Surface Defects and Corrosions Developed on Copper Clad Aluminium Wires Investigated by Scanning Electron Microscope Analysis and X-Ray Mappings

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ABSTRACT

Copper-clad aluminium (CCA) is a bi-metal electrical conductor consisting of an outer sleeve of copper that is metallurgically bonded to a solid aluminium core. In the market, CCA has started to replace copper wire for several decades because of its low cost and light weight. The demand for CCA wire has increased parallel to industrial and technological development in many sectors over the last decades. The structural surface defects and corrosion affect the quality of CCA wires. Corrosion deterioration can be detected visually and chemically; hence it was subjected to imaging and microchemical mapping. Textural defects such as significant abrasion grooves, tensional cracks, delamination of copper, pit corrosion, fatigue failure have been found. Silicon Drift Detector-Electron Dispersive Spectrometer-Scanning Electron Microscope (SDD-EDS-SEM) X-Ray mappings and chemical analysis exhibit that the corrosion has happened along with the textural defects. The oxidation is widely observed, and some electrolyte-related chemicals have been detected as deposited substances. The corrosion types have also been classified as galvanic corrosion, pitting corrosion. It is recommended to inspect the products with SEM studies before or during trade, as structural defects formed during manufacturing facilitate corrosion.

Keywords: CCA wires; cracks; delamination; pit corrosion; galvanic corrosion; X-Ray mapping.

Defectos superficiales y corrosión desarrollada en alambres de aluminio revestidos con cobre, estudiados mediante análisis por Microscopía Electrónica de Barrido y mapas de Rayos X

RESUMEN

El aluminio revestido con cobre (CCA, por sus siglas en inglés) es un conductor eléctrico bimetálico que consta de una funda exterior de cobre unida metalúrgicamente a un núcleo de aluminio sólido. En el mercado, el CCA ha comenzado a reemplazar al alambre de cobre desde hace varias décadas debido a su bajo costo y peso ligero. La demanda de alambre CCA ha aumentado paralelamente junto al desarrollo industrial y tecnológico en muchos sectores durante las últimas décadas. Los defectos superficiales estructurales y la corrosión afectan la calidad de los cables CCA. El deterioro por corrosión se puede detectar visual y químicamente; es por ello que, en la presente investigación, los cables CCA se examinaron mediante imágenes y mapeo microquímico. Como resultado, se encontraron defectos texturales tales como ranuras significativas por abrasión, grietas por tensión, deslaminación del cobre, corrosión por picaduras y fallas por fatiga. Las técnicas de Detector de Deriva de Silicio-Espectrometría de Dispersión de Electrones-Microscopía Electrónica de Barrido (referidas como SDD-EDS-SEM, por sus siglas en inlgés), así como los mapeos de Rayos X y el análisis químico mostraron que la corrosión se ha producido junto con los defectos de textura. La oxidación se observa ampliamente y se han detectado algunos productos químicos relacionados con electrolitos como sustancias despositadas. Los tipos de corrosión también se clasificaron como corrosión galvánica y corrosión por picaduras. Se recomienda inspeccionar los productos con estudios mediante Microscopía Electrónica de Barrido antes o durante la comercialización, ya que los defectos estructurales formados durante la fabricación facilitan la corrosión.

Palabras clave: Alambres de CCA, grietas, deslaminación, corrosión picadura, corrosión galvánica, mapeo de Rayos X.

INTRODUCTION

Corrosion is a process that causes deterioration of the material and its properties as a result of a chemical or electrochemical reaction between a metal or alloy material and its environment [1], affecting all metals by physical, chemical, electrochemical processes [2]. There are several types of corrosion: general corrosion, galvanic corrosion, pitting corrosion, intergranular corrosion, and atmospheric corrosion [3]. Palit [4] explains that galvanic corrosion occurs when two dissimilar metals in physical or electrical contact with each other are immersed in a common electrolyte or exposed to an electrolyte of different concentrations. The metals that make up the bimetal exhibit the behavior of the anode and the cathode, and the anode corrodes more slowly and the cathode faster [3, 4]. Conditions such as temperature, humidity, and salinity of the environment, metal types, dimensions are seen as parameters that affect galvanic corrosion [4]. Metals and alloys have different electrode potentials [3]. Especially in the alloys of metals such as aluminium and copper, there is an electrical potential difference between both metals and represent a bimetallic galvanic corrosion potential in the case of an electrolytic liquid in the environment [3]. As a result, the metal or alloy's physical, chemical, mechanical, or electrical properties undergo undesirable changes. Aluminium metal is metalurgically coated by the copper to obtain CCA wire. CCA wires have high electrical and thermal conductivity, are less dense than copper and are economically advantageous [5]. In the market, CCA is gaining more and more attention, and it is widely used in electric and electronic fields due to its lower weight and cost than pure Cu, and CCA has started to replace copper wire for several decades [6, 7]. The World's copper production reaches 20 million tons [8] and constitutes a market of around 10 Billion USD yearly (about 5000 USD/tonne). In order to use fewer copper reserves in nature, copper-clad aluminium wires in shielding cables are commonly replacing Cu wires [9]. In addition to Cu and Al produced by mining activities, the amount recovered from waste copper-clad aluminium (CCA) scraps has reached significant amounts [10].The demand for CCA has increased parallel to industrial and technological development in many sectors over the last decades. Those wires find some specific applications in high-frequency signal or power or electromagnetic transmission sectors, specifically in the production of kitchen utensils, automobile industry, aerospace, shipbuilding, biomedical devices, heat exchangers, telecommunications, headphone, internet cables, etc [11]. CCA can be broken due to rapid corrosion when exposed to air or grounded, preventing the quality of the transmission of the signals, electricity, sound, or other transmitted elements [9]. Zhang et al. [9] also defined three corrosion mechanisms in the copper clad aluminium wire in the terminal box of substation: chemical corrosion of acidic atmosphere, corrosion of primary battery and corrosion of electrolytic pool. Corrosion deterioration of bimetals can be detected both visually and chemically; hence they were subjected to imaging and microchemical mapping. In this paper, SEM researches have been reported on problematic CCA wires. The principal aim of the work is to demonstrate the mechanical deformations and electrochemical corrosions on the wire and the necessity of technical investigation of CCA wires by Electron Microscope Studies, X-Ray Maps, and Chemical analysis prior to trade procedures of this very demanding product in technology.

MATERIALS AND METHODS

SEM analysis was carried out on two different CCA cables with 0.18, 0.24 and 0.25 mm diameters. Since the samples are already bi-metals, no surface coating is required for SEM analysis.To dehumidify samples, they were placed in the oven at 25°C for 2 hours. Then, CCA wire samples were emplaced on carbon stubs. Zeiss EVO-50 with Bruker-Axs XFlash 3001 SDD-EDX installed in Hacettepe University, Department of Geological Engineering, Ankara, Turkey has been used and operated under 15 kV accelerating voltage, 15 nA probe current. First of all, the samples have been visualized in BSE mode. Then, X-Ray chemical maps have been generated with at least 5 minutes of scanning. Line scan profiles along the zones of the corrosion have been applied. Qualitative chemical analyses have also been performed on the wire and the chemical substances.

RESULTS

Textural discontinuities and deformations.

Figure 1 shows images obtained by SEM of the textural discontinuities, and corrosion in the CCA wires.

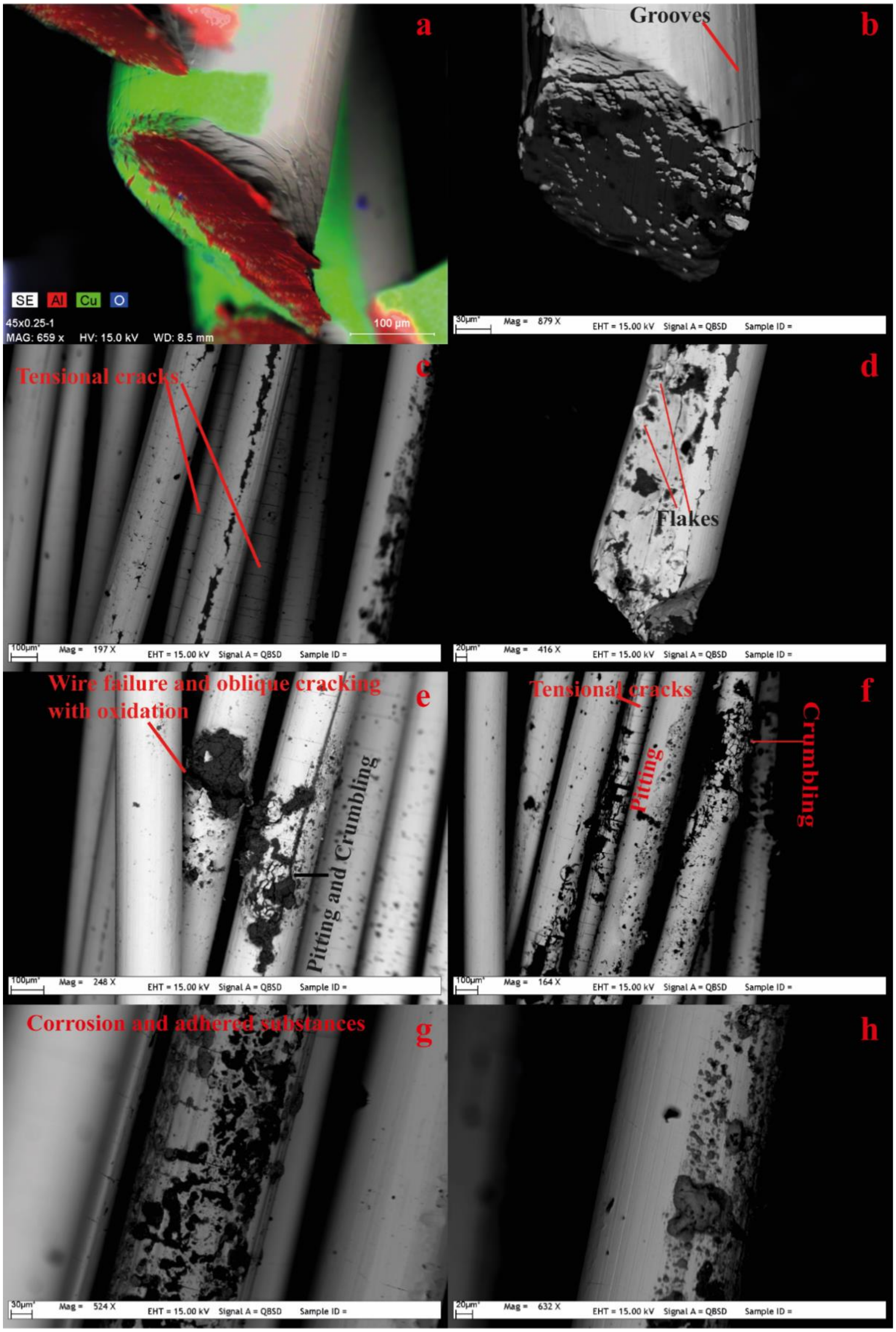

Fig. 1. Visualization of textural discontinuities, deformations, chemical substances, and corrosions in CCA by SEM study: Chemical mapping of the non-corroded section of the Copper Clad Aluminium wire; b) CCA wire with grooves; c) Tensional cracks together with other type surface defects; d) Delamination of copper in the form of flakes and tearings; e) Oblique cracking and wire failure and crumbling around the pits; f) Pits developed on tensional cracks and the grooves, and its progression is expressed by the crumbling; g) Blacks spots as the pits and adhered substances as the products of corrosion; h) The exposed side of CCA wire to electrolytic liquid expressed with the substances.

CCA wire has been visualized in figure 1a. The gray segments are not colored because they remain in the shadow segment of the detector. Color selection is entirely operator preference, and there is no genetic representation. Concentric deformation in the SE image and on the chemical mapping image (figure 1a and 1b) occurred during sample preparation with scissors. Some wires represent very regular, and continuous grooves tracked along the wire (figure 1b). These grooves create a corrugated surface that continues along the cable. In addition, very fine cracks as another textural deformation perpendicular to the long axis of wires have also developed on some wires (figure 1c, 1e, and 1f). The cracks are not separated from each other yet and are observed as many parallel cracks.

The outer layer made of copper peels off in some places corresponding to the delamination of copper in the form of flakes and tearings. The cable delaminates (flake) in areas where dark-colored substances are dense (figure 1d). They are constantly parallel to each other. Some oblique cracks, wire ruptures, and crumbling have been occasionally observed around the pits (figure 1e).

Some pits are also present on deformed wires (figure 1e, 1f, and 1h). The number of pits is greatly increased in areas with deformation and textural discontinuities. Besides, some crumbled deformations with random cracking have also been observed which may be related to pit corrosion (figure 1e, and 1f).

The substances have adhered to the grooves and developed over the fractures. (figure 1g, and 1h). A general impression that the corrosion has mainly happened following the groove

Chemical Investigation.

Various methods such as X-Ray mappings, X-Ray line scan analysis, point analysis have been helpful to demonstrate corrosion products. A-line scan of X-Ray on the predefined trajectory is presented in figure 2.

The change of chemical composition is tracked along the line shown at the bottom of the graph. Accordingly, while the Cu concentration at the cable edge reaches 80%, the Al content in the cable's center approaches 100%.

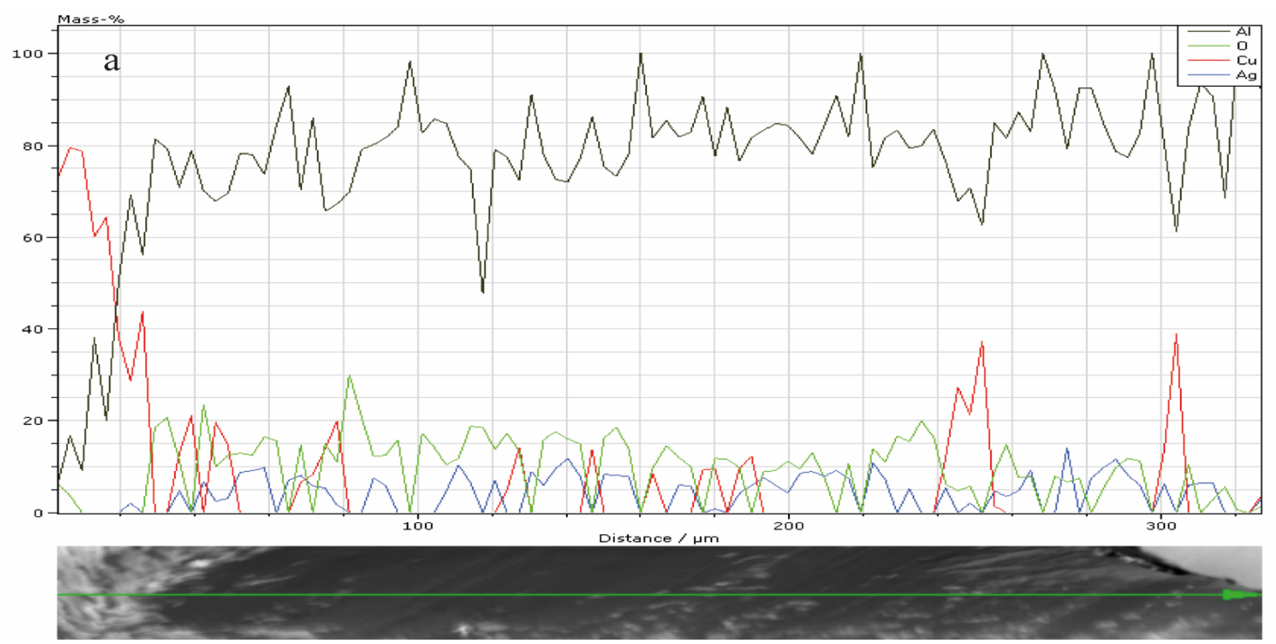

Fig. 2a. Line scan and chemistry of CCA interior (same sample as illustrated on figure 1a). Oxidation of copper is well expressed. Al appears on the black spots and other chemical substances are present in the dark area.

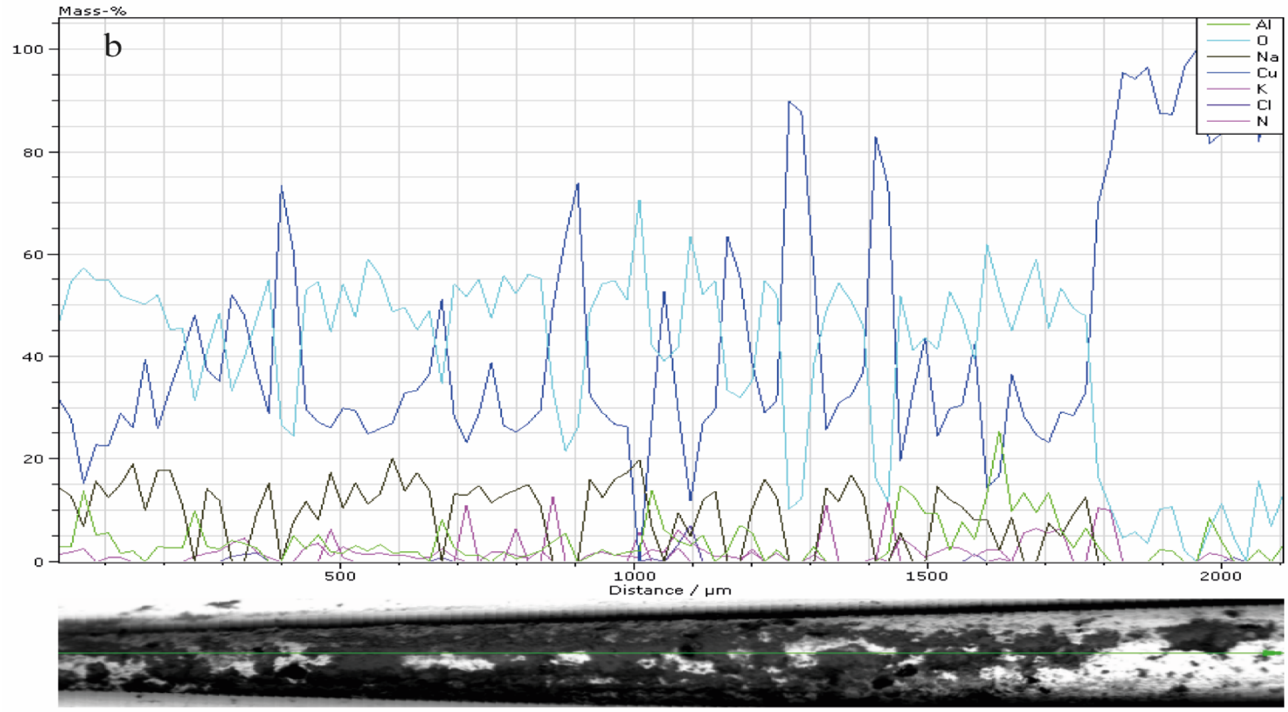

Fig. 2b. Line scan and chemistry of a corroded wire. Oxidation of copper is well expressed. Al appears on the black spots and other chemical substances are present in the dark area.

Besides, a qualitative chemical analysis profile, presented in figure 2a, exhibits that the non-corroded outer part of the wire consists mainly of Cu as it is expected. No other elements related to galvanic corrosion were found.

Numerous black spots on the wires appear on the general view of CCA (figure 1). Highly developed corrosion is also visualized in figure 3a and 3b. The observed dark zones correspond to the areas where the corrosion occurs and progresses (figure 2b; figure 3a and 3b).

The qualitative analyses of the black spots are presented in figure 3c and 3d. They show that besides copper and aluminium, other elements such as Na, Si, K, and Cl give some peaks together with oxygen.

The high level of oxidation has also developed. The oxidation is dominant, but also exist the salt chemistry (figure 3c and 3d). The presence of many different elements besides pure metal Cu and Al indicates that the general structure is chemically degraded.

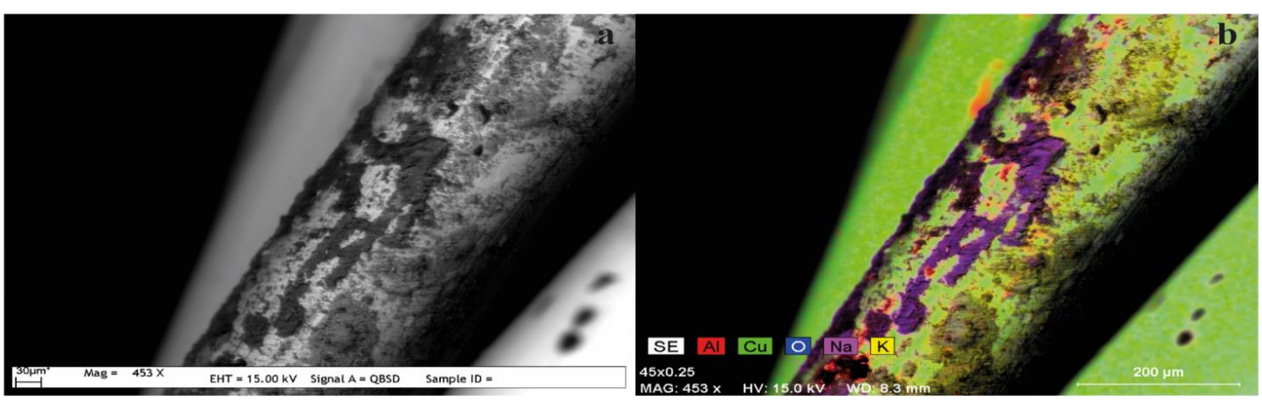

Fig. 3. a) Backscatter image of a highly corroded CCA wire with chemical substances; b) Chemical mapping of the same image.

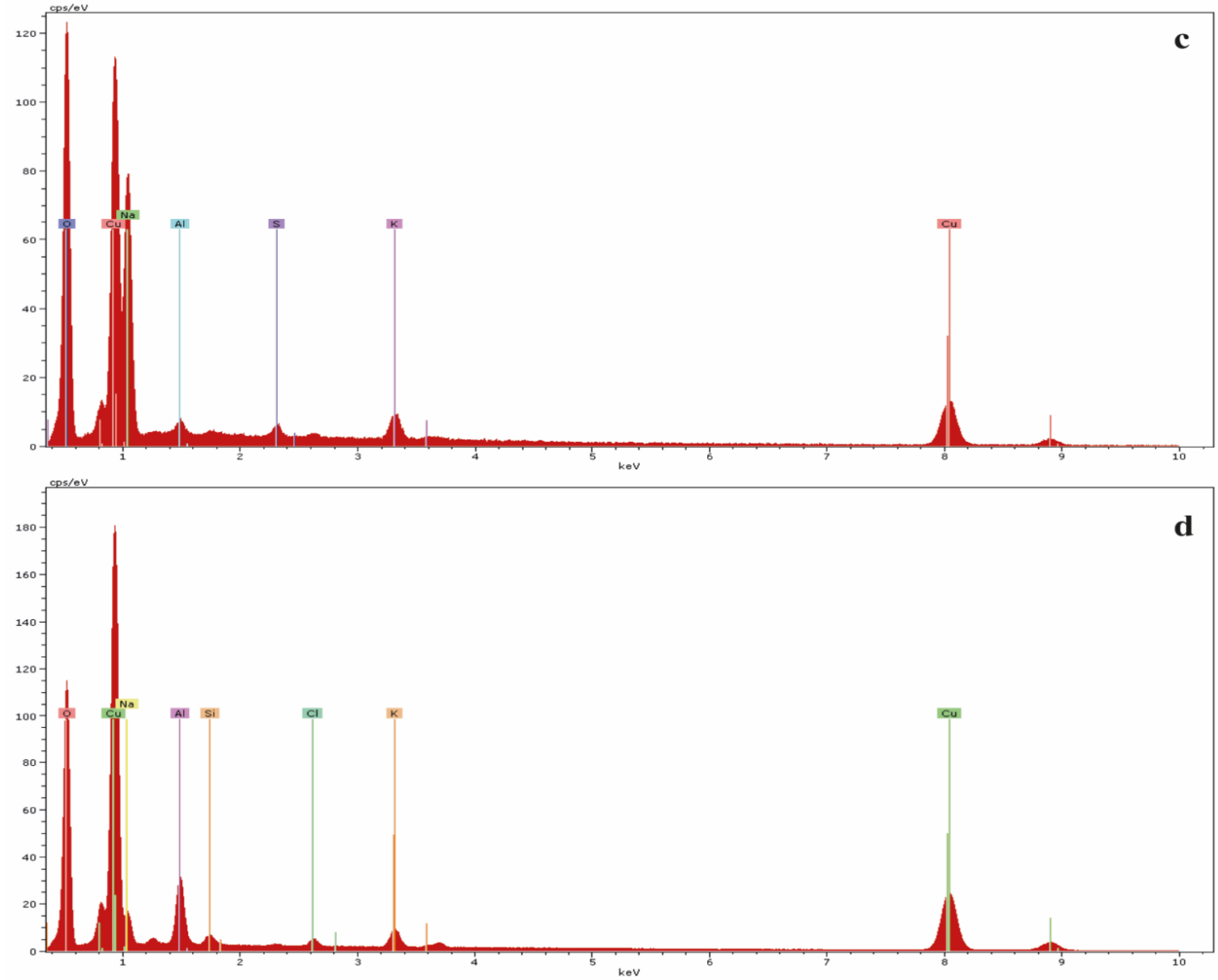

Fig. 3. c) Chemical analysis of the same cable section with line scanning; d) Qualitative analysis of the corrosion-free outer part of the wire.

Corrosion sometimes covers the whole cable (figure 3). Sulphurous compounds have also been detected in figure 3c on those completely corroded wires. Obviously, the corrosion and chemical substances have been emplaced along the grooves, fissures, and cracks.

DISCUSSION

Pournazari et al. [12], treated the Al-Cu alloy with artificial seawater and examined its corrosion with the FIB-SEM (Focused Ion Beam-SEM). Study and stated that the pitting and intergranular corrosion developed. The service performance and the lifetime of CCA are controlled by its quality which is a function of the material characteristics, surface properties, manufacturing conditions.

The micro defects in the wire surface may lead to excessive wear, crack initiation and propagation, and inadequate weldability [13]. Bernabeu et al [14] have classified into categories the surface structures of fine metallic wires according to their shapes. They have provided a terminology of the surface structure as surface scrap, spills, flakes, holes, inclusions, pores, protuberances, die lines, drawing grooves, ridges, chatter marks, flattened areas, scratches, notches. They also proposed possible causes of these surface defects. While examining corrosion monitoring techniques, Cragnolino [1] states that EDS-SEM is especially used for microscopic imaging of the surface structure and elemental identification of the surface species, among other inspection techniques such as XRD, FTIR, Raman, ICP-MS AAS. SEM studies allowed to determine corrosion and deformations of the examined CCA wires. Accordingly, the presence of surface discontinuities such as abrasion grooves, tensional cracks (that are perpendicular to the long axis and parallel to each other), delamination of copper, pit corrosion, fatigue failures were detected. Grooves are developed in the form of wear tracks caused by drawing die. The wire drawing process creates the surface flaws [15]. So, they were formed during cable production. On the other hand, since those very fine cracks are not present in each of the braided wires, the tension cracks are also thought to occur during production. It is observed that the corrosion has developed on only one side of the cables (figure 1h), indicating the exposed surface to the electrolytic solution. Apart from Cu and Al, especially oxidized copper, NaCl, and sulphureous substances are encountered on CCA. These chemicals show that the wires were in contact with an electrolytic liquid, causing galvanic corrosion. Otherwise, it is not possible to react between Cu and Al in the case of Cathode and Anode. The most crucial point is that CCA is insulated against all kinds of corrosion if the required conditions are met. Properly manufactured CCA cables should not be expected to be corroded in dry, well-insulated environments. So, the protection against corrosion starts with the manufacturing process. This work shows that corrosion has been mainly developed on structural defects like die lines and drawing grooves, and the failed part of the cables. So, the mechanical defects are affected by the humidity (causing oxidation) and Cl and S bearing electrolytic substances. As there is no iron within the copper, it does not rust, but the reaction between the copper and oxygen can happen and copper may be oxidized. The most expected corrosion type that can be developed on CCA is galvanic corrosion, namely bi-metal corrosion. This type of corrosion is commonly seen when two metals are in electrical contact while moisture (or any conducting corrosive electrolyte) is present. The result is enhanced and aggressive corrosion of one metal at the joint area together with partial or complete protection of the other metal [13]. The presence of an electrolyte, deformed wires, and humidity forms the worst conditions to keep CCA intact, as it is the case that has happened and targetted in this paper.

CONCLUSION

CCA wire trade in the world is increasing day by day due to its technical and commercial advantages. It has been proved by SEM analysis that the manufacturing defects make CCA wires prone to corrosion. The die lines, grooves, or tensional fractures formed during CCA manufacturing predispose a suitable environment for the corrosion. This article has revealed the corrosion of CCA wire and its reasons.

It is concluded that the surface defects of the CCA wire due to production facilitate the corrosion phenomenon under the influence of galvanic solutions. In other words, the quality of the CCA wire, and therefore its service life, is a function of the production quality and the production-dependent surface defects become vulnerable to corrosion agents during use.

CCA, widely used in consumer electronics cables invisible to the naked eye, will inevitably affect the product quality directly. The consumer can't see these defects while purchasing the electronic or technological product. For this reason, it is necessary to integrate electron microscopy studies into commercial activities, which are expressed in billions of dollars through methods such as certification, etc. It is recommended to inspect the products with SEM studies before or during trade, as structural defects that occur during manufacturing facilitate corrosion.

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CONFLICT OF INTEREST

The author declares no conflict of interest.

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