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Evaluation of materials used for coatings of electrical connectors used in the electrical harness of passengers cars

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Automotive electrical connectors are the essential components of a wiring harness. They are typically made of copper, which has excellent electrical conductivity. Due to the limited corrosion resistance of pure copper, connectors are often coated with other metals. In this paper, the qualities of coatings made of gold and tin are investigated and compared. The samples were examined by a metallographic microscope and scanning electron microscope (SEM). The examination revealed uneven thickness, delamination of the coatings, and issues with the preparation of the core material for coating. Numerous burrs and irregularities were observed. Selected samples were examined in salt solution to test their corrosion resistance. Even though gold is a noble metal and its electrochemical potential is higher, the tin coating was more resistant to corrosion.

Key words: *automotive electrical connectors, metal coatings, anodic protection, cathodic protection, corrosion*

1. Introduction

Almost every part of a car is supported by electronics, from very obvious examples like radio to brake assist. To make electronics work, the automotive wiring harness is essential. Its main components are circuits, housing, connectors, wrapping material and additional components [1]. A connector is a piece which enables an easy way to connect wires or whole circuits. It provides good electrical conductivity and a stable connection between components [2]. With the development of technology, the number of connectors is increasing, which can range from several hundred to several thousand in one vehicle [3]. As part of the wiring harness, connectors must be characterized by very good electrical conductivity. The conditions in which car connectors work are related not only to weather conditions and season, but also to temperature changes and vibrations caused by the engine operation [4]. Vibration contributes to faster degradation of components and can cause failure [5]. According to Abdi and Benjemâa, the operating temperature of connectors ranges from –40°C to 80–120°C, depending on the location of the connector. The vibration frequency ranges from 10 to 2000 Hz [6]. The operating environmental conditions of the connectors are conducive to the occurrence of corrosion, which promotes faster wear of the components [7]. For this reason, the materials from which the connectors are made should be resistant to high humidity, high and low temperatures and the presence of acid oxides in the air, including nitrogen oxides and sulfur oxides [3].

Automotive connectors are typically made of copper, due to the excellent electrical conductivity of this metal. There is one primary disadvantage of choosing copper as a connector material. Its resistance to harsh environment is not particularly good in comparison to other conducting metals like silver or gold [2]. Noble metals are unfortunately much more expensive than copper, due to limited resources and increasing demand for them [8], and are not used as a material for manufacturing automotive wiring. To preserve electrical properties and achieve anticorrosive abilities, connectors are coated with different metals. Gold, silver and tin are the most commonly used [2].

Noble metals, such as gold and silver, can be used to produce cathodic coatings, which provide anodic protection. These metals have higher electrochemical potential compared to copper and act as a cathode, which means that they are resistant to environmental conditions. They create a barrier between copper and the environment, providing protection against corrosion. Apart from the high price of noble metals, there is one disadvantage of such coatings. The coating must cover a core material evenly to protect it. Every discontinuity can result in a very deep corrosion pit, because copper, as a metal with lower electrochemical potential than gold or silver, will be exposed to environmental conditions. It is important to notice, that copper without any protection would corrode at a slower rate than copper coated with damaged cathodic coating [9].

Tin is a metal with lower electrochemical potential than copper, hence it is used as an anodic coating, which provides cathodic protection. Sometimes such protection is called sacrificial protection, because the coating acts as an anode, which corrodes instead of the core material. This method provides protection of core material even when the coating is not continuous [9, 10]. Another positive aspect of anodic coatings is the lower price compared to coatings made of noble metals.

In this paper, we examine and compare the properties of anodic and cathodic coatings on automotive connectors.

2. Methodology

2.1. Microscopy

Five different samples of automotive connectors were examined. According to the manufacturer, three of them were coated with tin and the other two had coatings made of gold. Energy-Dispersive X-ray Spectroscopy (EDX) was performed to verify the manufacturer's claims and detect possible injections of different metals. Two measurement points were chosen for each sample, one for coating material and one for core material. Connectors were examined by microscopy (Nikon Eclipse MA200) and Scanning Electron Microscopy (FEI Phenom G2 Pro) to determine coatings quality and thickness.

2.2. Roughness and corrosion tests

Two samples, one coated with tin and one coated with gold, were selected for the topography examination. The roughness of each connector was measured according to PN-87/M-04256/02. The topography picture was prepared via SEM. The corrosion resistance of these two samples was examined. Two tests, open circuit potential and potentiodynamic polarization, were performed on an automated measurements site (Fig. 1), which consisted of a vessel, a potentiostat ATLAS 0531 – ELECTROCHEMICAL UNIT&IMPEDANCE ANALYSER, computer controller and three electrodes: calomel electrode as a reference electrode, platinum electrode as a counter electrode and connector as a working electrode. The open-circuit test in 3% sodium chloride solution lasted 40 minutes and took place at room temperature. This test was performed in order to find a resting potential of a system, which is necessary for the second test. During potentiodynamic polarization measurement, potentiodynamic curves were registered and a pitting susceptibility of material was evaluated.

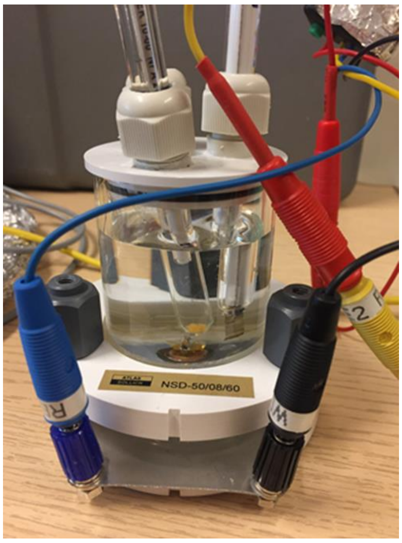

Fig. 1. The measurement site for corrosion tests

3. Results

3.1. EDX analysis

EDX analysis revealed that one of five samples did not match the manufacturer's specification and one of the gold coatings was actually made of silver (Table 1). The core material in each sample was copper, with a small amount of metal of a coating in sample number 1. EDX analysis detected copper injections in all coatings (Table 2). Coating made of gold contained the smallest amount of copper – 2.06%. Tin coatings contained more copper injections. It was especially noticeable in sample number 5, which consisted of 52.77% copper. Sample number 1 was excluded from further analysis due to inconsistency between specification and analysis results.

Table 1. Coating materials according to specification and EDX analysis

Sample	Specification	EDX results
1	Au	Ag
2	Au	Au
3	Sn	Sn
4	Sn	Sn
5	Sn	Sn

Table 2. EDX analysis results

Sample	Coating	Core
1	Ag – 84.17% Cu – 15.83%	Ag – 1.01% Cu – 98.99%
2	Au – 97.94% Cu – 2.06%	Cu – 100%
3	Sn – 73.21% Cu – 26.79%	Cu – 100%
4	Sn – 82.70% Cu – 17.30%	Cu – 100%
5	Sn – 47.23% Cu – 52.77%	Cu – 100%

3.2. Structure and thickness

Four connectors were examined by regular microscopy with magnification from 100× to 500× in order to briefly evaluate the quality of coatings. In some cases, magnification was not sufficient to notice and examine very thin coatings. SEM examination was performed for more accurate observation using magnification 10000×. The coating on sample number 2, which was the only connector coated with gold, was continuous, without any fractures, or delamination, but the thickness was uneven (Fig. 2 and Fig. 3). The gold coating covered the connector partially, only at the point of contact. The core material was prepared correctly before coating deposition. It was even, with no burrs. Connector number 3 was the only one with visible discontinuity of a coating (Fig. 4 and Fig. 5). Delamination was observed within a coating and between coating and core material. The thickness of the coating varied in different areas. Core material preparation was performed poorly, as there was noticeable roughness of the surface and numerous burrs. Sample number 4 had continuous coating (Fig. 6 and Fig. 7). The thickness of the coating was generally even. There were thinner and thicker areas, but not many. Some injections and delamination of the coating were noticed. The core material surface was not smooth, but there were no huge burrs. Coating number 5 was of poor quality (Fig. 8 and Fig. 9). Delamination between coating and core material, delamination within the coating and numerous injections were detected. The coating was continuous but its thickness was uneven. The core material surface was not prepared correctly before coating. It was uneven with visible burrs.

Coating thickness was measured with SEM. For each sample minimum and maximum thickness were measured. Depending on the material used, typical coatings on connectors range in thickness from 0.1 to 30 µm [11]. The average thickness of all coatings was calculated based on eight measurements. Values of all coatings thickness were presented in Table 3. The only gold coating was the thinnest of all samples, with an average thickness of 0.91 µm. Tin coatings were visibly thicker. Sample number 4 had the thickest coating – 6.61 µm. Significant differences between minimum and maximum thickness were noticed for each sample. According to Meyyappan et al. [12], typical gold coating thickness on connectors ranges from 400 to 800 nm, while the coating of sample 2 exhibited an average thickness of 910 nm. The highest coating thickness was 1420 nm, while in some areas it was only 170 nm. In the publication by Monlevade et al., the thickness of the gold coating ranged from 0.8 to 1.35 µm [13]. The biggest value of maximum thickness was registered for sample number 4 – 8.57 µm. It is worth noting that Yuan et al. [14] showed an inverse relationship between tin coating thickness and connector resistance.

Table 3. Coating thickness

Sample	Material	Coating thickness		Average thickness [µm]
		Minimum [µm]	Maximum [µm]	
2	Au	0.17	1.42	0.91
3	Sn	1.60	4.34	2.71
4	Sn	4.85	8.57	6.61
5	Sn	2.57	8.19	4.98

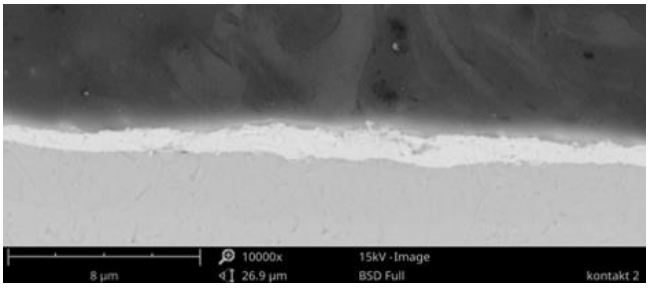

Fig. 2. Scanning microscope image of sample number 2 – a continuous, well-made coating of variable thickness, a substrate for coating application well prepared

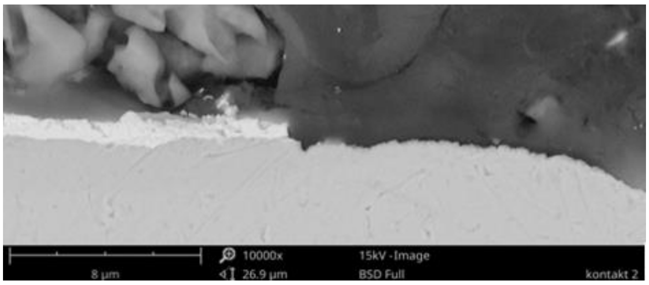

Fig. 3. Scanning microscope image of sample number 2 – the place of the beginning of coating application – visible layer break

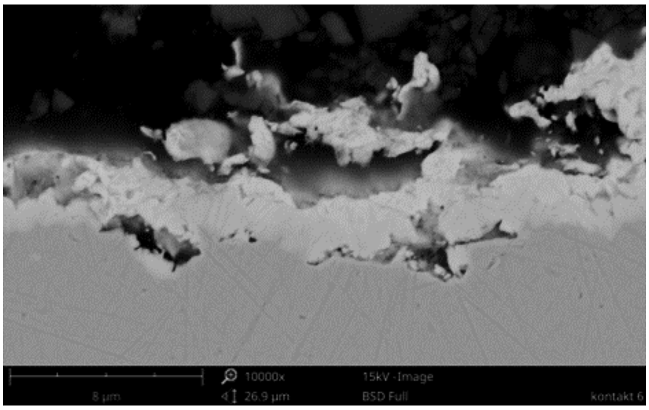

Fig. 4. Scanning microscope image of sample number 3 – a continuous layer, uneven coating thickness, visible delamination

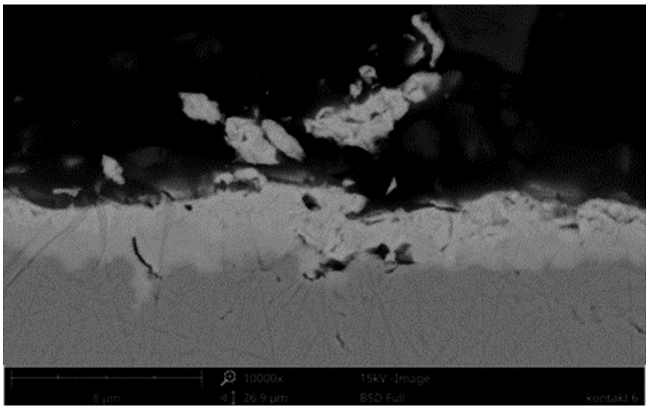

Fig. 5. Scanning microscope image of sample number 3 – differences in coating thickness with continuity, visible delamination at the border of coating and core material

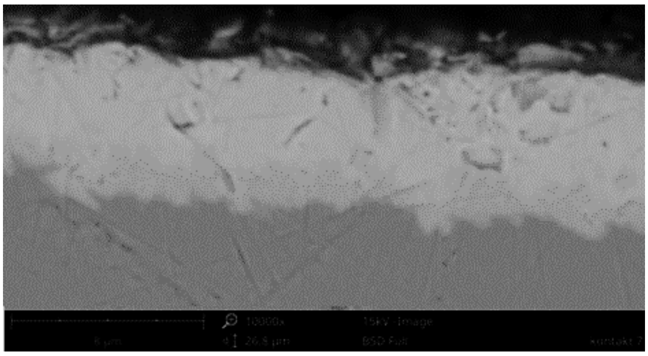

Fig. 6. Scanning microscope image of sample number 4 – a continuous layer with even coating thickness, visible impurities in the coating

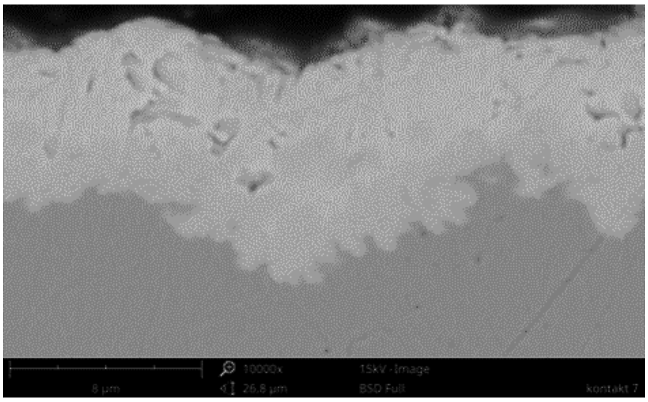

Fig. 7. Scanning microscope image of sample number 4 – a continuous layer with uneven coating thickness. Coating material with numerous irregularities

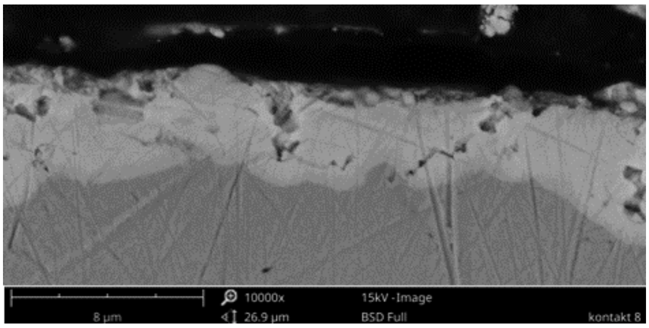

Fig. 8. Scanning microscope image of sample number 5 – a continuous layer, with varied coating thickness, numerous impurities

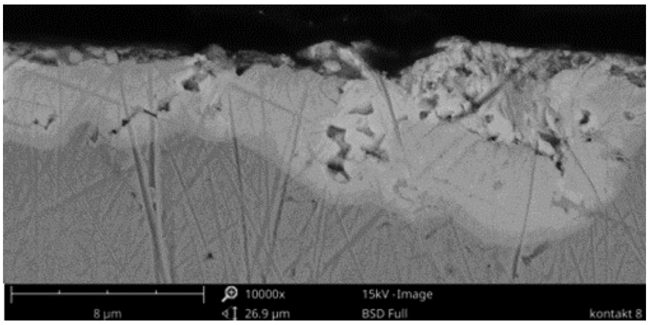

Fig. 9. Scanning microscope image of sample number 5 – a continuous layer, with uneven coating thickness, and numerous impurities

3.3. Roughness

The results of the roughness measurements of the selected specimens, number 2 and 3, were collected and presented in Table 4. It also includes the average roughness values of the Ra and Rz parameters calculated from the two measurements taken for each specimen.

Under each figure showing the measurement of roughness profile is a cross-section of the profile of roughness height in the given measurement lines for the sample indicated in the description.

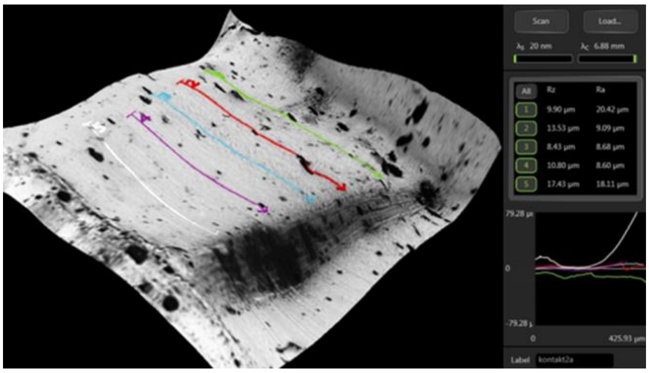

Fig. 10. Sample number 2, measurement 1 – 3D view of the test surface

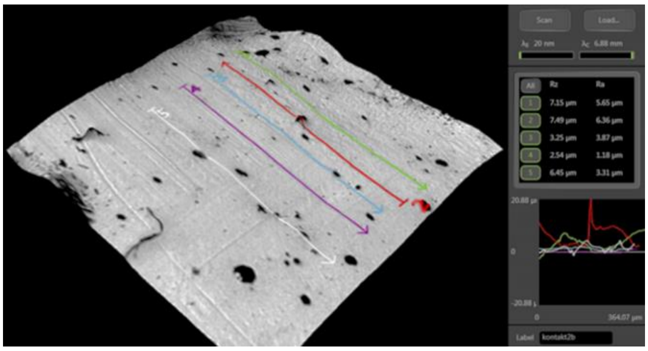

Fig. 11. Sample number 2, measurement 2 – 3D view of the test surface

Observations of the material of sample number 2 indicate a high presence of surface contaminants of various sizes but regular round shapes. Longitudinal cracks can be observed. In places of inclusions on the roughness profile, large differences in height appear (Fig. 11). In places without inclusions, the roughness profile shows very small differences in height. In the results for measurement 1 – line 5 (white) has a clearly increasing shape (Fig. 10). After analyzing this shape, this result is not considered a roughness measurement because the differences in profile height are too large – 79.3 μm – to qualify this shape irregularity as roughness. It is also not taken into account when calculating the average roughness value for the sample, which is for parameter Rz = 8.03 μm and for parameter Ra = 7.89 μm. The Ra value for gold coating is higher than that found in the literature, where it was 0.5715 μm and 0.3827 μm. The surface of the samples examined by Ren et al. was also less wavy and did not have large cracks and inclusions, which translates to lower roughness parameters [15].

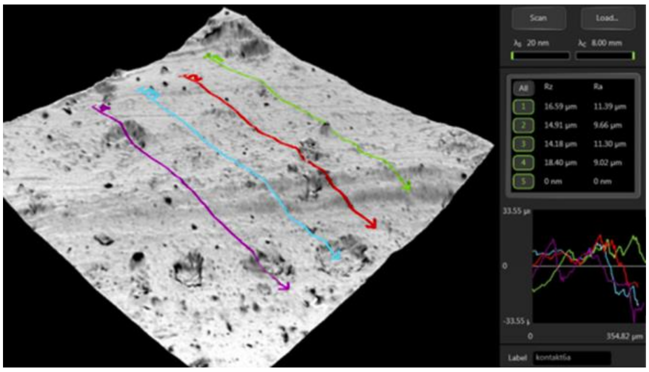

Fig. 12. Sample number 3, measurement 1 – 3D view of the test surface

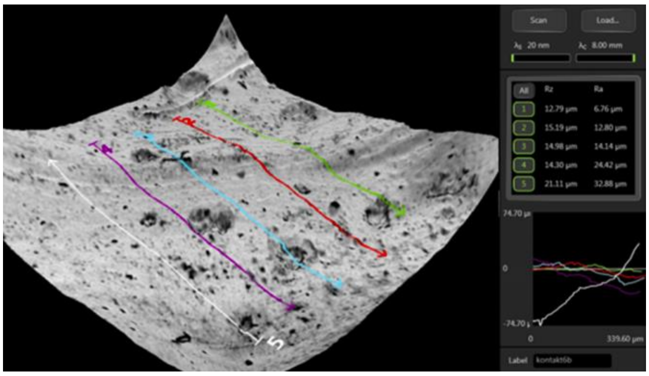

Fig. 13. Sample number 3, measurement 2 – 3D view of the test surface

The surface irregularities observed in the material of specimen number 3 are predominantly concave depressions – dark grey patches with irregular shapes visible in Fig. 12. and Fig. 13. A small number of convex, fine surface contaminations (black dots) with regular shapes and a small (several or even several times smaller) size compared to the depressions can also be observed. The sample has visible longitudinal scratches occurring in one direction. On the 3D image in places of surface roughness (convex and concave) on the roughness profile appear large differences in height. The indices of surface roughness for sample number 3 are for the parameter Rz = 13.58 μm and for the parameter Ra = 13.24 μm. Narayanan et al. examined the roughness of tin-coated connectors after 20000 fretting cycles at various temperatures. The Ra value they measured ranged from 1.71 to 2.77. This indicates that the samples they examined had lower roughness, despite being subjected to destructive testing, than sample number 3 [16].

Table 4. Surface roughness values

Sample	1st measurement – roughness values [μm]		2nd measurement – roughness values [μm]		Average roughness value [μm]	
	Rz	Ra	Rz	Ra	Rz	Ra
2	9.90	20.42	7.15	5.65	8.03	7.89
	13.53	9.09	7.49	6.36		
	8.43	8.68	3.25	3.87		
	10.80	8.60	2.54	1.18		
	~~17.43~~	~~18.11~~	6.45	3.31		
Average	10.67	11.70	5.38	4.07		
3	16.59	11.39	12.79	6.76	13.58	13.24
	14.91	9.66	15.19	12.80		
	14.18	11.30	14.98	14.14		
	18.40	9.02	14.30	24.42		
	~~0.00~~	~~0.00~~	~~21.11~~	~~32.88~~		
Average	12.82	8.27	14.32	14.53		

3.4. Corrosion tests

The corrosion resistance tests were carried out on two samples, number 2 and 3. The measurement of the stationary potential as a function of time for the open circuit of both samples showed that after 40 minutes both samples had very similar potential. The sample coated with gold, showed a potential E^0 = –421 mV, while the sample coated with tin, showed a potential E^0 = –422mV – the result is shown in Fig. 14.

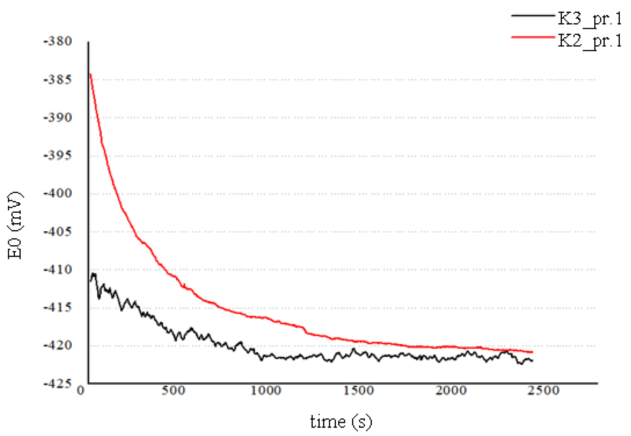

Fig. 14. Open circuit stationary potential as a function of time for samples number 2 and 3

Potentiodynamic results were obtained by performing anodic polarization and applying the Tafel method. These made it possible to obtain potentiodynamic curves, which were subsequently analyzed. On their basis the values of corrosion parameters were determined, i.e. corrosion potential (E_{cor}) and corrosion current (i_{cor}) – Table 5. The highest value of the corrosion potential was found for sample number 2 and the lowest value for sample number 3. The values of the corrosion potential translate into the results of the corrosion current. The values obtained for gold were similar to those in the literature, where E_{corr} was –359 mV and i_{corr} was $93 \cdot 10^{-6}$ A/cm^2. According to the authors, these parameters are unfavorable and imply the inability of the gold coating, made by the traditional method, to protect copper from corrosion and may even enhance it [17]. The values of polarization parameters reported by Arazna et al. differed from those obtained in this publication and were E_{corr} = –520 mV and i_{corr} = $5.8 \cdot 10^{-6}$ A/cm^2 [18]. However, in both cases, the parameters indicated better corrosion resistance of tin than that of gold.

Table 5. Results of corrosion tests carried out on samples number 2 and 3

Sample	Coating material	E_{cor} [mV]	i_{cor} [A/cm^2]
2	Au	–572.61	$75.85 \cdot 10^{-6}$
3	Sn	–489.5	$12.65 \cdot 10^{-6}$

4. Conclusion

EDX analysis found inconsistencies in the manufacturer's specification. One connector was coated with a different metal than it should have been. The fact that sample number 1 according to the manufacturer is coated with gold, while the tests show that it is coated with silver, may lead to electrical harness damage, due to differences in electrochemical potential of these two elements. This mistake may lead to unreliable operation of receivers for which gold and not silver connector is dedicated. The cause of the mistake may be insufficient quality control at the production unit.

The chemical composition analysis of the gold coating (sample 2) revealed injections of copper. They were small, so they should not influence the maintenance of the correct connection between terminals and receivers. They can, however, have an influence on the quicker appearance of corrosion centers in the contact area than in the case of a coating with a lower level of copper contamination. With samples that are tin-plated (samples 3, 4 and 5) the copper content of the coating is higher than with precious metals (from 17 to 53%). This may be due to the greater ability of tin to react with other elements due to its lower (negative) electrochemical potential than the precious metals and copper (positive potential). This level of core element's presence in the coated layer may be a residue from chemical reactions occurring during the coating process. A break in the continuity of the tin coating is not detrimental to the beam as tin has a lower electrochemical potential than copper. It is the tin that will be chemically active so the quality of the bond will be maintained and will not be exposed to the environment and corrosion.

Observation of specimens performed by light microscope revealed very thin layers of coated metal, but did not allow for detecting coatings defects and measuring coating thickness due to insufficient magnification. SEM exposed many coating defects, such as impurities, injections, and delamination, which could not be revealed by light microscopy. It was also possible to measure coating thickness. Examination revealed the poor quality of all tin coatings. All samples had uneven coatings thickness. The coating on sample number 3 was not continuous. Many injections and impurities as well as delamination within the coating and between coating and core material were observed. The surface of the connector was not prepared correctly as there were lots of burrs and irregularities. Samples number 4 and 5 had continuous coatings, but also many injections and delamination. The gold coating was free from injections, delamination and discontinuities. The surface of the connector was prepared correctly for coating. The main issue with sample number 2 was the thickness of the coating. It was thinner than tin coatings, presumably due to the higher price of gold. It makes this coating vulnerable to mechanical damage. While it is not crucial for tin coatings to be continuous, because they work as an anode and protect core material even with discontinuities, it is extremely important for a noble metal coating to cover protected material completely. Copper is a metal of lower electrochemical potential than gold, which means that if both of them are present in the same environment, copper will start to corrode. Every single discontinuity in the gold coating is a possible place for a corrosion pit.

The main irregularities concerning the coating itself are significant variations in layer thickness and delamination. Less common irregularities are pinholes which only occur in tin-coated samples. Differences in the preparation of the surface for the metal coating can also be observed. An unevenly prepared substrate significantly affects the difference in film thickness. The biggest problem in the use of connector terminals is the influence of the environment and thus the corrosion of the element, because all the above-mentioned defects and damages increase the susceptibility of the element to this phenomenon.

On the basis of the measurement of the surface roughness of the samples, it can be observed that the one coated with gold shows lower values of surface roughness for both indices (Ra and Rz) than the sample coated with tin. Sample number 2 has a greater difference in the height of the lowest and highest elevations examined on the roughness profile. The reason for this is point-like inclusions (black color in Fig. 10 and Fig. 11), which cause a peak change in the height of the roughness profile. Sample number 3 – coated with tin – shows a greater presence of pits on the surface than convexities on the surface. Sample number 2 shows a higher proportion of surface impurities in the form of inclusions, which are convex.

The surface roughness at the contact point of the connector is needed to ensure a connection at the contact point. However, large values of roughness (large peaks in the direction of lower or higher values) can have the opposite effect to that desired – they can cause surface deviation and poorer contact quality of the mating surfaces. All of the samples tested for roughness (samples 2 and 3) show significant surface irregularities at the roughness level. Inclusions or pits are present in each sample. Each sample is scratched – these are long straight scratches of varying depth. This damage is caused by the storage of the connector ends. They are stored in containers where they are exposed to each other. This causes scratches and micro-damage such as indentations. These containers are not particularly tightly sealed and are not isolated from the external environment, which gives rise to the possibility of contamination adhering to the surface. Spot contamination of the samples may also be a result of the chemical composition of the material used to coat the tips and the sterile conditions under which the coating process is carried out.

The corrosion resistance tests were conducted in a humid environment – in a 3% sodium chloride solution. This type of environment was chosen to imitate winter conditions of car operation in countries where winters with snow occur, and road salt is used on roads to prevent icing.

Research about the corrosion resistance of the samples has shown that the tin-coated tips have higher overall corrosion resistance. They have a higher corrosion potential (E_{cor}) and corrosion current (i_{cor}) than gold-plated samples. The higher the value of the corrosion potential, the higher the corrosion resistance of the metal and the lower the surface impact of the aggressive environment on the sample.

Research shows that gold-plated terminals, often chosen for responsible vehicle components, are actually a less safe choice than tin-plated connectors. In order to protect gold coated connector terminals well against corrosion, they should be very tightly manufactured to avoid discontinuities. Improving the quality of the coating can also be achieved by increasing its thickness, but this can result in a significant increase in production costs.

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