Interreg
ITALIA-SLOVENIJA
UNIONE EUROPEA
EVROPSKA UNIJA
NANO-REGION
Progetto strategico co-finanziato dal Fondo europeo di sviluppo regionale
Strateški projekt sofinancira Evropski sklad za regionalni razvoj

PROOF-OF-CONCEPT EXPERIMENT REPORT

ANALYSIS OF ANOMALIES IN ENAMEL INSULATION ON COPPER WIRE

Authors:

Gregor Kapun

CENN - Nanocenter

Jamova 39, 1000 Slovenija

Mattia Fanetti

Materials Research Laboratory, University of Nova Gorica

Vipavska 11c, 5270 Ajdovščina, Slovenija

Nanocenter

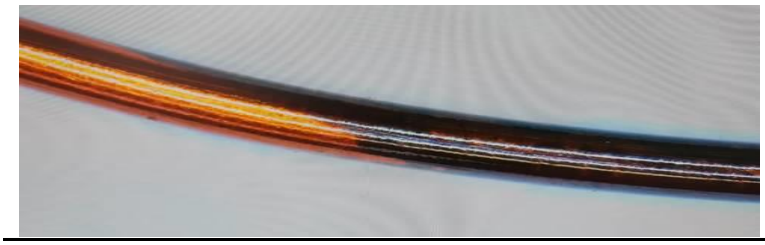
UNIVERZA V NOVI GORICI
SCIENTIA VINCES
1995

Proof-of-Concept experiment details

Received sample:

Three copper wires (diameter of ~ 1 mm) insulated by several THEIC-PEI (polyesterimide) layers in thickness of ~10-15 μm and ~10 μm topcoat PAI (polyamide-imide) layer. The wires were sampled from different part of motor stator pack which was subjected to lifetime test. Digital image of the delivered samples with given names are listed in Table 1.

Table 1: Samples delivered by the company

	Sample 4 Delivery date: October 14th 2020
	Sample 5 Delivery date: March 8th 2021

Planned analysis:

1st Binocular microscope inspection followed by SEM preliminary analysis to localize the defects. The preliminary analysis was aimed to obtain first insight of the wire protection defects and elaborate the best strategy for analysis.

2nd Surface SEM-EDX analysis of target locations on top Cu wire enamel protection i.e. healthy region, blue colored region and degraded region.

3rd FIB-SEM cross-sectional analysis at three target regions of the enamel protection for the case of Sample 4. Site specific FIB cross sections were chosen at the healthiest region, blue colored region (middle between healthy and most degraded part) and in near proximity of the most degraded part of the enamel protection.

4th Generation of a large cross-section throughout healthy and color changed region of the Sample 5 by using Ar^+ ion cross-section polisher. Subsequently, SEM-EDX analysis of the obtained cross-section.

Sample preparation:

SEM-EDX and FIB-SEM analysis: samples were attached to Al stubs using double adhesive conductive carbon tape. Subsequently, conductive contacts were made at both wire edges with quick drying Ag conductive paste. In a final stage, samples were sputter-coated with 6 nm layer of C.

Ar^+ ion cross section polisher: sample wire was embedded into epoxy resin, covered with a thin glass slice (150 μm) and cured at ~100 °C.

Measurement author, dates and place:

All analyses were performed within the framework of NANOREGION project, following the POC proposal submitted on 01/10/2020 and approved on 07/10/2020.

SEM-EDX and FIB-SEM analyses, together with required sample preparation, have been performed by Gregor Kapun in time period from 04/11/2020 to 11/06/2021 at Nanocenter, Jamova cesta 39, SI-1000 Ljubljana, Slovenia). Analyses were performed with FIB-SEM Helios Nanolab 650 (Thermo Fisher, The Netherlands) equipped with SDD X-Max 50 EDX detector (Oxford Instruments, UK). Carbon conductive coatings were made on precision etching coating system - PECS 682, (Gatan, US).

Large cross-section on Sample 3a, together with required sample preparation, have been performed by dr. Mattia Fanetti and dr. Andraž Mavrič in time period from 13/05/2021 to 08/06/2021 at University of Nova Gorica, Materials Research Laboratory, Vipavska 11c, SI-5270 Ajdovščina, Slovenia. Ar^+ ion beam polished cross-section was performed with Cross Section Polisher – model IB-09010CP (JEOL, Japan). Initial SEM observations of a cross-sections was performed on JEM-7100f-TTLS microscope (JEOL, Japan).

Preliminary measurements:

Initial sample observations and localization of defects was done with binocular stereo microscope followed by low kV SEM surface analysis.

Observation conditions:

Preliminary low kV SEM imaging on intrinsic samples (not coated): beam energy 1 kV, probe current 40 pA, ETD secondary electron (SE)detector and in-cloumn TLD SE detector

SEM and FIB-SEM imaging:

- surface and cross-sectional imaging: beam energy 1-2 kV, probe current 50-100 pA, ETD, ICE or in-column TLD-SE detector
- surface and cross-sectional Z-contrast imaging: beam energy 1-2 kV with probe current 400 pA for the case of ETD-BSE and in-column TLD-BSE detector or beam energy of 2-5 kV with probe current 400 pA for the case of retractable CBS detector.

The point, area, linescan or mapping EDX analyses were performed with the following parameters:

- Full energy range quantitative EDX analysis: beam energy 15-20 kV, probe current 200 pA, process time (PT): 5, Live Time (LT): 60 s; for the case of mapping PT:4, Dwell Time (DT): 350 ms, 10 frames,
- Low kV quantitative EDX analysis: beam energy 7kV, probe current 800 pA, PT:6, Livetime: 60 s; for the case of mapping PT:5, Dwell Time (DT): 350 ms, 10 frames,
- Detector energy quant optimization and beam measurement was done on Co standard following the same parameters as used in above-described EDX measurements.

EDX data processing was done in AZtec 4.3 software (Oxford, UK) by using TrueQ algorithm for elemental quantification while linescan and mapping data were processed with TruLine and TruMap algorithm, respectively.

FIB cross-section of selected regions on the sample was fabricated after deposition of a platinum protective layer on the surface (first 0.3 µm thick layer with EBID at 2 kV, 0.8 nA, second 1,2 µm thick layer deposited with IBID at 30 kV, 0.40 nA). Subsequently, material in front of Pt protection was milled away with FIB (30 kV, 64 nA), by generating special ROI geometry which enable cross-sectional analysis to the depth of 60 µm without shadowing of imaging and EDX signals. Freshly exposed cross-sections were made with FIB at 30 kV and 45 nA by sequential reducing ion beam currents down to 9.4 nA in a final polishing step. Imaging and EDX analysis along cross-section was performed with SEM at an angle of 38° by using same conditions as previously described for surface analysis.

Large cross-section was made with broad ion beam Ar^+ polishing at 5.5 kV with 140 µA beam current for 5 hours.

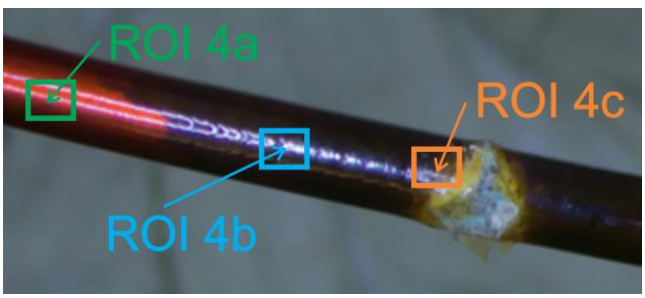
Main aim of the proposal:

The aim of the proposal was to verify if X-section preparation by FIB or by Ar+ polishing, combined with subsequent SEM/EDX analysis, are effective in the examination of degraded copper wires, and useful in the identification of the source of degradation. To this purpose, the analysis was focused onto polyesterimide/polyamideimide enamel protected Cu wires where enamel (insulation) degradation was observed during lifetime test of the electrical motor stator pack. Degradation of enamel was observed at various wire locations as color change, enamel cracking or heavily enamel degradation followed by insulating shell peeling. Within the proposed proof of concept experiment most typical failure areas, which visually shows different stages of wire enamel degradation, should be examined for surface contamination or potential inclusion of foreign material in the enamel protective layer. To avoid mechanical damage and possible contaminations, intrinsic cross-sectional areas must be produced at target enamel protection/Cu wire locations. For that purpose, FIB microscopy and/or Ar+ cross-section polisher, followed by SEM and EDX elemental analysis should be used for detailed examination of freshly exposed cross-sectional areas related to site-specific location of enamel insulated Cu wire.

Results

1. FIB-SEM analysis of Sample 4

Prior SEM-EDX and FIB-SEM analysis, region of interest (ROI) was coordinated with the company. Target ROI locations with corresponding names are shown in Figure 1.



Legend:

ROI 4a: healthy region

ROI 4b: blue colored region

ROI 4c: heavily degraded region

Figure 1: Sample 4 with selected ROI locations and corresponding names

1.1 Surface SEM-EDX analysis

SEM analysis shown that the surface morphology and topography of enamel protection was very similar at healthy (ROI 4a) and blue colored region (ROI 4b) of insulated wire (Figure 2-3). At this locations cracking, degradation or any foreign contaminant on enamel surface was not detected. The later was confirmed also with EDX analysis (Table 2) which shown very similar elemental compositions on both locations (EDX 4a and EDX 4b). Contrary, at the ROI 4c, heavily enamel degradation was found which resulted in enamel layer cracking and insulation peeling of the Cu wire as shown in Figure 4. Moreover, phase contrast images shown in Figure 5 revealed presence of additional phases on top of unprotected Cu wire (at cracked part) as well as on enamel surface near the cracked region. These phases include potassium as well as traces of sodium and chlorine elements, which were not seen at healthy or blue colored enamel surfaces (Table 2). According to elemental analysis in Table 2 (EDX 4c-2 to EDX 4c-4), the content of potassium increases from the cracked enamel edge toward "peeled of" Cu wire region. This indicates that the potassium/sodium contamination was most likely present locally at the Cu wire surface, where the corrosion/degradation effect was most intense, and from there degradation process advanced in the near surrounding which caused defects in enamel insulation layers.

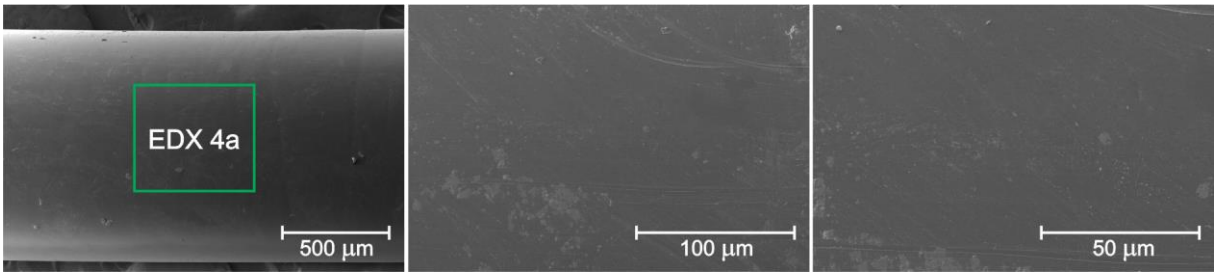


Figure 2: Surface SEM images of healthy region (ROI 4a) with denoted EDX analysis position

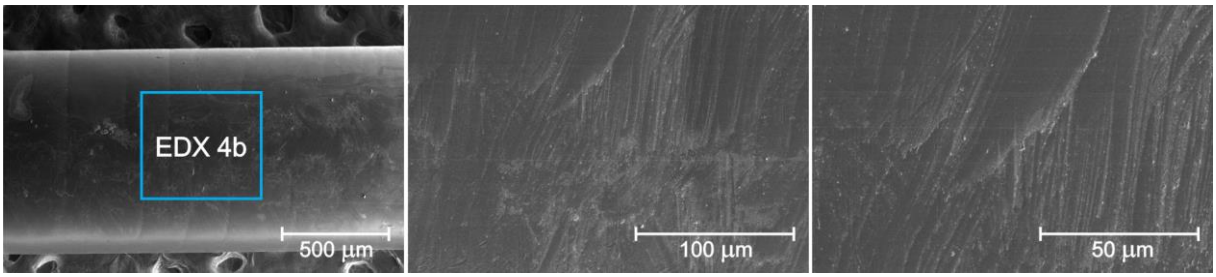


Figure 3: Surface SEM images of blue colored region (ROI 4b) with denoted EDX analysis position

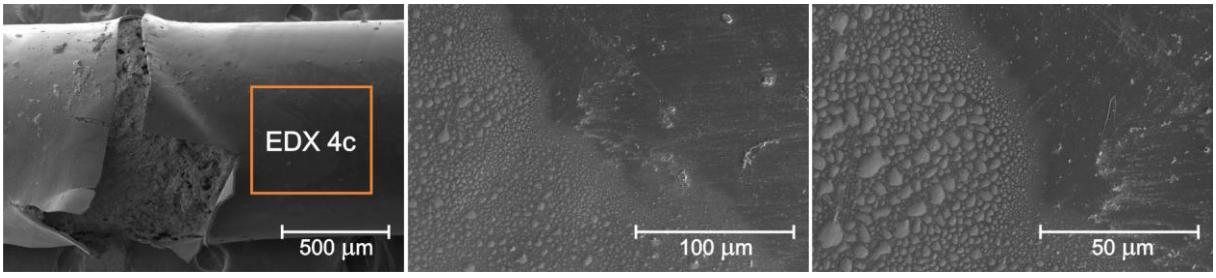


Figure 4: Surface SEM images of heavily degraded region (ROI 4c) with denoted EDX analysis positions

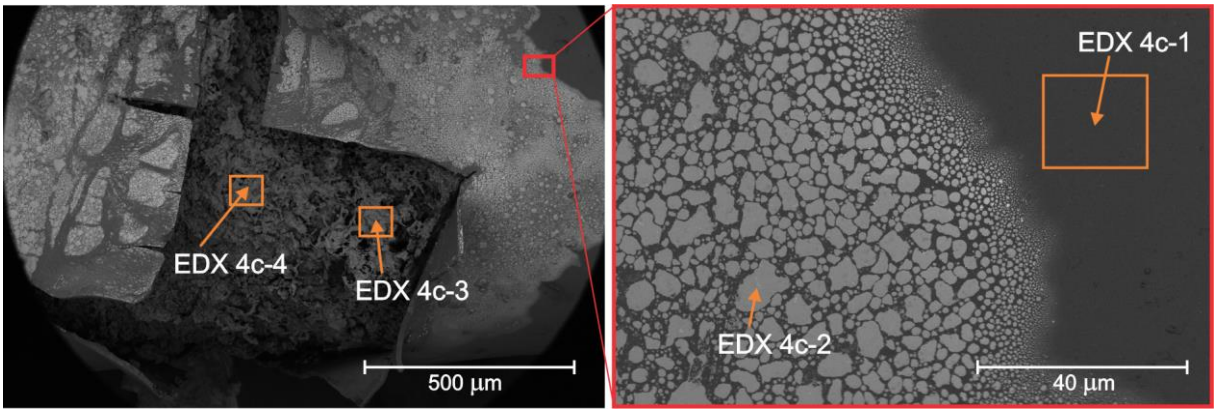


Figure 5: Phase contrast SEM images of heavily degraded region (ROI 4c) with enlarged detail (enamel surface) and denoted EDX analysis positions

Table 2: Quantitative EDX elemental analysis of the Sample 4 surfaces at denoted locations

EDX analysis location	Elemental composition / Wt%								
	C	N	O	F	Na	Cl	K	Cu	Total
EDX 4a	78.7	7.2	13.0	1.2					100.0
EDX 4b	78.1	7.3	13.4	1.2					100.0
EDX 4c	68.4	6.5	21.1	0.4	0.3	0.1	2.9		100.0
EDX 4c-1	79.2	6.4	13.3	1.1					100.0
EDX 4c-2	26.4	0.3	28.9	0.2	1.5	0.8	41.9		100.0
EDX 4c-3	7.7		38.3		0.5	0.2	49.7	3.9	100.0
EDX 4c-4	5.9		24.5		0.5	0.3	58.9	9.9	100.0

1.2 FIB-SEM cross-sectional analysis at healthy region (ROI 4a)

FIB-SEM cross-sectional analysis of healthy region (ROI 4a) shown that total thickness of enamel insulation on top of Cu wire was 49.5 µm. Phase contrast images in Figure 6 revealed two different types of enamel layers which were firmly sandwiched together without any traces of foreign contaminations between them. According to the company description, the first enamel protection part

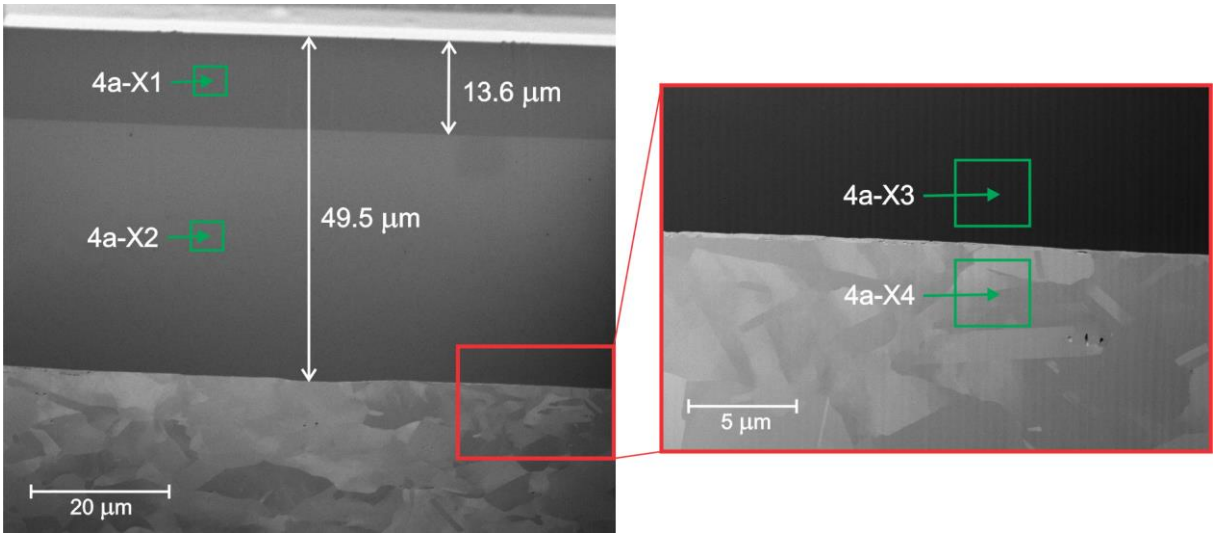


Figure 6: FIB cross-sectional analysis of Sample 4 healthy region (ROI 4a) with enlarged detail (enamel protection/copper interface) and denoted EDX analysis positions

on top of Cu wire should be composed of 2-3 polyesterimide (THEIC-PEI) layers with individual thickness of ~ 10-15 μm. However, (THEIC-PEI) layers cannot be individually distinguished by phase contrast imaging (same material) and therefore are shown on phase contrast image (Figure 6) as one combined layer with total thickness of 32.9 μm. By the contrast, the topcoat polyamide-imide (PAI) layer was clearly distinguished from the initial layers and shown its uniform thickness of 13.6 μm. The difference between two different types of enamel layers was also confirmed by EDX elemental composition shown in Table 3. The interface between Cu and enamel protection presented in enlarged image in Figure 6 shown flawless adhesion of first protection layer without any cracks or defects. The wire composition near the interface shown practically pure copper with some traces of carbon which is related to Cu X-ray secondary fluorescence with enamel layers (Table 3). At the Cu/enamel interface there were not found any traces of foreign contaminants or Cu surface degradation. In addition, EDX linescan (4a-X) shown in Figure 7 confirms uniform elemental profile along both types of enamel layers (in terms of C and O) and stepwise change of C, O and Cu signals at the Cu interface without any traces of foreign contamination elements. Related to EDX linescan analysis it is also important to note that Cu signals in enamel layers could be effect of two contributions: Cu diffusion toward enamel layers and/or beam scattering effect from supporting copper due to large depth of FIB cross-sectional geometry.

Table 3: Quantitative EDX elemental analysis along ROI 4a cross-section, acquired at locations denoted in Figure 6

EDX analysis location	Elemental composition / Wt%					
	C	N	O	F	Cu	Total
4a-X1	77.8	4.5	9.7	2.5	5.6	100.0
4a-X2	67.8	4.4	16.1	3.1	8.6	100.0
4a-X3	63.6	4.2	15.8	2.8	13.7	100.0
4a-X4	1.6				98.4	100.0

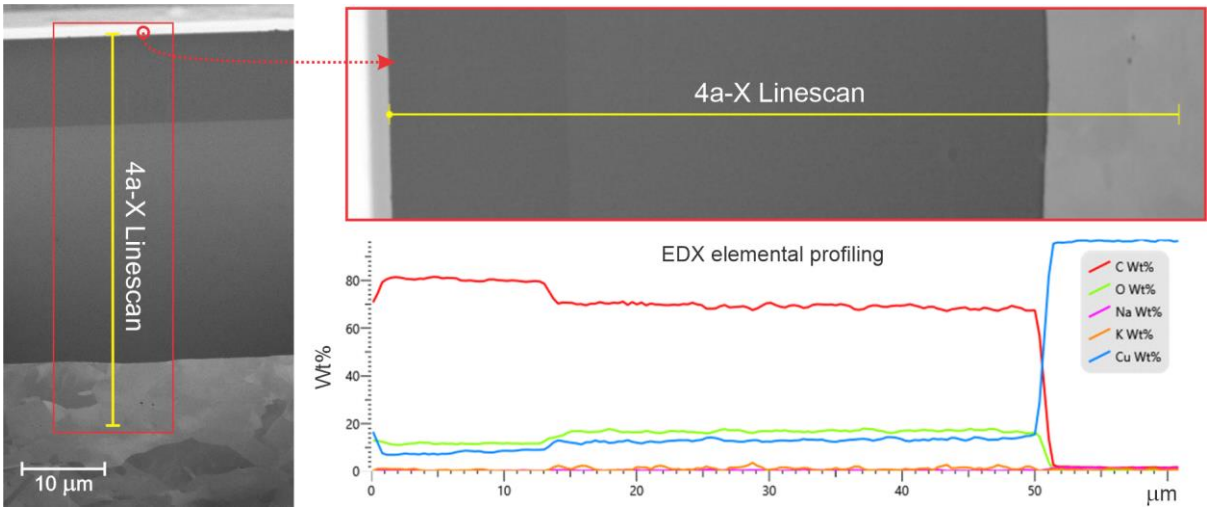


Figure 7: EDX linescan analysis along cross-section of healthy region (ROI 4a) with enlarged linescan acquisition detail and corresponding EDX elemental profiles

1.3 FIB-SEM cross-sectional analysis at blue colored region (ROI 4b)

FIB-SEM cross-sectional analysis of blue colored region (ROI 4b) shown that total thickness of enamel insulation on top of Cu wire was 46.1 μm (Figure 8). Enamel layered insulation was found very similar to healthy region (ROI 4a), composed of two different enamel types with the thickness of 32.9 μm and 31.2 μm for the combined THEIC-PEI layer pack and topcoat PAI layer, respectively. All enamel layers were firmly sandwiched together and there were not found any traces of foreign contaminants between them. However, Phase contrast image in Figure 8 clearly shown corrosion/degradation of the Cu wire surface at the Cu/enamel interface. The corroded Cu surface layer at ROI 4b location was found to be 7.4 μm thick. EDX elemental analysis shown in Table 4 revealed presence of potassium (up to 27.5 Wt%) and sodium (up to 2.2 Wt%) in the Cu degraded layer. EDX linescan (4b-X) presented in Figure 9 shown uniform elemental profile along both types of enamel layers (in terms of C and O) similar as in healthy region. At the enamel/Cu wire interface K and Na elemental signals appeared and were present, together with O element, throughout entire Cu degraded surface layer (7.4 mm) until healthy Cu wire was reached at the depth of 56 μm. This indicates that the traces of K and Na contaminants were present at the Cu/enamel interface within the blue colored wire region and caused surface degradation processes of the Cu wire.

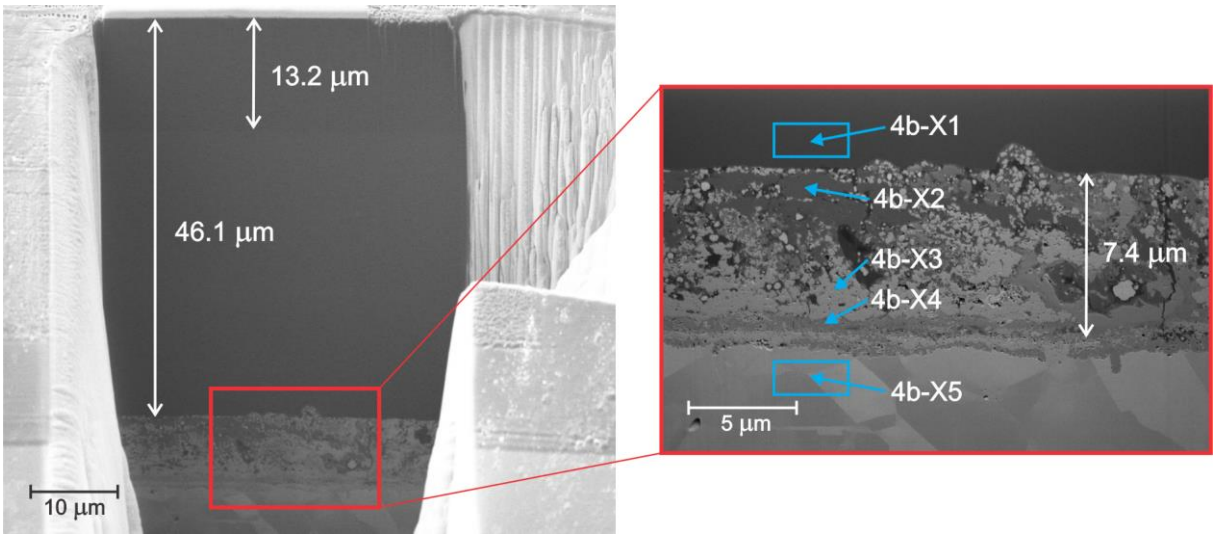


Figure 8: FIB cross-sectional analysis of blue colored region (ROI 4b) with enlarged detail (enamel protection/copper interface) and denoted EDX analysis positions

Table 4: Quantitative EDX elemental analysis along ROI 4b cross-section, acquired at locations denoted in Figure 8

EDX analysis location	Elemental composition / Wt%							
	C	N	O	F	Na	K	Cu	Total
4b-X1	63.9	5.4	18.6	1.3			10.9	100
4b-X2	37.2	0.9	17.6		2.2	25.7	16.5	100
4b-X3	2.5		16.4		0.5	4.7	75.8	100
4b-X4	2.6		13.9		1.9	16.0	65.6	100
4b-X5	1.2						98.8	100

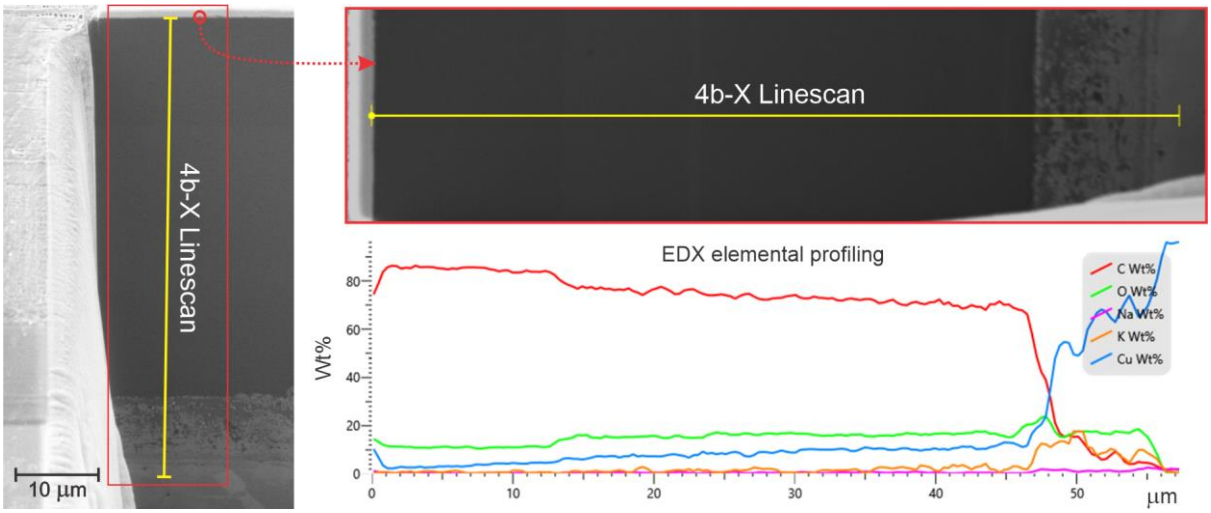


Figure 9: EDX linescan analysis along blue colored region (ROI 4b) with enlarged linescan acquisition detail and corresponding EDX elemental profiles

1.4 FIB-SEM cross-sectional analysis of heavily degraded region (ROI 4c)

FIB-SEM cross-sectional analysis was performed 400 µm away from the peeled (cracked) insulation, where enamel protection was still in plain with normally attached insulation. Phase contrast image of the cross section presented in Figure 10 shown intense corrosion of Cu wire surface in terms of large pore, cracks, and secondary phase formation. Moreover, degradation of enamel protection layers was observed in several location. The enamel degradation was found most intense at the first THEIC-PEI layer (at Cu interface), where secondary phase, cracks and pores were seen over complete layer. The degradation affected also next two THEIC-PEI layers and part of the PAI layer at the THEIC-PEI interface. Phase contrast image in Figure 10 confirmed presence of secondary phase in enamel layers. EDX elemental analysis revealed that potassium element (8.1 – 17 Wt%) was present in secondary phases in enamel layers as well as in corroded Cu surface. In addition, high content of sodium element (15.8 Wt%) was found in the first enamel layer, while in all above layers its concentration was found much lower. Elemental distribution along cross-section is evident from EDX mapping shown in Figure 11.

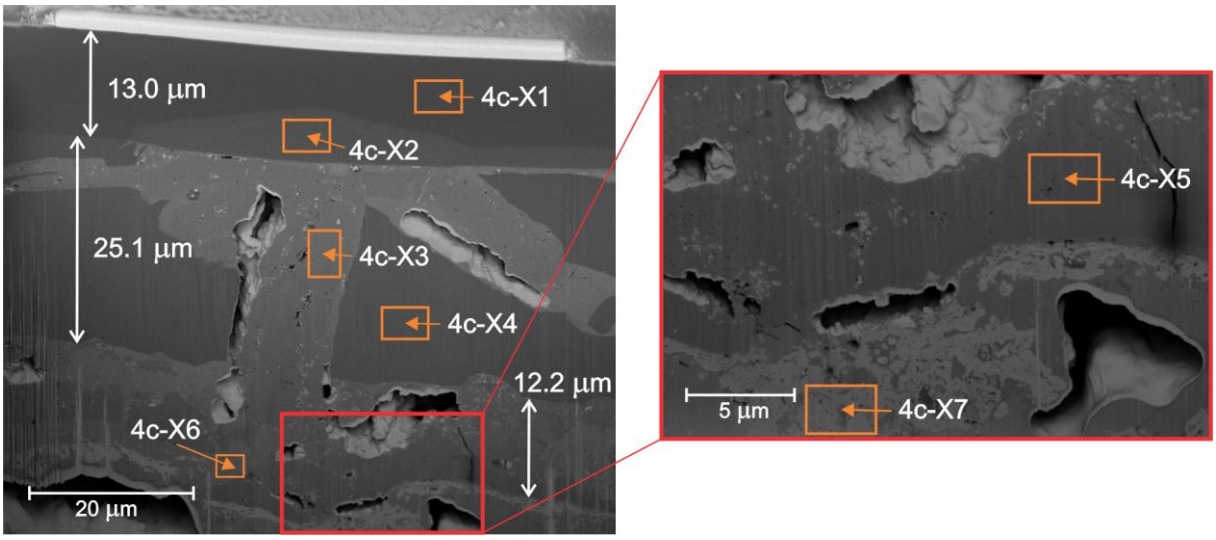


Figure 10: FIB cross-sectional analysis near heavily degraded region (ROI 4c) with enlarged detail (enamel protection/copper interface) and denoted EDX analysis positions

Table 5: Quantitative EDX elemental analysis along ROI 4b cross-section, acquired at locations denoted in Figure 10

EDX analysis location	Elemental composition / Wt%							
	C	N	O	F	Na	K	Cu	Total
4c-X1	81.5	4.8	10.3	1.0			2.4	100
4c-X2	66.8	3.5	12.7		0.6	11.4	5.0	100
4c-X3	48.9	1.3	20.2		2.0	17.3	10.4	100
4c-X4	73.0	4.5	18.4	0.3			3.9	100
4c-X5	21.4	0.5	62.2		0.9	8.1	6.9	100
4c-X6	5.8		32.5		15.8		46.0	100
4c-X7	7.4		18.3			8.2	66.0	100

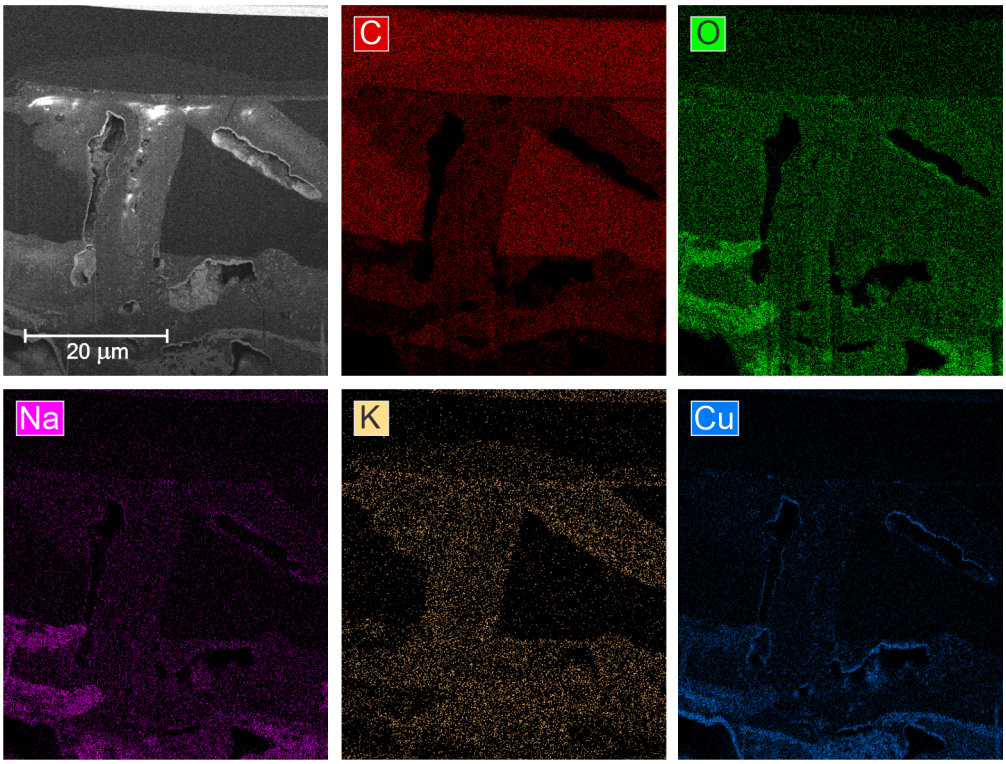
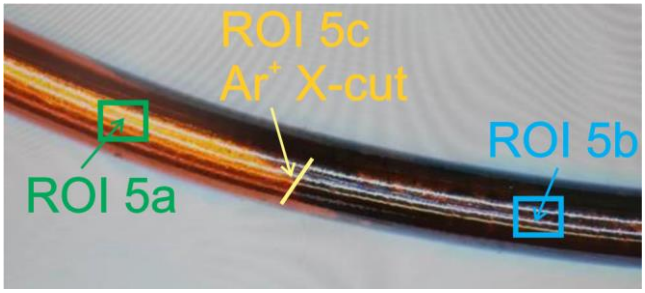


Figure 11: EDX elemental mapping along FIB cross-section near heavily degraded region (ROI 4c) with phase contrast SEM image and corresponding EDX elemental maps (C, O, Na, K and Cu)

2. SEM-EDX analysis of Sample 5

Sample 5 was taken from the motor stator wire pack, where the initial stage of enamel degradation was visually observed. Prior surface SEM-EDX analysis, region of interest (ROI) was coordinated with the company. Target ROI locations with corresponding names are shown in Figure 12.



Legend:

ROI 5a: healthy region

ROI 5b: blue colored region

ROI 5c: transition between healthy and blue colored region

Figure 12: Sample 5 with selected ROI locations and corresponding names

2.1 Surface SEM-EDX analysis

Surface SEM analysis (Figure 13) of insulated copper wire 5 shown that the surface morphology and topography of enamel protection was very similar at healthy (ROI 5a) and blue colored region (ROI 5b). Cracking, degradation, or foreign contaminant elements were not detected at any of those locations. The later was confirmed also with EDX analysis (Table 6) which shown very similar elemental compositions on both locations (EDX 5a and EDX 5b).

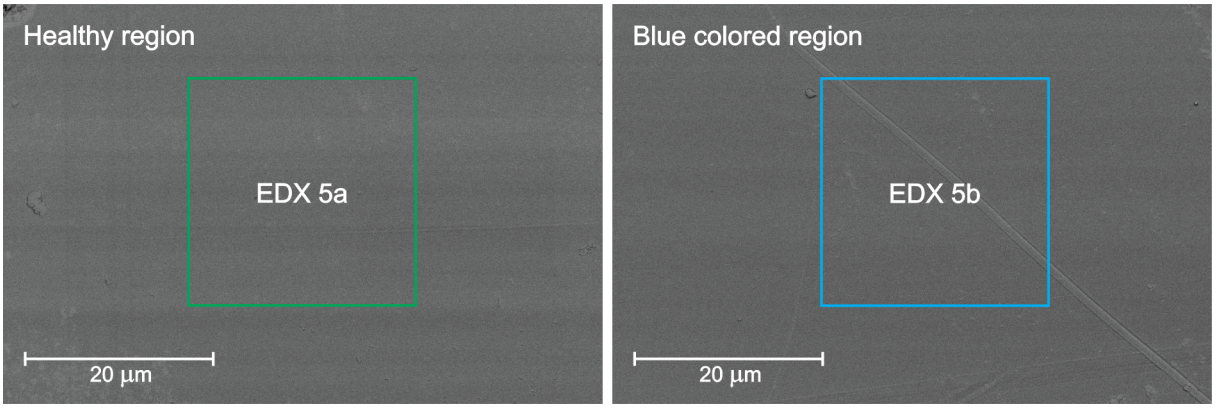


Figure 13: Surface SEM images of Sample 5 healthy (ROI 5a) and blue colored region (ROI 5b) with denoted EDX analysis positions

Table 6: Quantitative EDX elemental analysis along ROI 4b cross-section, acquired at locations denoted in Figure 13

EDX analysis location	Elemental composition / Wt%				
	C	N	O	F	Total
EDX 5a	80.3	4.8	13.7	1.2	100.0
EDX 5b	77.7	6.6	15.0	0.7	100.0

2.2 SEM-EDX analysis of Ar ion polished cross section at color transition region (ROI 5c)

Ar ion cross-section polisher enabled generation of ~500 mm wide cross-section of insulated Cu wire without any mechanical damage or contamination of the interfaces. With this technique large cross-sectional area was exposed which included healthy (right side), blue colored (left side) and transition region between them as shown in enlarged images in Figure 14.

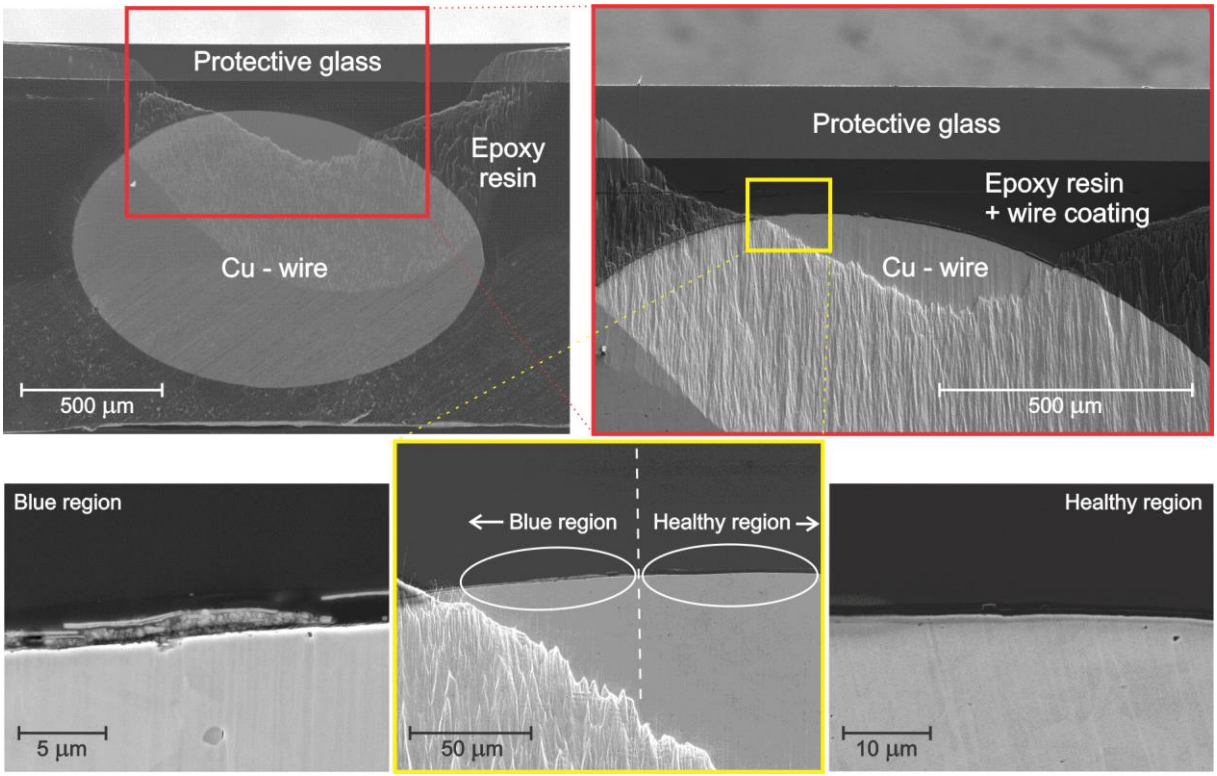


Figure 14: SEM images of Ar ion polished cross-section of insulated Cu wire (Sample 5) at color transition region (ROI 5c) with magnified blue colored and health region.

Phase contrast cross-sectional images shown in Figure 15 revealed the presence of secondary phase between first enamel layer and Cu surface at the blue colored region. At the healthy insulation side, enamel coating/Cu interface was found flawless. EDX analysis shown that the secondary phase found at the blue colored region included potassium and traces of sodium element (Table 7).

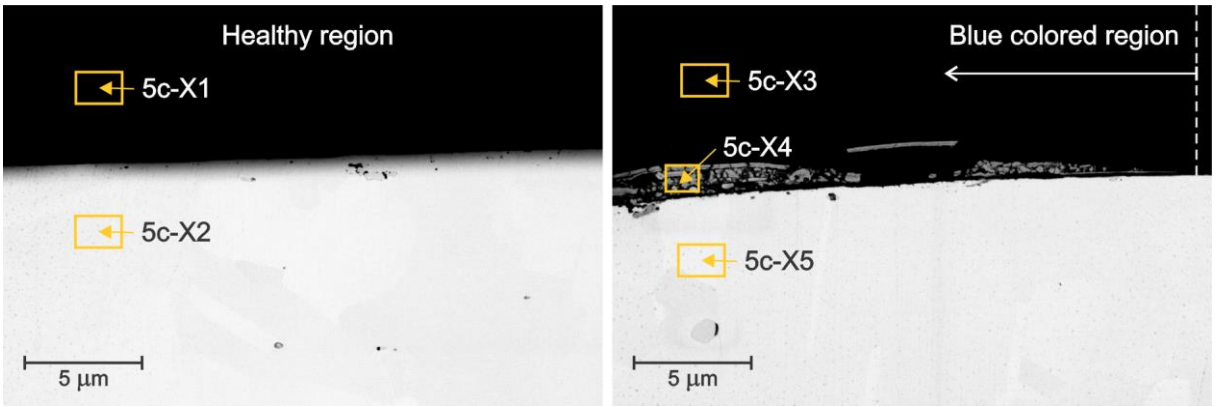


Figure 15: Phase contrast SEM images of Ar ion polished cross-section (ROI-5c) at healthy (left) and blue colored region side (right) with the denoted EDX analysis positions

Table 7: Quantitative EDX elemental of Sample 5 surfaces at locations denoted in Figure 15

EDX analysis location	Elemental composition / Wt%							
	C	N	O	F	Na	K	Cu	Total
5c-X1	66.1	5.3	24.9	2.4			1.3	100
5c-X2	7.5						92.5	100
5c-X3	62.9	7.2	26.3	2.1			1.5	100
5c-X4	5.8	0.4	16.1	3.9	0.3	3.8	69.6	100
5c-X5	7.8						92.2	100

EDX linescan analysis (Figure 16) shown that total enamel insulation thickness was ~38 μm. According to the C and O elemental profiles the enamel layer thickness corresponded to ~12 μm and ~26 μm for the topcoat layer (PAI) and sum of THEIC-PEI layers, respectively. At the enamel/Cu wire interface K and Na elemental signals were clearly identified which indicates the presence of K and Na contaminants at the Cu/enamel interface within the blue colored region.

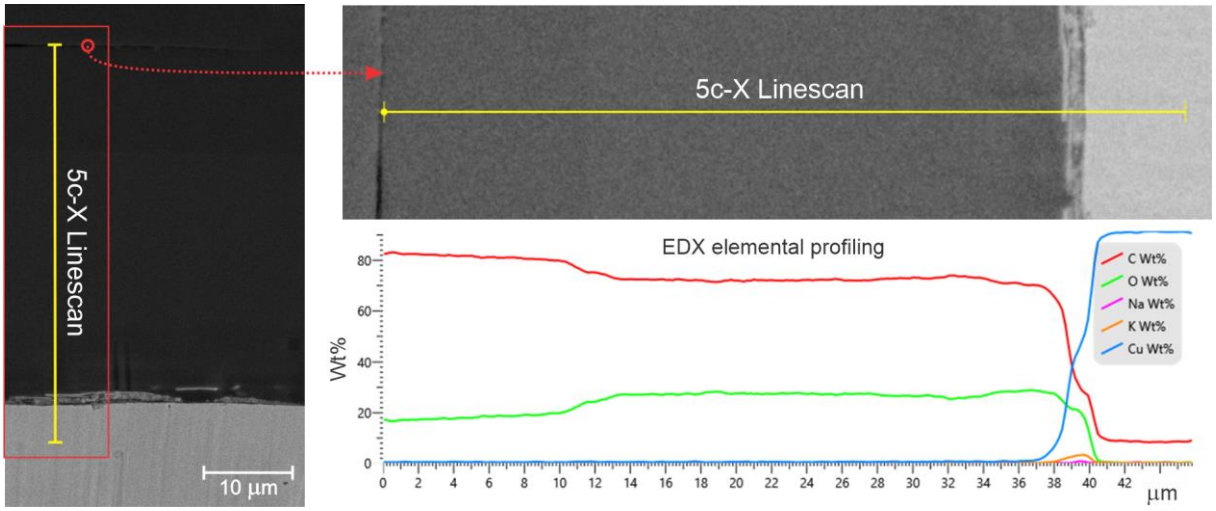


Figure 16: EDX linescan analysis along Sample 5 cross-section at blue colored region, with enlarged linescan acquisition detail and corresponding EDX elemental profiles

Summary

The obtained results gave detailed insight into the anomalies of the enamel protected copper wires. FIB-SEM surface and cross-sectional analysis of insulated Cu wire - Sample 4 revealed the following details:

1. Surface morphology and EDX elemental composition was found very similar at healthy and blue colored enamel region. At this locations cracking, degradation or any foreign contaminants on wire insulation surface were not detected.
2. Cross-sectional analysis shown that total thickness of insulation protection on Cu wire was 49.5 μm. Phase contrast images and EDX elemental analysis confirmed two different types of enamel layers, where the thickness of combined polyester amide (THEIC-PEI) layers and topcoat polyamide-imide (PAI) layer were 32.9 μm and 13.6 μm, respectively.
3. All the enamel layers at healthy and blue colored region were found firmly sandwiched together without anomalies or any traces of foreign contaminants between them. However, at the blue colored region, potassium and sodium contaminants were found at the enamel/copper interface. At this location potassium and sodium elements were confirmed also in the first 7.4 μm of copper wire surface, where initial copper corrosion effect was observed.
4. At heavily degraded region, enamel layer cracking and insulation peeling of the copper wire was observed. Presence of potassium and sodium elements were found on top of unprotected copper wire and on enamel surface near the cracked region. Their concentration was most intense at the coper wire surface and decreased towards edge of cracked enamel insulation.
5. Cross-sectional analysis at the heavily degraded region shown intense corrosion of Cu wire surface in terms of large pore, cracks, and secondary phase formation. At this location various anomalies were found in all enamel layers. The enamel degradation was found most intense at the first THEIC-PEI layer (at Cu interface), where secondary phase, cracks and pores were seen over entire layer. The degradation was seen also in all above layers including with part of the topcoat PAI layer. Presence of potassium and sodium phases were confirmed in all enamel layers as well as in corroded copper wire surface. High content of sodium element was localized near the first enamel layer, while in above layers its concentration was lower.

SEM-EDX analysis of Ar ion polished cross-section of insulated Cu wire - Sample 5 revealed the following details:

1. Surface morphology and EDX elemental composition was found very similar at healthy and blue colored enamel protection. Enamel cacking or degradation were not observed.
2. Cross-sectional analysis shown that total thickness of enamel protection was 38 μm. Two different types of enamel coating were confirmed, where the thickness of combined polyester amide (THEIC-PEI) layers and topcoat polyamide-imide (PAI) layer was found to be ~26 μm and ~12 μm, respectively.
3. At blue colored coating region, potassium and sodium phases were found between first enamel layer and Cu surface while at healthy insulation region foreign contaminants were not detected.

Final remarks about the effectiveness of the demonstrated techniques

Within presented PoC experiment we demonstrated that both, FIB-SEM analysis, and Ar^+ ion cross-sectional polishing combined with EDX analysis are effective in the identification of failures in the copper wire insulation. For example, in the present case both techniques allow detailed insight into wire coating and identification of foreign contaminants. Compared to conventional mechanical polishing, both techniques enabled generation of site-specific cross-section without any mechanical damage or contamination of the exposed interfaces.

Further advices

Related to insulation color change phenomena we also suggest analysis of the enamel coating with IR Raman Spectroscopy which may give additional details in terms of chemical structure, polymorphy and crystallinity.

This report has been written by Gregor Kapun and Mattia Fanetti (18/10/2021)