Manufacturing*, Vol. 38, pp. 637-645, 2019.
- [12] Moreira, B.M.D.N.; Gouveia, R.M.; Silva, F.J.G.; Campilho, R.D.S.G.: A Novel Concept Of Production And Assembly Processes Integration, *Procedia Manufacturing*, 2017, Vigo, Spain, Vol. 11, pp. 1385-95, 2017.
- [13] Martins, N.; Silva, F. J. G.; Campilho, R. D. S. G.; Ferreira, L. P.: A novel concept of Bowden cables flexible and full-automated manufacturing process improving quality and productivity, *Procedia Manufacturing*, Athens, Greece, Vol. 51, pp. 438-445, 2020.
- [14] Santos, P.R.; Silva, F.J.G.; Campilho, R.D.S.G.; Pinto, G.F.L.; Baptista, A.: A novel concept of a conduit transport system, *Procedia Manufacturing*, Vol. 38, pp. 848-57, 2019.
- [15] Pinto, H.; Silva, F.J.G.: Optimisation of die casting process in Zamak alloys, *Procedia Manufacturing*, 2017, Vol. 11, pp. 517-25, 2017.
- [16] Pinto, H.; Silva, F.J.G.; Martinho, R.P.; Campilho, R.D.S.G.; Pinto, A.G.: Improvement and validation of zamak die casting moulds, *Procedia Manufacturing*, Vol. 38, pp. 1547-57, 2019.
- [17] Silva, F. J. G.; Morgado, L.; Teixeira, A.; Sá, J. C.; Ferreira, L. P.; Almeida, F.: Analysis and Development of a Failure Prediction Model for Electrical Terminals Used in the Automotive

- Industry, *Procedia Manufacturing*, Vol. 51, pp. 207-214, 2020.
- [18] Silva, F.J.G.; Campilho, R.D.S.G.; Ferreira, L.P.; Pereira, M.T.: Establishing guidelines to improve the high-pressure die casting process of complex aesthetics parts. *Transdisciplinary Engineering Methods for Social Innovation of Industry 4.0*, Peruzzini M et al (Eds.), IOP Press, 2018.
- [19] Nunes, V.; Silva, F.J.G.; Andrade, M.F.; Alexandre, R.; Baptista, A.P.M.: Increasing the lifespan of high-pressure die cast molds subjected to severe wear, *Surf Coat Tech*, Vol. 332, pp. 319-331, 2017.
- [20] Ribeiro, R.; Silva, F.J.G.; Pinto, A.G.; Campilho, R.D.S.G.; Pinto, H.A.: Designing a Novel System for the Introduction of Lubricant in Control Cables for the Automotive Industry, *Procedia Manufacturing*, Vol. 38, pp. 715-25, 2019.
- [21] Silva, F.J.G.; Gouveia, R.M.: *Cleaner production – Toward a better future*. Springer Nature, Switzerland, 2020.
- [22] Yendrapati, T.P.; Gautam, A.; Bojja, S.; Pal, U.: Formation of ZnO-CuS nanorods for efficient photocatalytic hydrogen generation, *Solar Energy*, Vol. 196, pp. 540-548, 2020.
- [23] Luévano-Hipólito, E.; Torres-Martínez, M.: Sonochemical synthesis of ZnO nanoparticles and its use as photocatalyst in H₂ generation, *Mater Sci Eng B-Adv*, Vol. 226, pp. 223-33, 2017.
- [24] Gorna, C. R.; Emanetoglu, N. W.; Liang, S.; Mayo, E. E.; Lu, Y.: Structural, optical, and surface acoustic wave properties of epitaxial ZnO films grown on (011 $\bar{2}$) sapphire by metalorganic chemical vapor deposition. *Journal of Applied Physics*, Vol. 85, pp. 2595, 1999.
- [25] Rocha-Mendoza, I.; Camacho-López, S.; Luna-Palacios, Y.Y.; Esqueda-Barrón, Y.; Camacho-López, M.A.; Camacho-López, M.; Aguilar, G.: Second-harmonic generation of ZnO nanoparticles synthesized by laser ablation of solids in liquids, *Optics & Laser Technology*, Vol. 99, pp. 118-23, 2018.
- [26] Özgür, Ü.; Alivov, Ya. I.; Liu, C.; Teke, A.; Reshchikov, M. A.; Doğan, S.; Avrutin, V.; Cho, S.-J.; Morkoç, H.: A comprehensive review of ZnO materials and devices, *Journal of Applied Physics* Vol. 98, 2005.
- [27] Sun, S.; Jiao, S; Zhang, K.; Wang, D.; Gao, S.; Li, H.; Wang, J.; Yu, Q.; Guo, F. Zhao, L.: Nucleation effect and growth mechanism of ZnO nanostructures by electrodeposition from aqueous zinc nitrate baths, *Journal of Crystal Growth*, Vol. 359, pp. 15-19, 2012.
- [28] Mayekar, J., Dhar, V., Radha, S.: Role of salt precursor in the synthesis of zinc oxide nanoparticles, *International Journal of Research in Engineering and Technology*, Vol. 3(3), pp. 43-45, 2014.
- [29] Kołodziejczak-Radzimska, A.; Jesionowski, A.: Zinc Oxide—From Synthesis to Application: A Review, *Materials*, Vol. 7, pp. 2833-2881, 2014.

ИСТРАЖИВАЊЕ ОКСИДАЦИЈЕ КОД ПОЦИНКОВАНИХ ЧЕЛИЧНИХ КАБЛОВА

Г. Пинто, Ф.Ј.Г. Силва, А. Бапטיста,
Р.Д.С.Г. Кампилхо, Ф. Виана

Индустрија аутомобилских компонената стално унапређује перформансе. Бовден каблова има код отварања врата, отварања и затварања прозора, итд. Код текстилних плетених каблова, израђених галванизацијом жица цинком, изложених условима спољашње средине, јавља се ZnO, појава позната као „бела корозија“. Истраживање има за циљ ублажавање узрочника ZnO. Применом технологије SEM и ЕРМА утврђено је да ZnO изазивају нуклеирајући елементи на површини челичног кабла пре галванизације са Zn. На интерфејсу између премаза и подлоге видљиви су S, Cl и O. Нађено је да се штетни продукти јављају испод премаза и узрокују ZnO нуклеирајућу реакцију. Према томе, складиштење и чишћење челичне жице пре галванизације је битно за спречавање настанка ZnO.