Innovative protective-conducting coatings based on silicon oxycarbide

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RESEARCH UNIVERSITY
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INTRODUCTION:

The main research objective of the project was to develop innovative protective coatings based on silicon oxycarbide (Si-O-C – so-called black glasses) to improve the resistance of individual metallic materials to high-temperature oxidation (e.g. ferritic steel for SOFC interconnects, TiAl alloys for aircraft turbine blades and Cr alloys as an alternative to Ni superalloys) and wet corrosion (e.g. austenitic steel for biomaterials).

Black glasses are ceramic materials with an amorphous silica structure in which some of the O^{2-} ions have been substituted with C^{4-} ions. Due to the difference in valence, this type of substitution leads to a local increase in bond density and thus a strengthening of the network, resulting in an increase in the mechanical strength and the thermal and chemical stability of the glass. However, the structure of silica glasses can only accept a limited number of carbon ions. Hence, black glasses usually contain so-called free carbon in addition to Si-C and Si-O bonds. The mutual dependence between the number of carbon ions introduced into the lattice and the amount of free carbon determine the properties of black glasses. The choice of the method for obtaining black glasses is crucial in this regard. The most efficient method for their preparation is the sol-gel method, which involves the catalytically controlled hydrolysis and polycondensation of suitable organosilicon precursors introducing a Si-C bond, which are then subjected to pyrolysis. The application of the sol-gel method offers great opportunities to 'design' the final properties of materials at each stage of their preparation by selecting appropriate precursors (amount of carbon introduced, modifying cations) as well as process conditions (pH, amount of water, catalysts, etc.). Therefore, the synthesis stage mainly determines the final properties of black glasses. Changing the proportion, or the type of used precursors, determines the ratio of carbon content in two forms – structural (Si-C bonds – structure strengthening - resistance to high temperatures and aggressive environments) and free carbon phase (nanodomains or percolation paths – electrical conductivity). Our experience with obtaining black glasses allowed us to consciously select precursors in order to obtain materials with the required properties. Thus, coatings for interconnects, in addition to high corrosion resistance, must have had adequate electrical conductivity, which means that it was necessary to use precursors that enable the generation of significant amounts of free carbon providing electrical conductivity while maintaining heat resistance. In the case of aircraft turbine blades, on the other hand, it was necessary to obtain black glasses with as low a free carbon content as possible and, therefore, maximum chemical and thermal resistance, which can also be achieved through the appropriate selection of precursors and the introduction of additional modifying cations (e.g. Al^{3+}) into the glass structure. Thus, by appropriately selecting the type and ratio of organosilicon precursors, as well as those introducing other cations, solvents were obtained, on the basis of which coatings (applied by dip-coating technique) were obtained on ferritic steel substrates, with properties appropriate to their purpose. At this stage, several different layers were obtained based on different amounts and types of preceramic precursors.

METHODOLOGY:

In order to obtain coating materials with variable chemical compositions tailored to specific applications, and thus the required performance properties, a series of organic syntheses was performed with the sol-gel method using organosilicon precursors (methyltriethoxysilane and dimethyldiethoxysilane). Subsequently, layers were applied to previously ground and degreased metallic substrates (Crofer 22APU ferritic steel, TiAl alloy 48-2-2, Cr 99.9% and 316L austenitic steel) using the dip-coating technique, which, together with the solid materials (as a reference), were subjected to a 2-stage thermal treatment (air drying at 70°C for one week and pyrolyzing for 30 minutes at 800°C in argon). The obtained materials were subjected to the following tests:

- Rheological studies of the obtained sols using the plate-plate technique.
- Structural (GIXRD, XRD, FTIR, Raman, MAS NMR, XPS) and microstructural (SEM) studies with chemical composition studies (EDS, EPMA) of bulk materials and coatings after thermal treatment and after oxidation studies at high temperatures and under wet corrosion conditions.
- Studies of selected functional properties, including bioactivity and biocompatibility, electrical conductivity (DC 2-point 2-probe technique), and resistance to high-temperature oxidation (isothermal oxidation using TGA) and wet corrosion (EIS).

RESULTS AND DISCUSSION:

As part of the research, innovative protective coatings based on Si-O-C system materials – the so-called black glasses – were developed to reduce high-temperature oxidation of metallic SOFC (Solid Oxide Fuel Cells) structural components and aircraft turbine blades, as well as wet corrosion in the case of metallic biomaterials.

As anticipated, the effect of varying humidity and atmosphere during sol-gel syntheses was minimised through the purchase of a glovebox, thus eliminating the problem of reproducibility of results almost completely.

The most important achievements in papers 1 and 3 were the development of a procedure for obtaining films based on SiOC black glasses doped with cerium ions (Figs. 1 and 2) and phosphorus ions on austenitic steel, respectively. The addition of cerium ions led to a significant improvement in the chemical resistance of the black glass-based layers (Figs. 3 and 4) and in their antibacterial properties – key factors for their practical use as biomaterials. In turn, the successful introduction of phosphorus ions into the structure of black glasses (the first such reports in the literature) allowed a significant improvement in the biocompatibility of the obtained materials, which is also critical from a utilitarian point of view. Procedures for obtaining layers based on SiOC glasses were developed on the basis of extensive studies of the structure (XRD, FTIR, Raman, MAS NMR, XPS – (Figs. 5 – 8)) and microstructure (SEM with EDX, Confocal) of the obtained materials and their functional properties (chemical resistance, bactericity, biocompatibility, wetting angle, cytotoxicity).

In turn, the most important results achieved in papers 2, 4 and 6 were the development of a procedure for obtaining layers based on black glasses from the SiAlOC system on three different metallic substrates (2 – Crofer 22APU steel, 4 – TiAl alloy and 6 – chromium alloy), where in each case the results obtained showed a significant improvement in the resistance of the substrate to high-temperature oxidation:

- the mass gains after application of the layers were at the level of the best results obtained in the literature (Figs. 9 and 13),
- the films exhibited very good adhesion, where the mechanism of action was to 'trap' the outwardly diffusing cations in the structure, thus slowing down the corrosion process (Figs. 10–12 and 14–16),
- the phase composition of the cross-sections was studied in detail using a novel confocal Raman imaging technique (Figs. 10, 11, 14 and 15), which provides a fast, simple and inexpensive way to circumvent the limitations of other commonly used methods such as XRD, EBSD or TEM.

Paper 5 is devoted to the preparation of layers (by electrophoretic deposition – EPD) based on suitably modified carbon nanotubes on austenitic steel. In this paper, on the basis of detailed studies of the structure (XRD, FTIR, Raman) and microstructure (SEM with EDX – (Figs. 17–20)), the phenomena accompanying the deposition process and the influence on this process of various factors (overpotential, concentration of modifying ions, etc.) were precisely described. It was clearly demonstrated that, by appropriate selection of the process parameters, the morphology and phase composition, and thus the functional properties of the obtained layers, can be controlled with relative ease. For the first time, the growth process of copper oxide crystals on carbon nanotubes during the EPD process was described in detail. This publication inspired the combination of the remarkable properties of black glasses (described above) and carbon nanotubes.

SUMMARY:

From the point of view of the project's objectives, where several different applications for the same layers were indicated, it was possible to demonstrate the beneficial effects of the developed coatings, for completely different metallic substrates, which indicates their versatility and gives hope for further, numerous research works in collaboration with strong foreign centres, for which further studies on other metallic substrates are already underway. Furthermore, extensive structural and microstructural studies (with an emphasis on Raman spectroscopy) have led to the publication of numerous papers in reputable journals, as well as numerous collaborations with centres at home and abroad.

The obtained results, the cooperation with foreign entities (DECHEMA), as well as the previous achievements, among others, during the implementation of this project, provide a solid foundation and give high hopes for obtaining funding from NCN and NCBiR, which in turn should contribute to the improvement of the AGH University coefficients, such as the number of awarded projects, the number of citations in connection with works in recognised journals, and the internationalisation of research work.

The research carried out has a significant impact on POB 7, due to the design and production of a state-of-the-art coating material that combines the fundamentals of materials science and chemistry, including in particular synthesis - microstructure - structure - properties - application. Thanks to the purchase of the glovebox, syntheses of coating materials were performed using the sol-gel method under strictly controlled conditions, making it even easier to design corrosion-resistant coatings for specific applications.

PUBLICATIONS (LISTED ACCORDING TO PUBLISHING DATE):

1. M. Gawęda, P. Jeleń, M. Bik, M. Leśniak, M. Sowa, W. Simka, M. Golda-Cepa, M. Brzychczy-Włoch, Z Olejniczak, Marek Nocuń, M. Sitarz „Modification of SiOC-based layers with cerium ions - influence on the structure, microstructure and corrosion resistance" Applied Surface Science 543 (2021).IF=7.392.
2. M. Bik, M. Galetz, J. Dąbrowa, K. Mroczka, P. Zając, A. Gil, P. Jeleń, M. Gawęda, M. Owińska, M. Stygar, M. Zajusz, J. Wyrwa, M. Sitarz "Polymer Derived Ceramics based on SiAlOC glasses as novel protective coatings for ferritic steel" Applied Surface Science 576 (2022) 151826. IF=7.392.
3. M. Gawęda, P. Jelen, M. Bik, M. Szumera, Z. Olejniczak, M. Sitarz "Spectroscopic studies on phosphate-modified silicon oxycarbide-based amorphous materials" Spectrochimica Acta Part A: Molecular and Biomolecular Spectroscopy 291 (2023).IF=4.4.
4. M. Bik, M. Galetz, L. Mengis, E. White, W. Wieczorek, K. Łyszczarz, K. Mroczka, J. Marchewka, M. Sitarz "Oxidation behaviour of uncoated and PDC-SiAlOC glass-coated TiAl at 750 °C in dry and humid air" Applied Surface Science 632 (2023). IF=7.392
5. J. Marchewka, E. Kołodziejczyk, P. Bezkosty, M. Sitarz "Characterization of electrochemical deposition of copper and copper(I) oxide on the carbon nanotubes coated stainless steel substrates" Scientific Reports 13 (2023).IF=4.6.
6. N. Petry, M. Bik, Ł. Wilk, R. Swadźba, A. Ulrich, M. Sitarz, M. Lepple, M. Galetz "Novel Polymer-derived SiAlOC Coating to Improve the High-Temperature Resistance of Chromium" Surface and Coatings Technology. Manuscript Number: SURFCOAT-D-23-03284 (status – under review). IF=5.4

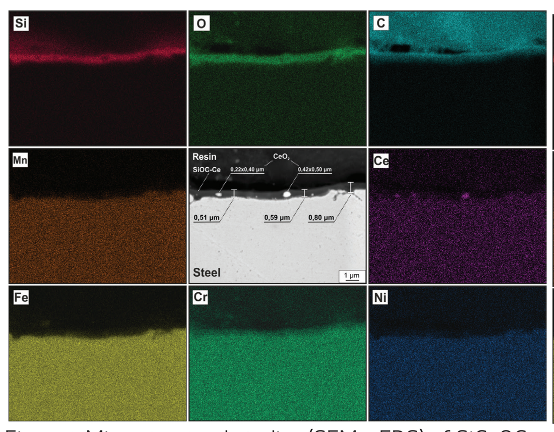

Figure 1. Microstructural studies (SEM + EDS) of SiCeOC coating with 1% of Ce - cross-section.

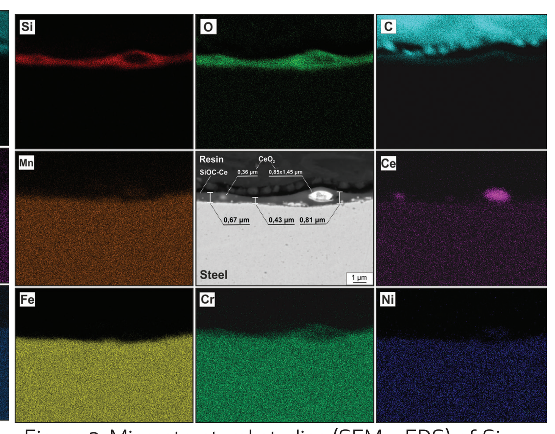

Figure 2. Microstructural studies (SEM + EDS) of SiCeOC coating with 2% of Ce - cross-section.

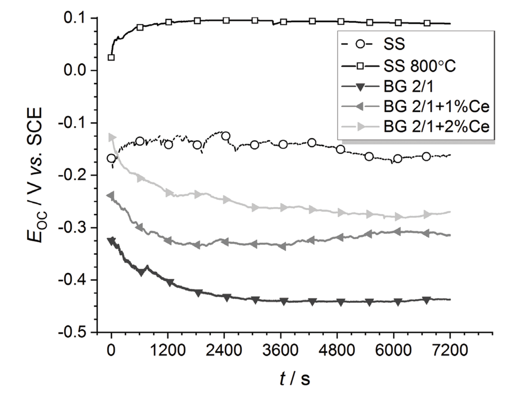

Figure 3. Open-circuit potential variation with time for the bare stainless steel before (SS) and after the heat treatment (SS 800°C) as well as samples coated with black glasses: TD (SiOC), TD_1Ce (SiOC with 1% of Ce) and TD_2Ce (SiOC with 2% of Ce)with 2% of Ce - cross-section.

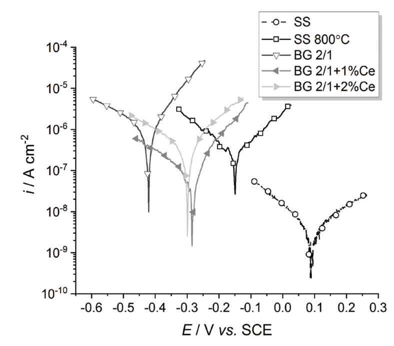

Figure 4. Potentiodynamic polarization curves obtained for the stainless steel specimens before and after coating with the amorphous layers.

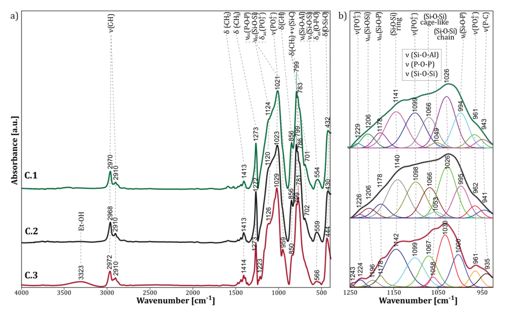

Figure 5. Infrared spectra of the polymeric precursors – ladder-like silsesquioxanes modified with phosphate ions (based on (2-diethylphosphatoethyl)-triethoxysilane) and co-dopped with aluminium ions: full-range spectra (a) followed by decomposition of the chosen region to component bands (b).

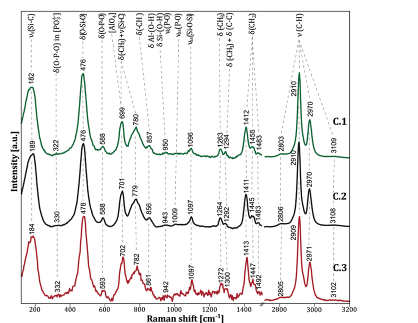

Figure 6. Raman spectra of xerogels from the SiAlPOC series.

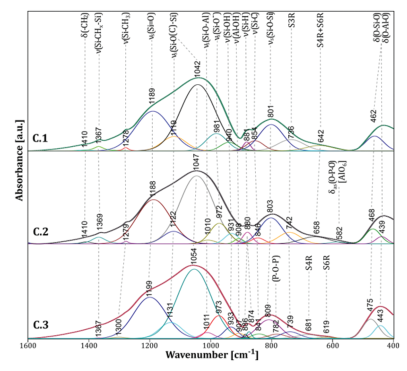

Figure 7. Decomposed FTIR spectra of ceremized SiOC-based modified amorphous materials modified with phosphate and co-doped with aluminium ions.

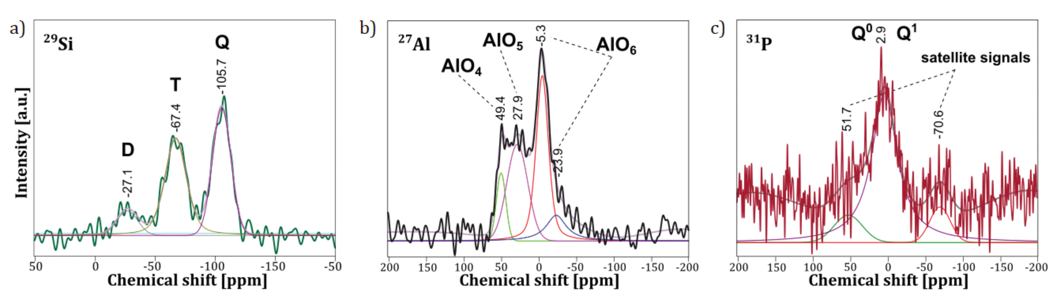

Figure 8. IMAS-NMR spectra of the ceramic C.1 sample from SiAlPOC system.

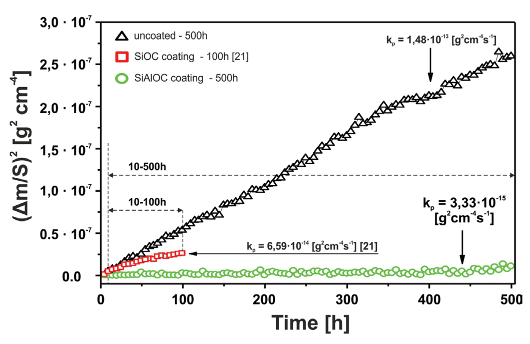

Figure 9. Mass changes of uncoated and SiAlOC-coated Crofer 22APU steel samples exposed at 800 °C for 500 h.

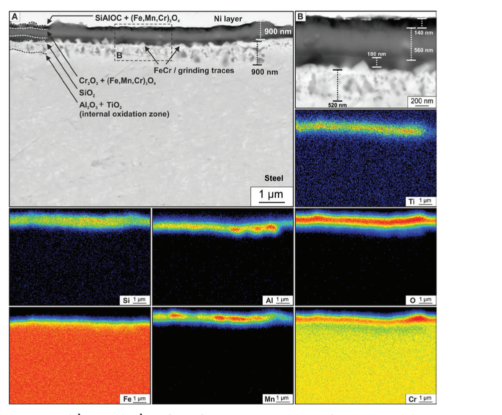

Figure 10. A) and B) BSE-SEM images of the cross section of the SiAlOC coated Crofer 22APU steel exposed at 800 °C for 500 h and elemental maps from EPMA analysis.

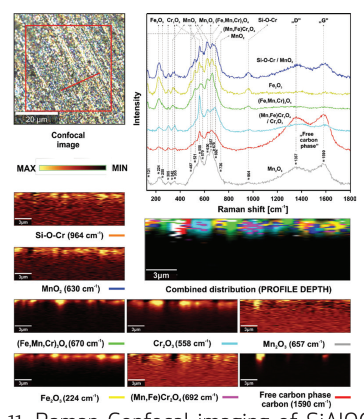

Figure 11. Raman Confocal imaging of SiAlOC coated sample exposed at 800 °C for 500 h – in case of all Raman results, distribution images of the phases (based on integration of the characteristic band with the Raman shift given in the brackets) are presented with the corresponding spectra.

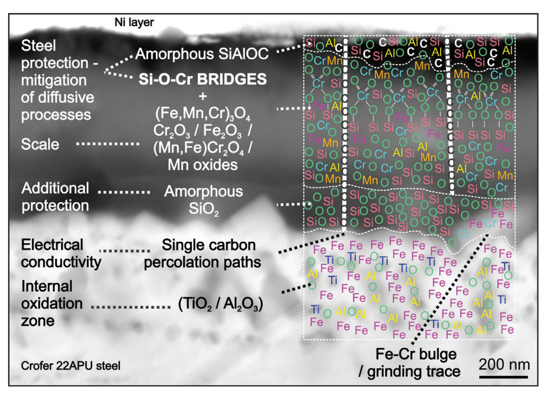

Figure 12. Morphology of oxidized SiAlOC glass coatings.

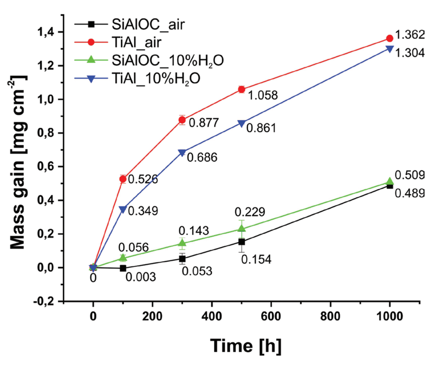

Figure 13.Oxidation kinetics of both uncoated and SiAlOC-coated 48-2-2 TiAl alloy in dry and humid air.

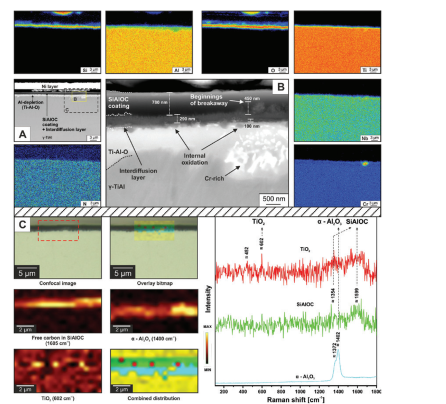

Figure 14. A) and B) Cross-sectional microstructure and EPMA analysis (taken from Fig. A); C) Raman confocal (imaging of SiAlOC-coated 4822 TiAl alloy oxidized for 300 h in dry air conditions.

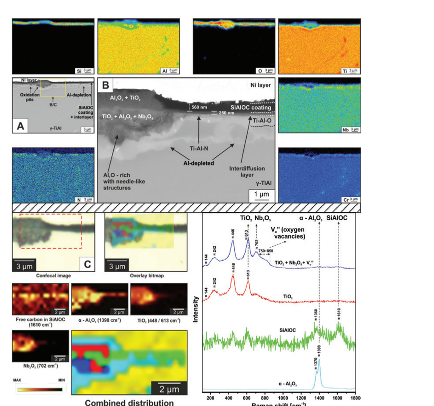

Figure 15. A) and B) Cross-sectional microstructure and EPMA analysis (taken from Fig. A); C) Raman confocal imaging of SiAlOC-coated 48-2-2 TiAl alloy oxidized for 300 h in humid air conditions.

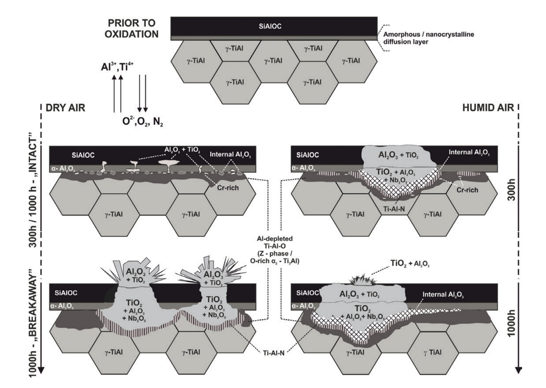

Figure 16.Overview of degradation for SiAlOC coated 48-2-2 TiAl alloy oxidized in both dry and humid air conditions.

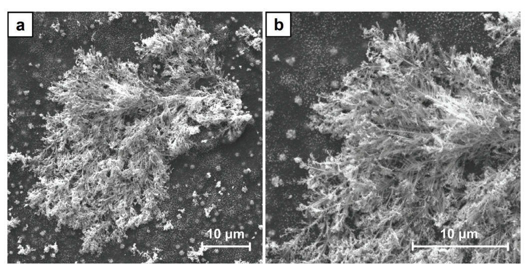

Figure 17. SEM images of the dendritic crystals formed on CNT layer (EPD deposition time of 450 s, CuSO4 concentration of 1 mM) at the magnification of ×5000 (a) and ×10,000 (b).

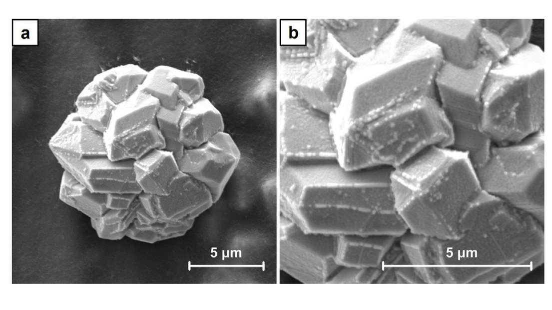

Figure 18. SEM images of the crystals agglomerate formed on CNT layer (EPD deposition time of 600 s, CuSO4 concentration of 100 mM) at the magnification of ×15,000 (a) and ×30,000 (b).

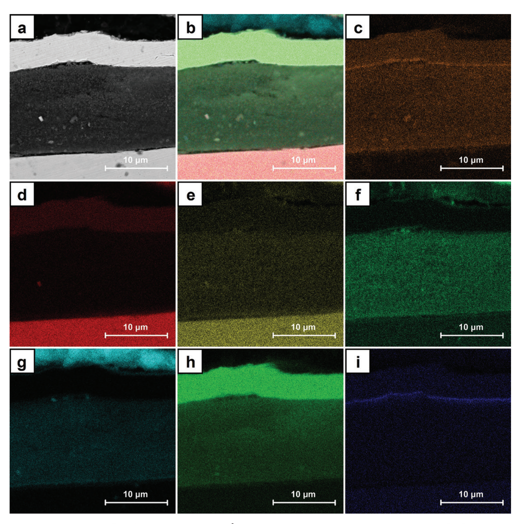

Figure 19. SEM images (EPD deposition time of 600 s, CuSO4 concentration of 1 mM): cross section (a), cross section with elements distribution (b), single element distribution (c–i) including copper (c), iron (d), chromium (e), oxygen (f), carbon (g), nickel (h) and gold (i).

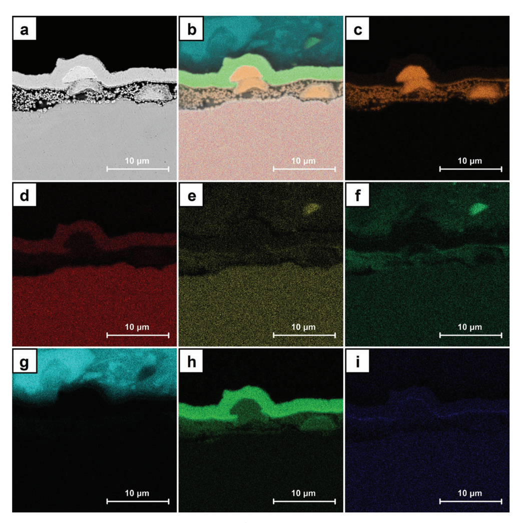

Figure 20. SEM images (EPD deposition time of 600 s, CuSO4 concentration of 100 mM): cross section (a), cross section with elements distribution (b), single element distribution (c–i) including copper (c), iron (d), chromium (e), oxygen (f), carbon (g), nickel (h) and gold (i).