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Studying the ZnO formation in coated steel wire ropes for the automotive industry

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Abstract

Bowden cables are abundantly applied in the automotive assembly lines leading to drive various devices, such as opening trunk or the fuel tank cap, triggering the handbrake, opening the doors, etc. The cable used in automotive metallic harness is commonly constituted of braided wire galvanized steel, which has been studied to resist the weather aggressions typically imposed by the conditions under which usually work. However, to allow this operating in a steady state way, the braided wire must have the appropriate quality. This work study the reasons of the formation of relatively abundant quantities of zinc oxide (ZnO) in metallic cables used in the automotive industry, a few weeks after their manufacture. It was concluded that there were serious shortcomings of cable cleaning between the wire forming operations and galvanizing, with deposition of ZnO enhancing elements in the interface, which would prove to be crucial to nucleation and development of ZnO on the surface. Thus, the main contribution of this work is to identify and describe the elements able to generate ZnO in coated steel wires, avoiding this phenomenon in the industry.

Keywords: Corrosion, Oxidation, Zinc Oxide, Zinc electroplated steel wire, Automotive harness, Bowden cables.

1. Introduction

The importance of the automotive industry to the world economy is incontestable. The sector has its own dynamic, capable of overcoming periods of crisis with relative ease, taking advantage of these moments to invest even more strongly in innovation. The safe use of motor vehicles is based on driving standards that comply with the stipulated traffic rules, but it also depends on the quality presented by the vehicles. Thus. quality in the automotive industry is seen as unquestionable, as the lack of quality can imply the loss of human lives, with severe consequences in economic and image terms for car manufacturers. This concern with quality extends to the entire supply chain in this sector.

Component manufacturers for the automotive industry are subject to constant audits and need to comply with very strict quality standards. This work intends to study a quality problem detected in Bowden cable. This problem is the zinc oxide (ZnO) white corrosion generation on steel-coated wire. Thus, it is intended to mitigate the root-causes behind the generation of the white corrosion above referred. To do that, it was necessary to perform a surface morphological analysis and microanalysis composition using Scanning Electron Microscopy (SEM), X-Ray Microanalysis by Energy Dispersive Spectroscopy (EDS) and Micro-Probe (EPMA) to detect unexpected products outside and inside the Zn-coated steel cable. Normally, these cables are inserted into the release command of the tilting tab on the rear seat of cars. For the correct releasing operation of the mechanism for tilting the rear seat, a maximum load of 240 N to be exerted by the consumer is allowed. The problem arose when it was verified that the load required for its activation reached 300 N, thus generating the alert for the necessary corrective measures to be taken. An initial research was carried out and it was detected that there was white corrosion in the

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steel cables of the aforementioned control cable of this mechanism, which was causing an increase in friction and, consequently, an increase in the driving force, which exceeded the maximum value specified by the customer.

This work is divided into five sections, beginning with this brief introduction that aims to contextualize the work. Section 2 aims to support the practical work developed with the necessary theoretical concepts around control cables. Section 3 aims to describe the approach methodology used in this work. Section 4 describes the results obtained and makes a critical analysis of them. Finally, section 5 outlines the main conclusions, highlighting the main contributions of this work.

2. Literature review

The dynamics imposed by car manufacturers generate countless research works in the most diverse areas, from the improvement of manufacturing processes [1,2] to the application of Lean tools for the elimination of waste [3,4], cost reduction [5], increasing product quality [6-8], reformulating concepts in production equipment with a view to minimizing downtime and maximizing equipment availability [9,10] or acting in logistic processes which improve the linkage between processes [11]. More recently, Smart Manufacturing and Industry 4.0 have gained particular highlight in many sectors, including the automotive industry [12].

The components industry is regulated by very demanding standards and by very frequent audits by OEMs, in order to strictly comply with previously established procedures, not allowing any deviation from the initially contracted standards. However, it is usually known that problems arise and, due to a component, OEMs need to call authorized repairers complete batches of vehicles manufactured with a certain component, 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 layouts, [13]. The simple opening of a door or the movement of the window glass in a vehicle, use this type of components. They are usually relatively complex components, but with low added value [14]. However, quality levels must be equally demanding. The combination of relatively low prices and the need for high quality has promoted a series of studies aimed at improving productivity, without affecting quality levels.

Bearing in mind that Bowden cables need a vast list of processes to reach the final product, Moreira et al. [13] developed a new concept for the manufacture of this product, combining different operations in single equipment. This aggregation brings advantages at different levels, as it avoids intermediate stocks and aggregates operations on the same equipment, reducing the load on work preparation and making production control much simpler. Any quality problem can be easily detected, allowing to stop the process and avoid adding value to components that will have to go to scrap. In addition, it should be noted that this concept can be easily integrated into the Industry 4.0 philosophy, linking it to other surrounding equipment and to the production management system.

Santos et al. [15] devoted his attention to the way Bowden cables are transported over equipment regarding some integrated operations. This study had as its main focus the reduction of setup times between different cable references and the drastic reduction in the stopping time of this equipment, a factor that was a major cause for concern. Significant improvements were achieved in the process: setup time was reduced by 97%, which dramatically increases equipment flexibility and production planning, as well as equipment availability. However, availability was also increased in another way: a 70% reduction in equipment downtime was expected due to breakdowns thanks to the simplicity of the systems now designed, thinking as well in facilitating replacement operations. Thus, availability and flexibility of fundamental equipment for the production of Bowden cables was vividly increase based on simple mechanical solutions.

For Bowden cables to promote the actions for which they were designed, it is necessary that they are equipped with terminals at the ends: a terminal near the end where 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 millimetres of metal, usually Zamak, pores have been detected. In order to eliminate this problem, Pinto et al. [16,17] carried out studies on the injection process of these terminals and on the design of the mould using simulation and analytical methods, verifying that improvements should essentially be made in the design of the mould, although the adjustment of parameters in the high pressure die casting also needed to be adjusted. In a first study [16], the main guidelines to be taken into account in the future design of the moulds were outlined, and in a later study [17], these guidelines became even more assertive, especially (1) with regard to turbulence during the filling process of the mould, (2) the need to properly study the flow of metal when it is injected into the mould, in order to avoid the formation of gas pockets, and (3) the need to include gas flow channels in the mould, preventing them from being trapped and creating porosities. Other studies around high pressure die casting has been performed, mainly with a view to eliminating quality problems in the manufactured products [18,19], or to reduce the typical wear of the moulds [20].

Bearing in mind that Bowden cables cross damp areas in vehicles, such as the area where the windows collapse, there are associated risks of corrosion, so that most models are filled with grease in the part covered by the outer spiral. The filling process of this grease also presented problems, which were properly studied by Ribeiro et al. [21]. Indeed, a significant waste of that grease was recorded in the reservoirs used for its storage immediately before injection, and significant logistical problems persisted due to differences between these reservoirs. The study allowed the creation of a new logistics system that significantly improved and made the process more flexible, but the main gains were obtained in terms of saving grease, through a new design of the system for extracting the mass from the reservoirs and injecting that mass into the cables, between the outer spiral and the inner metallic cable. In addition to the benefits in terms of competitiveness, there are also significant gains for the environment, as the wasted grease was a threat to the environment [22].

This study intends to mitigate the problems behind the generation of ZnO in steel coated wire-ropes used in Bowden cables. To the best of the authors' knowledge, there are no studies already published about this issue. The formation of ZnO has been studied by several authors [23-25], but with very different purposes.

3. Methodology

The investigation of the white corrosion root-causes was essentially based on two steps: firstly, a SEM + EDS analysis of the cable wires surface and, after that, an EPMA analysis to assess the coating interface. In order to carry out the requested analysis, a FEI Quanta 400FEG SEM provided with an EDAX Genesis EDS was used. Initially, a careful analysis of the Zn-coated steel cable was done leading to identify areas affected by corrosion. Subsequently, also the areas among wires of the cable were investigated in order to find possible contaminants. Moreover, a CAMECA model SX-50 EPMA was used to identify specific compositions in certain areas of interest.

Samples were bonded to a holder system through a carbon/graphite tape. In those analyses, Secondary Electrons (SE) were predominantly used and the magnifications were kept standardized regarding each main goal: low magnification for global views mentioned in the work as "Area" and medium magnification for details referred to in the work as "Zone".

The internal polymer tube was also investigated in order to collect important information about the root of some products found on the cables, correlating them with the polymer constitution used as cover. In order to carry out the analysis, three new cables and three others manufactured three weeks ago were used. Four samples were taken from each cable cut in different sections, as shown in Fig. 2. There are a total of twelve "area" samples analyzed in the three new cables and another twelve in the 3 cables manufactured three weeks ago. Each sample was marked, allowing a better correlation between the detected phenomenon and the eventual area from which it was extracted. In total, in the twenty-four samples, ninety zones were analyzed. This study was grounded on a practical analysis based on empirical principles based on the results that were obtained.

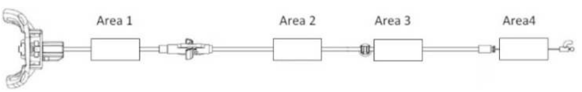

Fig. 2. Location of the different samples taken from each of the cables.

All samples collected for analysis were catalogued, and a reference was assigned to each sample. For example, the new cable 1 (CN1), in area 2 (A2) and in zone 3 (Z3) was catalogued with the reference **CN1A2Z3** (table 1), cable 2 manufactured 3 weeks ago (CM2), in area 1 (A1) and zone 4 (Z4) was referred to as CM2A1Z4.

Table 1. Example of the cable 1 samples collected for analysis.

Cable (**N**ew) **1**														
A1		**A2**				A3						A4		
Z1	Z2	Z1	Z2	**Z3**	Z4	Z1	Z2	Z3	Z4	Z5	Z6	Z1	Z2	Z3

An initial analysis makes it possible to observe the existence of lubricant as well as other constituent elements. After being properly cut and separated 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. In these analyzes, the secondary electron system (SE) was predominantly used, and the magnifications were kept standardized for each type of analysis: low magnification for global views and medium magnification for obtaining details. The beam potential was maintained at 15 kV for practically all the analyzes performed. In situations where this was justified, micro-analyzes were carried out in order to identify particular zones that, for this reason, stimulated the curiosity to find any anomaly. Subsequent investigations were also carried out on the same samples to identify some flaws in the preparation process for the same cables (cleaning process), or lack of adherence of the coating to the steel wire (substrate) due to lack of cleaning, which will be described later.

4. Results

In this chapter the samples analyzed and their respective connections are shown, allowing the understanding of the phenomena presented in specific areas, Fig. 3, such as the genesis of ZnO and its evolution, the particles type and fluids.

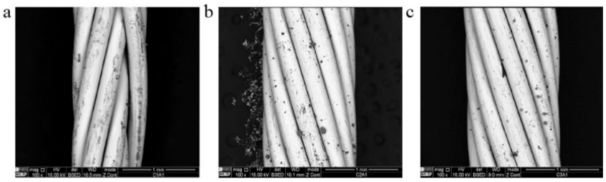

Fig. 3. Three new cables in area 1, (a) CN1A1, (b) CN2A1 and (c) CN3A1.

After the observations made by SEM in area 1, on the three new cables, it is possible to expose some ideas, such as:

- No corrosion was detected in this area, and only cable 1 presents some heterogeneity in terms of general aspect.
- The presence of these trails in areas not affected by corrosion allows to state that this fact cannot be considered as one of the possible root-causes of the corrosion felt in other samples.
- The presence of some dark stains on and between wires will be showed ahead in detail, revealing a strong peak of C, accomplished or not by K. The composition of the internal polymer tube was also studied in order to understand if these stains could result of cable friction on the polymer or if it is another product. No correlation was obtained between these stains and the polymer pipe, and it can be believed that those stains are wire lubricant rests. However, its presence is major in cables 2 and 3 but in very small concentration.

Important note: In further references to the substances found on the surface, the "dark substances" or "dark stains" just correspond to the colour observed on the SEM pictures, not to the substance real colour.

After the observations made by SEM in area 2, on the three new cables, it is possible to conclude the following:

- The behaviour among samples (cables) is very different, regarding that they provide from the different cables, despite corresponding to the same area.
- The presence of lubricant in this area is extremely low.

- Cable 1 shows the initial stage of the ZnO formation, while cable 2 shows some small aggregates of ZnO, but starting from a different basis. Cable 3 shows uniform layer of fine ZnO formation, which leaves easily the wires under a white powder form. This powder is depicted and dissected ahead.
- The adhesion of some small clusters of ZnO seems to be very poor, detaching easily and showing pitiable intimate contact with the Zn surface layer, particularly in cable 3.
- The ZnO appears around all the wires, not just on the external area of the cable.

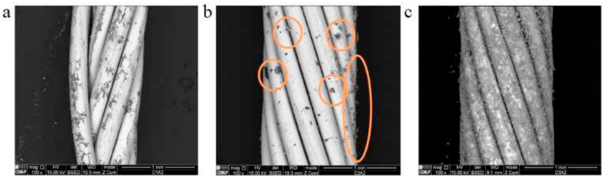

Fig. 4. Three new cables in area 2, (a) CN1A2, (b) CN2A2 and (c) CN3A2.

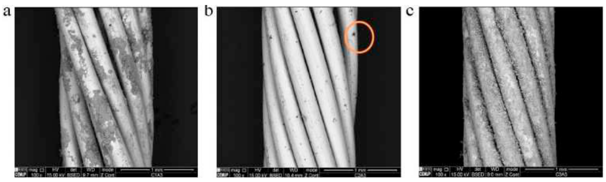

Fig. 5. Three new cables in area 3, (a) CN1A3, (b) CN2A3 and (c) CN3A3.

After the observations of area 3, it can be concluded that:

- Attending to area 2, it can be stated that just cable 1 presents an increase in terms of ZnO formation.
- Cable 2 seems not to be affected by ZnO formation.
- Cable 3 presents behaviour extremely similar between area 3 and area 2, previously shown in Fig. 2. The concentration of ZnO formed seems a little bit lower but it cannot be stated 100% safely.
- Just cable 1 shows a consistent increase in ZnO formation since area 1 to area 3, revealing one possible way about how the ZnO beginnings to be created.
- Some aggregates of ZnO seem stand-alone, being easily extracted when in contact with a carbon (C) tape.

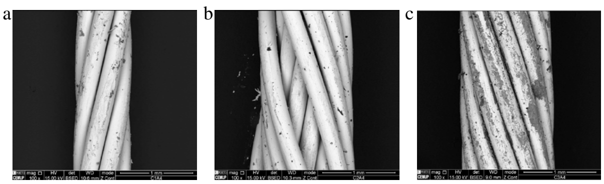

Fig. 6. Three new cables in area 4, (a) CN1A4; (b) CN2A4; (c) CN3A4.

Considering the observation of area 4, it can be concluded that:

- In general, this area presents results similar to area 1, and much better than areas 2 and 3.
- It is clear that the four areas considered in this study present different results.

Regarding the generic analysis previously presented, a deeper analysis was carried out leading to better realize what is going on in particular areas, how the ZnO is generated and how it evolves, as well as the kind of other particles or fluids present on the areas considered.

4.1. Confined dark areas and tracks

The presence of dark areas over the wire coating was investigated. Thus, micro-analyses were performed in specific areas where there are dark areas to analyze. It will be noted that concentration of these dark areas, considering the four areas in analysis, is a little bit more pronounced in area 1, see fig 7.

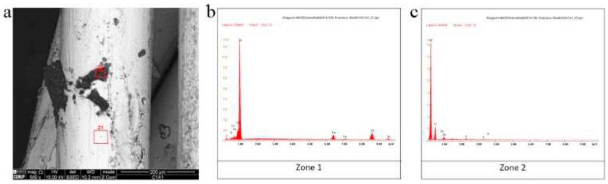

Fig. 7. Dark areas on (a) CN1A1; (b) and (c) micro-analyses.

The areas highlighted in Fig. 7 correspond to microanalyses carried out with a beam potential of 15 kV. Zone 1 corresponds to the wire coating (Zn), Fig. 7(a, b), and Zone 2 can be linked to some lubricant or polymer substance, due to the strong peak of C, Fig 7(a, c).

After these previous analyses, it is necessary to observe a new sample. Now, the same cable was analyzed in area 2. Observing Fig. 8, it follows that:

- There are two different kinds of grooves on the wire surface: the vertical grooves, perfectly organized, generated by the wire drawing process, and the inclined grooves, randomly distributed, which cause some surface cracks.
- Despite some surface cracks, no ZnO formation takes place in these cracks or nearby them, even though the coating is affected. Thus, ZnO formation seems not be related to wire protection due to Zn coating lack.
- The randomly distributed grooves and deformations seen on the left side of Fig. 8 (a) do not seem to be generated by the wire drawing process, having been formed by high stress.
- The ZnO formation is insipid in area 2. Indeed, the zone 2 of the Fig. 8 (a) shows the first step of the ZnO formation, which, under favorable conditions, will develop to the situation presented ahead.
- The ZnO formation takes place as an external body, easily detachable under the powder form.

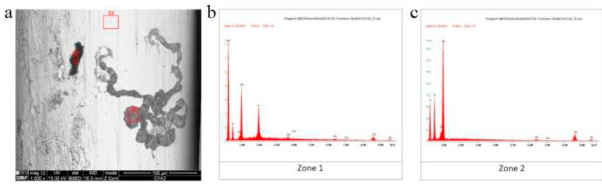

Fig. 8. Different morphologies on (a) CN1A2; (b) and (c) micro-analysis.

Zone 1 corresponds to substances or Carbon-rich (C-rich) and Phosphorous (P) products, strange to the wires, whereas zone 2 shows the presence of ZnO but, at this time, accomplished by an unexpected peak of C. In order to understand if there is different behaviour of the dark substances in or out the trail along the cable, a fourth zone was studied, Fig. 9. A similar analysis was performed on the same cable, but now on area 3, leading to the results shown in Figs 10 and 11.

a b

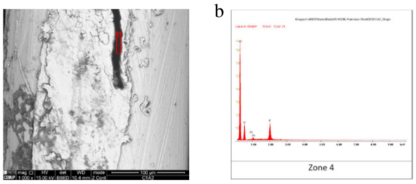

Fig. 9. Analysis of the dark substance on the trail, (a) in CN1A2, and (b) Micro-analysis corresponding to zone 4.

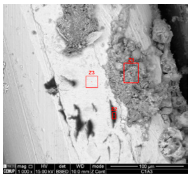

Fig. 10. Different colours and morphologies on CN1A3.

Whereas in zone 1 there is a clear presence of ZnO, which can be observed as aggregates over the Zn coating, zone 2 shows the presence of a dark substance rich in C as well as in Fig. 7 (a): New cable1, area 1, zone 2 (CN1A1Z2). However, at this time, C is accomplished by a non-negligible peak of P and some oxygen (O). The presence of C could be attributed to lubricants or polymers, however, P is commonly associated to lubricants so, the most probable is that the detected substance is a lubricant, see Fig. 8 (a), CN1A2Z1.

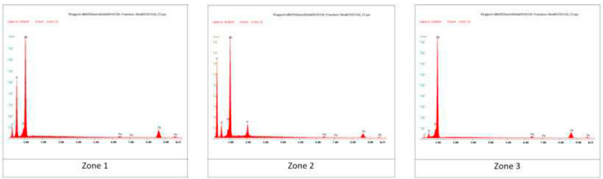

Fig. 11. Dark areas on CN1A3, zone 1, 2 and 3 of the Fig. 10.

From this analysis, some conclusions can be drawn:

- There is a presence of some strange substances over the wire coating of the cables, independently of the area considered.
- These substances appear randomly on the different areas. Micro-analysis performed allows conclude that these substances may come from the internal polymer tube used in this kind of harness or from lubricant used to protect the metallic cable. The first analysis leaves opened both hypotheses, because just C was detected. However, the second analysis led to observe that also P can be found on these substances. Hence, two situations can occur: the dark substances provide from different situations and products or they are heterogeneous enough to allow slight different compositions on different sites.
- Because dark substances and ZnO coexist in the same area, it can be stated that: the dark substances are not the cause of the ZnO formation and the dark substances do not inhibit the ZnO formation due to the fact that coexist Zn coating, ZnO and dark substances on the surface of each area.
- Taking into account the left side of the Fig. 8 (a), it can be observed some grooves, which may have as source one of the following mechanical processes: (a) Wire drawing: the grooves were made during the section reduction, being further covered by the Zn coating; (b) Matting process: the wires, already coated, were subjected to contact with the driving holes whose let the wires flow to the head responsible by the cable matting process. In this case, the coating would present more or less wear due to contact and friction. Fig. 8 (a) induces that this is not the case, being the grooves originated by the wire drawing process, because the coating seems to accomplish adequately the substrate (wire).
- Regarding also the Fig. 8 (a), even the Zn coating seems affected this is not the cause to generate ZnO.

Area 4 of the cable was also dissected, Fig. 12. Following the analyses previously presented, the micro-analyses and corresponding comments are presented in Fig. 13.

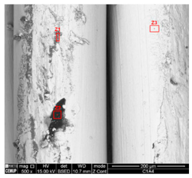

Fig. 12. Different colours and morphologies on CN1A4.

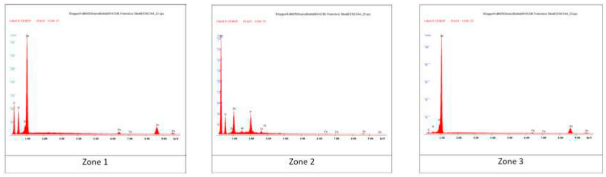

Fig. 13. Micro-analysis corresponding to zone 1, 2 and 3 of the Fig. 12.

Regarding the micro-analyses of Fig. 13, it can be stated that:

- The formation of ZnO in zone 1 is insipid yet.
- Zone 2 presents a wide range of elements, despite some of them in very small quantities. C is predominant and the P apears again. Other elements are present in a non-influent content but the presence of Chlorine (Cl) can be correlated to eventual material released by the internal polymer pipe and the Al can be related to the Zamak terminal sliding.
- In some situations, the presence of dark substances is more intense and continuous, as shown in the Fig. 14.

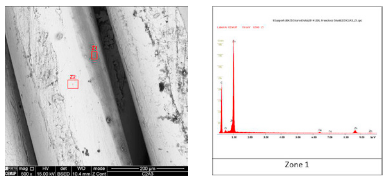

Fig. 14. Extended dark zone on CN2A3.

The dark larger area of the Fig. 14 seems to be a thin film of lubricant over the Zn coating, due to the composition (C-rich) and the modest peak, corresponding to a small thickness.

4.2. ZnO formation and development

The presence of ZnO is more intense on cables 1 and 3. The following sequence of images intends to show how the ZnO formation starts, how it develops and the final stage, with generalized formation of ZnO over the Zn coating. In Fig. 15 it can be seen the first stage of ZnO formation (cable 1, area 2).

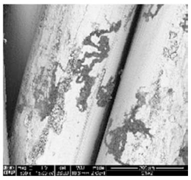

Fig. 15. Initial stage of the ZnO formation on CN1A2.

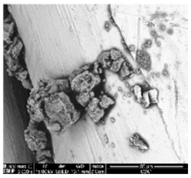

Fig. 16. Intermediary stage of the ZnO formation on CN2A1.

The development of the ZnO formations is performed by a notorious growing of the oxide particles, as can be seen in the Fig. 16, showing that they enlarge around themselves, after the initial stage. It can be noted that there is no enlargement of the area affected, but the particles present a larger size than in the case shown before, Fig. 15. Furthermore, in Fig. 16 it is possible to realize that ZnO particles are weakly bonded to the Zn coating. However, there are other cases where the ZnO is a mix between thin film formation and large agglomerates formation. This is the case depicted in Fig. 17, relative to cable 1, area 3. The same situation can be observed in Fig. 18 where there is almost generalized formation of ZnO. However, it can be seen that the evolution of the ZnO layer seems do not follow a well-established pattern, leaving some areas let off from the ZnO formation in this stage. Furthermore, it is notorious to observe that there are different stages of ZnO formation with grains from several sizes. This observation allows conclude that ZnO growth, as stated before, takes place around the ZnO particles themselves. The mechanism that feed this development is not known and cannot be revealed through this work. However, some partial conclusions can be drawn at this moment:

- No iron oxide was detected, showing that Zn coating protection is effective.
- The Zn layer thickness was not measured but the level of Fe detected under an electron beam potential of 15 kV through the Zn layer shows that the thickness of this layer is thick.
- The ZnO presents a first stage of nucleation, followed by continuous growth around the small crystal initially nucleated but, the larger are the ZnO particles, the weaker seems the connection between ZnO layer and wire coating.

Fig. 18 depicts the final stage of the ZnO formation, showing how the wires that constitute a cable stay full covered by ZnO film and aggregates. The areas where the ZnO nucleation took place firstly, developed bigger aggregates (red circles/ovals). Other areas such as highlighted with yellow cicles/oval show the absence of ZnO formation. This reveals that the surface potential for ZnO formation is not the same along the whole wire surface. The interval between wires seems to be a preferred local for ZnO large particles growth or, on the other hand, these particles are protected from the external surface of the cable, keeping better the ZnO particles formed.

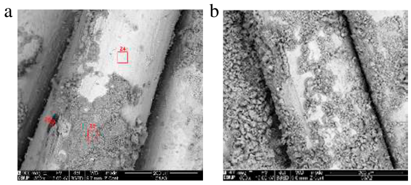

Fig. 17. (a) intermediary; (b) generalized stage of the ZnO formation, CN1A3 and CN3A2, respectively.

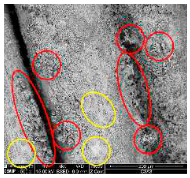

Fig. 18. Generalized stage of the ZnO formation, CN3A3.

4.3. Analyzing the presence of C and other elements along the wires

The presence of some stains reveals the persistent presence of C. However, sometimes, the C appears accomplished by phosphorus and other elements in very small contents. A deeper analysis was performed in order to realize where the C appears isolated or accomplished. Regarding the spectra in Fig. 19, it can be seen that P is not detectable on sample providing from area 1, but it is common in all the remaining samples.

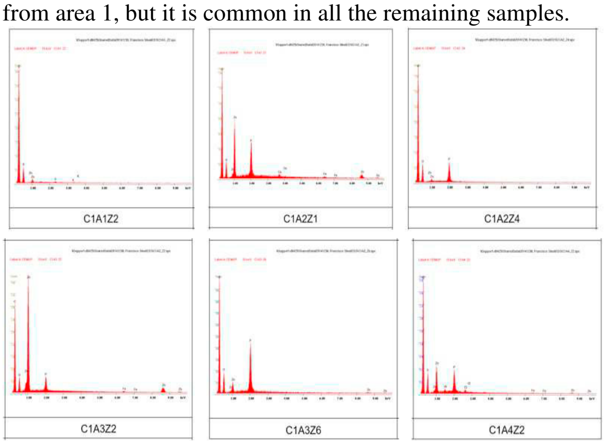

Fig. 19. Analyses of different areas containing C providing from the cable 1.

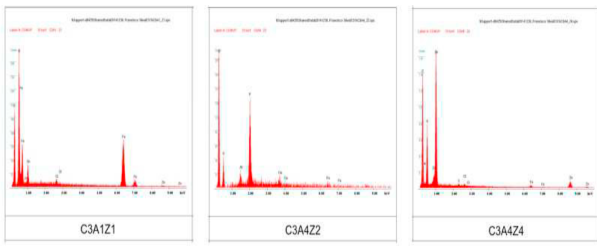

Fig. 20. Analyses of different areas containing C providing from the cable 3.

Fig. 20 depicts the spectra corresponding to areas 1 and 4 of the cable 3, because areas 2 and 3 do not present particles rich in C. These spectra allow realize that there are different kinds of dark particles (stains) in the same area, some of them containing P, whereas others contain just C or C and other elements in very small contents, such as Ca and/or Cl. Both in cable 1 and 3, area 1 does not present any P content allowing conclude that area 1 seems to be preserved from P content, whereas the other areas seem to contain different kinds of dark particles, providing from the internal polymer tube or resting from the lubricant used during the cable production.

4.4. ZnO powder extracted

In samples like in Fig. 19, and as referred previously, the ZnO aggregates give off easily. Thus, some wires were passed slightly over a C tape, leaving the ZnO on the tape. The overall aspect of the tape after this operation can be seen in Fig. 21, showing that the dispersion of the ZnO particles is high, having many small particles but there are also large ZnO particles over 40 µm size. It is believed that the dimension of the particles is directly related to the developing/growing time.

4.5. Internal polymer pipe

To realize a possible effect of the internal polymer tube interaction with the cable, a portion of this tube was cut and analyzed, Fig. 22. There are some embedded particles in the inner side of the tube, which show a lighter colour. In order to confirm what kind of particles are embedded, its composition was investigated by micro-analysis. As expected, the particles are essentially ZnO, whereas the tube wall contains almost exclusively C, and the initial hypothesis that polymer could contain P or another different content can be discarded.

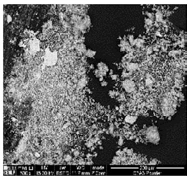

Fig. 21. General view of the ZnO powder left on the C tape.

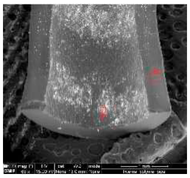

Fig. 22. General view of the internal polymer tube.

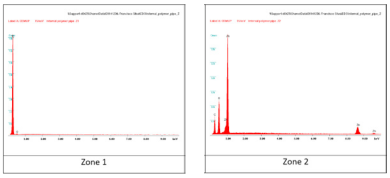

Fig. 23. Micro-analysis of the internal polymer pipe.

4.6. EPMA Analysis

In order to identify possible foreign contents between the steel wire and the Zn coating, Microanalysis by Electronic Probe (EPMA) was performed. The cable area analysed allows obtain a generic spectrum, which contains the main information about the elements present on the area under analysis. Regarding Fig. 24, it is possible to realize that Zn and Oxigen (O) are usually together but, where the intensity of O is more pronounced, the intensity of Zn is lower. Thus, O takes the Zn place. Furthermore, the Sulfur (S) presence is notorious and its presence is clearly related to O incidence. The presence of Cl is quite reduced, but not negligible, due to its effect in ZnO formation, being finely dispersed into the coating/substrate interface. In order to investigate if these elements are in the external face of the coating or in the interface coating/substrate, new analyses were carried out crossing the coating from the external wax used on the sample mounting process to the steel substrate. Four channels were used in order to divide the intensity and area where each element is present, considering the left side of the graphics as the external wax and the right side as the steel substrate, Fig. 25. Each channel was linked to a specific element: cyan to the O, blue to the Cl, green to the S and red to the Zn. The Cl and O are clearly presented on the external wax. After that, the Zn becomes visible and the S, Cl and O become newly visible in the interface between coating and substrate. This allows to conclude, under the coating, there are harmful products capable of triggering the ZnO nucleation reaction.

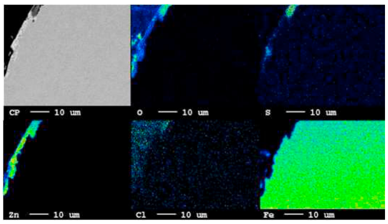

Fig. 24. Spectra obtained for each element detected.

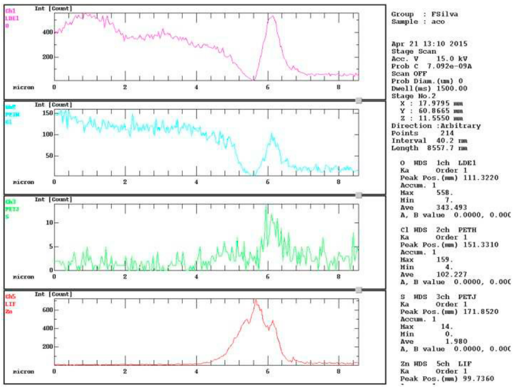

Fig. 25. EPMA analyses from the external to the steel substrate and isolating the intensity and area where each element.

4.7. Discussion about the results

The results show that the wires used on the metallic cable formation are provided with an affordable Zn coating. The presence of ZnO was felt in all the cables analyzed. Regarding the four areas analyzed of cables without working yet, it is strange that areas 2 and 3 are the most affected by the ZnO formation, whereas areas 1 and 4 are almost free of ZnO formation. The ZnO formation is gradual. Initially, there is a nucleation process, followed by the particles growth and dissemination of new areas of nucleation and strong dissemination on the surface. The size of the ZnO particles is time-dependent. Some strange substances were detected on the Zn coating. Micro-analyses performed allow determine that there are differences among them. The presence of P, in a first approach, indicates that would be some kind of lubricant. However, there are samples with and without the presence of P, which avoid to be absolutely sure about this situation. Some cracks were also detected on the Zn coating surface. No correlation was found between cracks, wire deformation or strange substances and the ZnO formation. The adhesion of the ZnO particles to the Zn coating is poor, leaving the surface under white powder form. The presence of P on the dark particles is 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 or not, 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 reveals a dangerous situation regarding the nucleation of ZnO, as referred in the literature [26,27]. Thus, the steel wire cleaning conditions played a crucial role in the ZnO formation on the surface of the Zn-coated steel wire.

5. Conclusions

This work presented an in-depth study of two series of steel cables, freshly-manufactured and with three weeks of manufacture, aimed at analyzing the formation of ZnO in the cables. The results showed that the main problem cause is the lack of cleaning of the cables, before zinc electro-plating. There are no bibliographic sources to support that the elements found are catalysts par excellence for ZnO, but some references were found (cited throughout the report), which mention that Cl and P, with the help of a little heat or even at room temperature, promote the formation of ZnO, which then proliferates on the surface of the zinc layer. It was proven the existence of foreign elements, Cl and S, at the interface between steel and Zn, which can induce the beginning of the ZnO nucleation. EPMA analyzes detected harmful elements, such as S and Cl, located at the coating/substrate interface. This allowed to conclude that these elements are in the steel wire before the Zn coating process, which was caused by the poor steel wire storage procedure and is in the origin of ZnO nucleation and growth.

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