

Surface microcracks in Cu-OFP exposed to air or water with sulphides

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Summary	
<p>Specimens manufactured from Cu-OFP were tested in air and in water with 80 mg/l sulphide. Post-test analysis of the surfaces of specimens tested in air by scanning electron microscope (SEM) revealed a large number of surface microcracks (in the range of several thousand per mm²) with a maximum length of not more than about 50 µm. Increasing the extent of plastic deformation resulted in an increasing number of surface microcracks.</p> <p>Specimen tested in water with 80 mg/l sulphide showed no details that could be positively identified as surface microcracks. This was proposed to result from surface microcracks forming on the surface due to plastic deformation being so low in depth that they are consumed by the few µm thick sulphide film when it forms and thus were not present on the surface anymore to be detected by SEM.</p> <p>The main conclusion from the work is that for the Cu-OFP batch used in the study the surface microcracks form due to plastic deformation only, and not due to the exposure to sulphide containing water. Additionally, exposure to water with 80 mg/l sulphide does not seem to result in environmentally induced growth of the surface microcracks forming due to plastic deformation.</p> <p>In order to verify that these main conclusions are not batch-dependent, several additional batches need to be investigated. Also, to verify that the small thickness of the specimens used in the present study (of the order of 3 to 6 grain sizes of the Cu-OFP used) does not affect the formation of the microcracks, specimens with a thicker gauge length need to be studied. Another task for future work is to check the depth of the microcracks forming in specimens tested in air.</p>	
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Preface

This report forms part of the year 2023 deliverables of the DEHYDSU-project within the SAFER2028 Research Programme.

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1. Introduction

The nuclear fuel disposal technology in Finland and Sweden (both based on the KBS-3 concept) is slowly maturing. Some issues regarding the main corrosion protection offered by the copper canister still remain to be further studied, among them the possibility of stress corrosion cracking (SCC) of Cu-OFP induced by sulphides in the ground water.

The Radiation safety authority in Sweden, SSM (Strål säkerhets myndigheten), in their report 2018:07 and the Land and Environmental Court in Sweden - in their statement of Yttrande M 1333-11, both express their concern about the possibility of the so-called Aaltonen mechanism in reference to the stress corrosion cracking of phosphorus micro-alloyed copper, Cu-OFP, in presence of sulphide in the repository environment. Recently, the so-called Aaltonen-mechanism of SCC was shown [1] to be a refinement of the common slip-oxidation mechanism of SCC, and not a separate new SCC mechanism per se.

Regarding specifically the possibility of SCC induced in Cu-OFP by sulphides, the early Japanese study by Taniguchi & Kawasaki [2] claimed SCC is possible for copper in presence of sulphide, but later investigations [3-8] have failed to unequivocally support the claim.

The main result supporting the hypothesis that Cu-OFP is susceptible to SCC in presence of sulphides is that several research groups have identified surface microcracks/defects on Cu-OFP samples mechanically tested to higher levels of plastic deformation. Becker and Öijerholm [7] studied Cu-OFP with tapered specimens and slow strain rate testing (SSRT) up to about 9% of total strain. They found microcracks/defects on the surface of the specimens, part of which were claimed to be SCC microcracks (Fig. 1b). The microcracks/defects size was a few tens of micrometers at maximum, roughly like those found by Taniguchi & Kawasaki [2]. Becker and Öijerholm also found similar microcracks/defects deep inside the material where an effect from the exposure environment could be excluded (Fig. 1c). Rantala [9] has found similar surface microcracks/defects in long term creep experiments tested in air at 152°C (Fig. 1a). It appears that this type of defects form in Cu-OFP under pure mechanical loading without sulphide exposure and without even an aqueous exposure. Thus, to investigate the possibility of SCC in Cu-OFP in the presence of sulphides it would be highly beneficial to study the nature of these microcracks/defects more carefully. Recently [10], surface microcracks found on Cu-OFP tested in water with 32 mg/l sulphide were interpreted to form as a result of preferential dissolution of grain boundaries, i.e. intergranular attack (IGA).

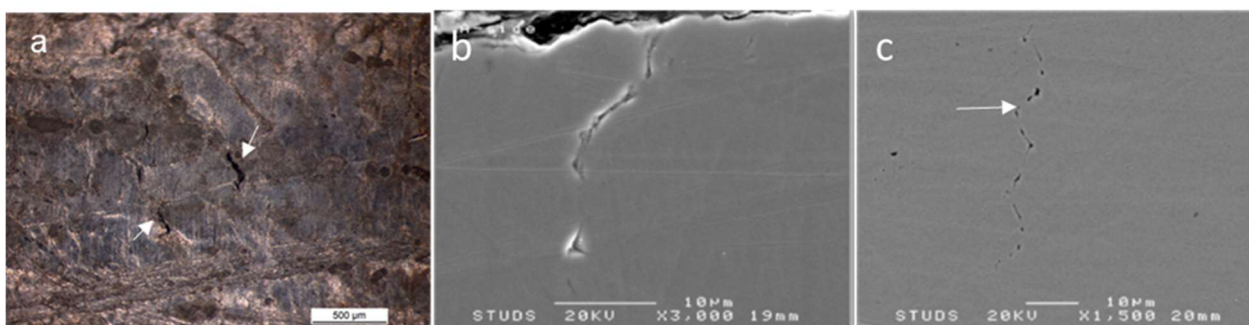


Figure 1. Surface microcracks/defects in Cu-OFP; a) creep specimen after testing in air at $T = 152^{\circ}\text{C}$ and 120 MPa for 73697h (8.4y) [9], b) tapered SSRT specimen tested at $T = 90^{\circ}\text{C}$ and $\sim 1.9 \text{ mg/l HS}^{-}$ [6], c) inside a tapered SSRT specimen tested at $T = 90^{\circ}\text{C}$ and $\sim 0.1 \text{ mg/l HS}^{-}$ [6].

2. Goal

The goal of the work is to examine the nature of the surface microcracks/defects found on Cu-OFPP and especially the possible role of sulphides in water in promoting the appearance and/or growth of them.

3. Description

The Cu-OFPP material studied was delivered by SKB (Svensk Kärnbränslehantering AB). The received material had approximate dimensions of 170x130x50 mm, cut from the tube T58. The material had been characterised and found to meet the requirements [11]. The average mechanical properties of nine samples representing different locations within the tube material are shown in Table 1. The average concentration of phosphorus and impurities is shown in Table 2. The average grain size in different parts of the tube varied between 0.07 and 0.16 mm [11], which averages to about 75 grains per mm².

Table 1. Average room temperature mechanical properties of the material [11].

R _{p0.2} N/mm ²	R _m N/mm ²	Elongation %	Hardness HV5
42	212	52	43

Table 2. The average phosphorus and impurity concentration of the material [11].

P ppm	S ppm	O ppm	H ppm
58.7	5.4	3.0	0.43

4. Limitations

Only one batch of Cu-OFPP was studied (delivered by SKB). The gauge thickness of the used tensile specimens was about 0.45 mm corresponding to roughly 3 to 6 grain sizes of the material. Both of these factors may affect the results, although it is expected that they will not influence the main conclusions made.

5. Methods

All tests were made at room temperature, T = 23°C. The tensile tests (using a strain rate of 3*10⁻⁵ s⁻¹) were performed with a slow strain rate testing (SSRT) device manufactured by Cornet Ltd. The Cu-OFPP specimen gauge part had dimensions of 0.5 mm (thickness before final surface finish), 8 mm (width) and 29 mm (length of the deforming part of the body). The specimen design is shown in Figure 1. The specimens were manufactured with Electric Discharge Machining (EDM), after which the EDM-affected layer was removed from the gauge part of the specimens using SiC-papers and polished up to a #1200 finish. The final thickness of the specimen gauge part (after removing the EDM- affected layer and polishing) was about 0.45 mm.

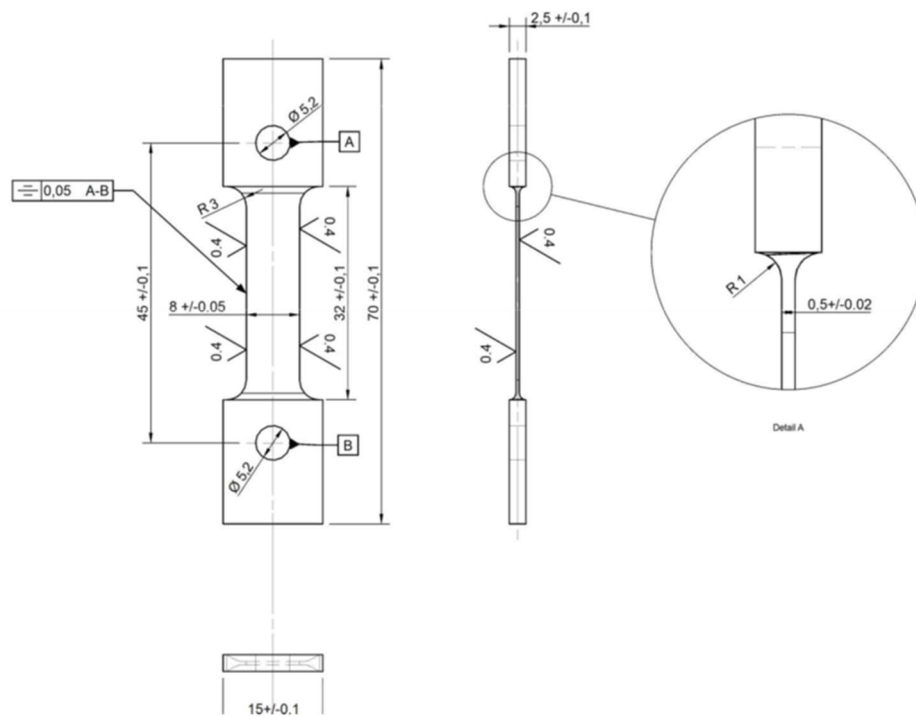


Figure 1. Specimen design.

The specimens were attached to the loading grips of the SSRT machine, electrically insulated from the grips by ZrO_2 parts. The loading part was attached to an autoclave lid. In the tensile tests performed in air, the temperature was 23 ± 1 °C. In the tensile tests performed in water, the loading part was placed inside the autoclave body. All autoclave parts were made of AISI 316L stainless steel. The pull rod extended through the autoclave lid via a Ballseal™ spring loaded sealing element, with a friction force of 59 N at room temperature. The autoclave was equipped with a Ag/AgCl(0.05 M KCl) reference electrode and a Pt counter electrode. An Autolab PGSTAT302F potentiostat with Nova 2.0 software was used to measure and control the potential and current of the specimen. Tube pumps (Cole-Parmer Instrument Co.) were used to pump the electrolyte through the autoclave. The loading of the specimen was controlled by Cornet SSRT system v. 4.03. The tensile tests were performed at a strain rate of $3 \times 10^{-5} \text{ s}^{-1}$.

The water used for the sulphide test was a buffer solution ($H_3BO_3 + NaOH$) with a target pH = 8.0. The pH was measured from grab samples using a Thermo Scientific Orion 5 Star pH-meter. The sulphide addition ($Na_2S \cdot xH_2O$, 60-63%) was made at a target concentration of 80 mg/l (2.5 mM) to a 10 l glass stock vessel filled with the buffer solution, which was previously bubbled oxygen free with 5N N_2 -gas (Aga Ltd). The glass stock vessel was then pressurized to 0.5 bar overpressure with 5N N_2 to keep oxygen out and to balance the pressure drop caused by the outgoing flow. Since no continuous bubbling through was used (only pressurization) gaseous H_2S was not able to escape from the stock solution and the sulphide concentration in the stock solution tended to stay constant.

After adding the sulphide to the stock vessel, the autoclave was bubbled oxygen free with 5N N_2 -gas and the tube pump was used to pump the electrolyte through the autoclave. After flowing through the autoclave, the solution was directed to a 40 l storage tank where $FeCl_3 \cdot 6H_2O$ was used to neutralize sulphide.

The sulphide concentration was measured from the autoclave outlet from grab samples using Chemetrics C-9510D-kit for large concentrations (5 to 300 mg/L).

In post-test examinations, a field emission gun - scanning electron microscope (FEG-SEM) Zeiss Crossbeam 540 equipped with solid-state four-quadrant backscatter detector were used to characterize the specimens.

The specimen surface and cross sections were analysed by SEM-secondary electron (SE) imaging and backscatter electron (BSE) imaging. SE imaging was performed with high voltage mode and low voltage mode at working distance (WD) of 10–15 mm. High voltage mode is with 15 keV, 1.5 nA, while low voltage mode is with 5 keV, 0.5 nA. High voltage mode is more sensitive to chemical composition difference while low voltage mode is more sensitive to surface layer topography. BSE are based on the dependence of the backscatter electron signal on the orientation of crystal lattice planes with respect to incident electron beam due to electron channelling. BSE images were acquired with the solid-state four-quadrant backscatter detector at 15 kV acceleration voltage with WD of 5–9 mm.

Inclusion and oxide layer chemical analysis was performed with SEM-Energy Dispersive X-Ray (EDS) with 15 keV, 1.5 nA. For the sub-micrometer structures, to reduce the interaction volume of the incident electrons, EDS with 5 keV, 1.5 nA was applied.

The SEM-pictures were analyzed for microcracks using the Image-J software. Note that the contrast in SEM-pictures was deliberately chosen greater than normally in order to facilitate the ability of the software to detect microcracks.

The sulphide film forming on copper in sulphide containing water needs to be removed to allow for a SEM-study of the metal surface beneath the sulphide film. The sulphide film was removed from the specimen tested in water with 80 mg/l HS⁻ using a procedure attained originally from University of Western Ontario, Canada (courtesy of SKB, Sweden). The procedure consists of eight steps as follows:

1. Pre-sparge 1 M HClO₄ + 0.025 M C₆H₁₂N₄ (hexamethylenetetramine) solution with high-purity Ar for at least 45 min;
2. Immerse the corroded Cu sample into the solution above for 3 min;
3. Rinse the Cu sample with ion pure water and dry with Ar gas;
4. Remove the corrosion products using an adhesive tape (e.g., package tape) by applying it to the surface and removing the tape rapidly;
5. Repeat (4) until no corrosion products can be removed, ensure by optical microscopy that tape residues are minimized;
6. Sonicate the Cu sample in methanol for 20 min;
7. If needed (i.e, the surface is still covered with corrosion products observed by optical microscope or scanning electron microscope), repeat steps 1 to 6;
8. Rinse the Cu sample with ion pure water, dry the sample using a jet of Ar stream, and store the sample in anaerobic chamber to minimize oxidation if needed.

To ensure that the glue from the tape used in the sulphide film removal procedure is thoroughly removed, an additional step was used involving soaking the specimen in a washing solution (EkoPuhto) for 10 minutes and then brushing gently with a soft toothbrush, followed by rinsing in ion pure water, acetone and ethanol. This was done since the SEM EDS results on the sulphide exposed specimen after using the original procedure showed suspiciously high carbon concentrations (85 to 95%), probably resulting from tape glue remains. This step was added between steps 5 and 6 in the original procedure, after which SEM EDS showed no carbon.

6. Results

Four polished specimens have been tested in air, one in air to about 5% deformation, one to about 10% deformation and two to fracture. One polished specimen has been tested to fracture in water with 80 mg/l HS⁻. These specimens have been investigated with SEM to check for microcracks. Additionally, three specimens have been tested as reference to fracture in air, without removing the EDM-affected layer from the surface.

6.1 Tensile tests results

Figure shows a comparison of the stress-strain curves of the polished specimens tested to fracture in air. Also shown are results from two polished specimens tested to fracture in air in an earlier assignment for SKB [12].

The fracture strain of all tested specimens falls clearly below that measured with standard specimens, 52%, Table 1. There can be several reasons for this. The gauge thickness of the specimens used here is about 0.45 mm, which means that the thickness covers roughly 3 to 6 grains of the material (grain size is about 0.07 to 0.16 mm [11]). Also, because of the specimen design (the gauge length is smaller than the heads), the removal of the EDM-affected layer and final polishing needs to be made by hand, which may introduce additional deformation to the material. This is seen e.g. as an elevated yield stress (about 75 N/mm² in Figure compared to 42 N/mm² in the standard tensile tests, Table 1). Also, the tensile tests presented here were performed with a smaller strain rate ($3 \times 10^{-5} \text{ s}^{-1}$) than that typically used in the standard tensile tests.

In order to check for the effect of the EDM-affected layer, three specimens were tested in air to fracture without removing the EDM-affected layer, the results are shown in Figure 4. The three tests made without removing the EDM-affected layer show a slightly higher fracture strain and a clearly higher tensile strength than the tests made after the EDM-affected layer was removed. This indicates that, with the specimen design used in this work, the EDM-affected layer does not deteriorate the tensile properties of the Cu-OFP material. The stress-strain curves of these two together with the "Air 1" curve are shown in Figure .

Figure shows the stress and elongation as well as the measured sulphide concentrations as a function of time for the test performed in water with 80 mg/l sulphide. The experiment was performed in two phases. In the first phase, the specimen was loaded to a stress level of 115 MPa and kept there for a period of 42 hrs, to allow for sulphide film formation process to reach a steady state. During this period, the specimen was subjected to creep, proceeding with a strain rate of about $1 \times 10^{-7} \text{ s}^{-1}$. At the end of this period, the loading was changed to a tensile test with the same strain rate as was used in the tests performed in air, i.e. $3 \times 10^{-5} \text{ s}^{-1}$. The fracture strain was 31.8%, thus slightly higher than for the specimens Air 1 and Air 2 tested in air, but within the expected scatter band. This indicates that the exposure to water with 80 mg/l HS⁻ did not have an adverse effect on the fracture strain, which further indicates that no SCC was taking place during the exposure.

The "Air 1" and the specimen tested in water with 80 mg/l HS⁻ were chosen for further study with SEM. In addition, two polished specimens were tested in air, one to about 5% deformation and the other to about 10% deformation. Both of these specimens were also used for further study with SEM.

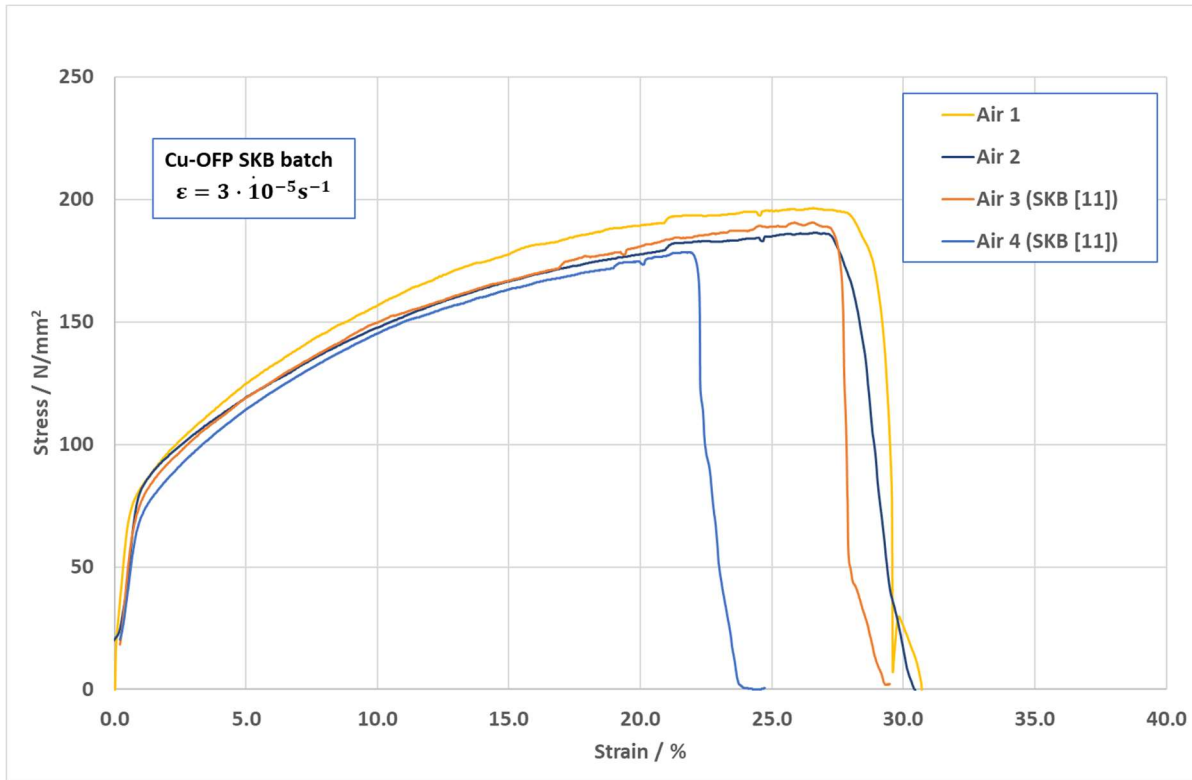


Figure 3. Comparison of tensile stress-strain curves tested in air (Air 1 and Air 2). Also shown are two tests performed earlier in air for the same material batch and specimen design (Air 3 and Air 4 [12]).

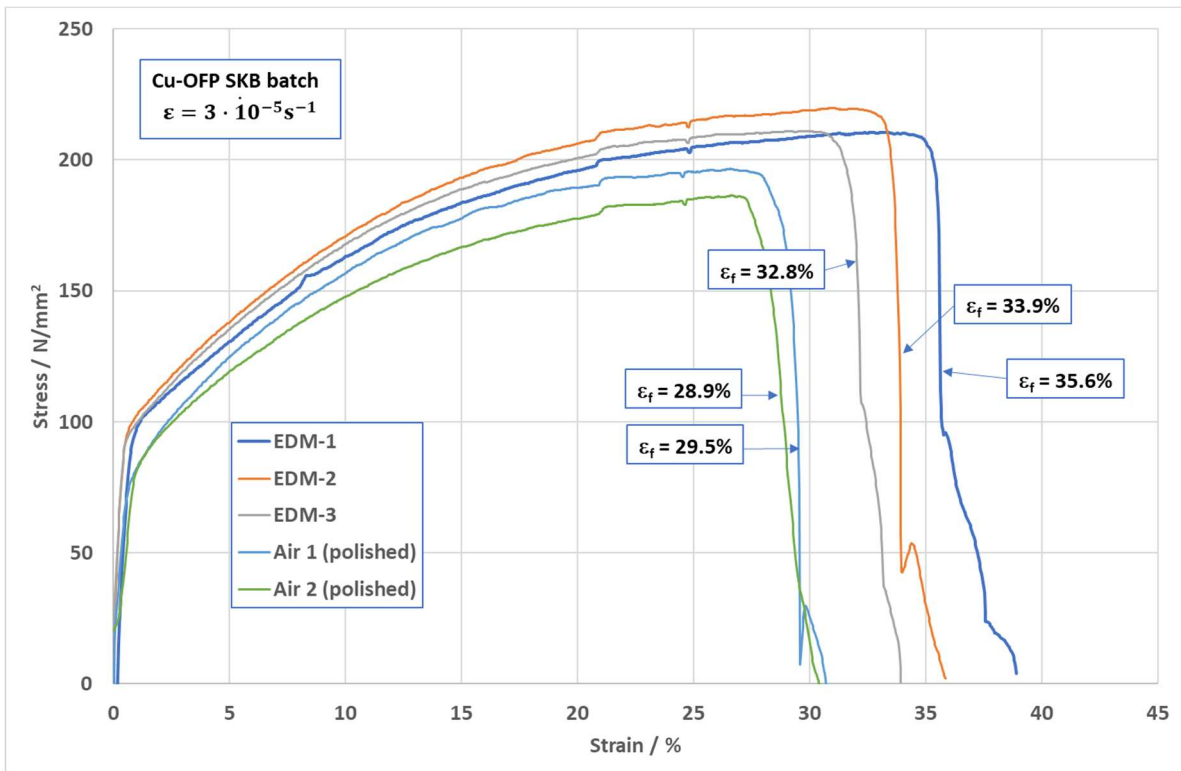


Figure 4. Comparison of tensile stress-strain curves tested in air (Air 1 and Air 2 EDM-affected layer removed, EDM-1 to EDM-3 with the EDM-affected layer).

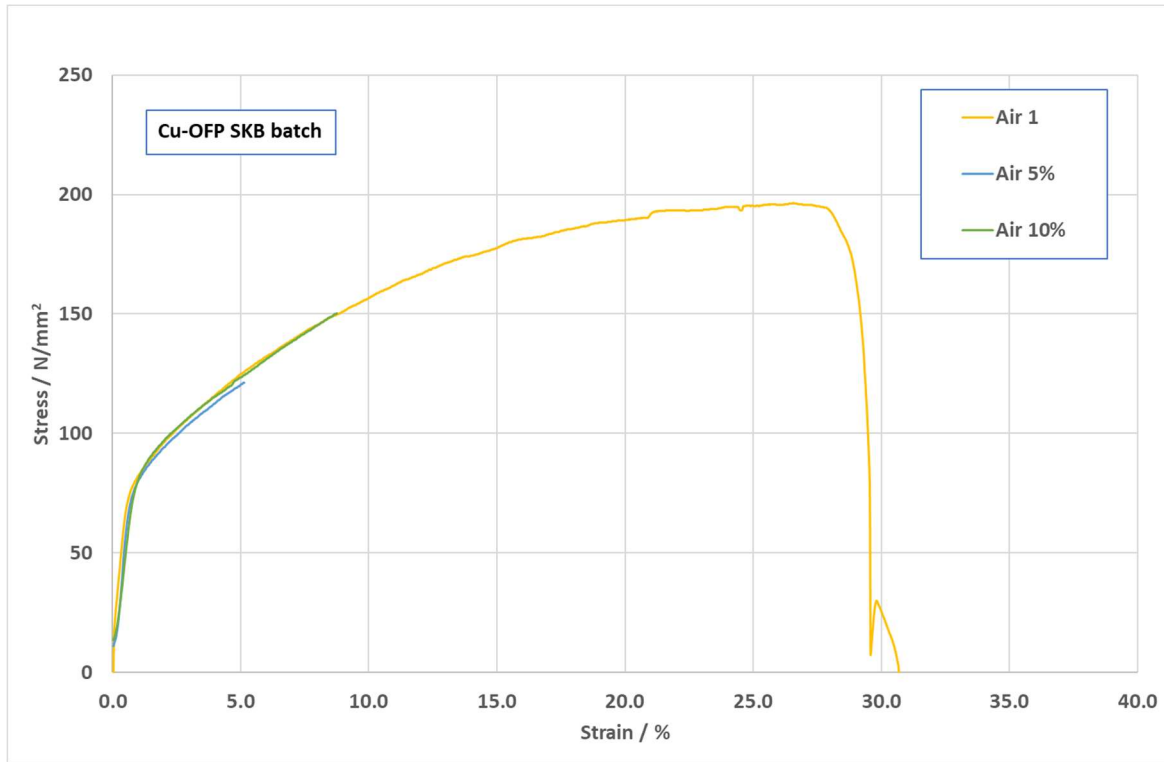


Figure 5. The stress-strain curves of two specimens tested to 5% and 10% strain, also shown the result for specimen Air 1 tested in air to fracture.

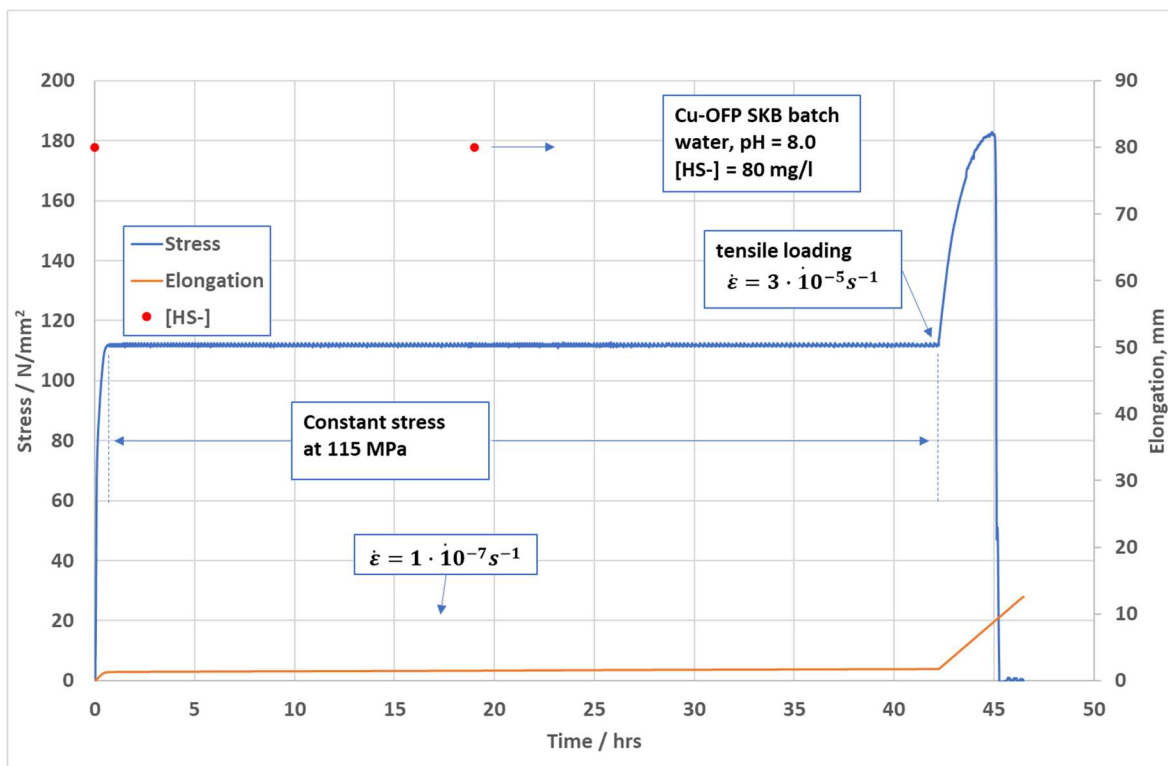


Figure 6. Stress and elongation as a function of time in water with 80 mg/l HS⁻. Fracture strain was 31.8%. The red dots mark the measured sulphide concentrations.

6.2 SEM study results

An example of the microcracks found on the surfaces of the specimens tested in air is shown in Figure . The size of the analysed area in one picture with this magnification (x1000) is about 0.009 mm². In this case, as shown in Figure b, altogether 56 microcracks were found, mostly in the size category of 1 to 6 µm. This adds to over 6000 microcracks per square millimetre. The largest microcrack found in all the investigated areas was about 50 µm. For each of the air-tested specimens analysed, four different areas were examined to provide a statistical average of microcracks found.

In order to verify that the sulphide film removal procedure does not affect the microcracks existing on the surface, the sulphide removal procedure was applied on specimen Air 2, tested to fracture in air. Comparing Figure C (1000X) with Figure A (1000X) shows that the sulphide film removal procedure does not affect the appearance of the microcracks, i.e. the chemicals used in the procedure do not e.g. dissolve the surface.

An example of surface microcracks found on the specimen tested in air to 5% deformation is shown in Figure . When comparing with Figure it is clear that fewer microcracks were present, i.e., the increase of deformation resulted in an increase in the number of microcracks.

The total number (average of four different areas for each specimen) of microcracks in the three air-tested specimens as a function of the extent of plastic deformation is shown in Figure . Almost half of the microcracks were found to have formed already at 5% plastic deformation. Figure shows the number of microcracks larger than 6 µm. It is clear that the formation of these larger microcracks is much more probable as the extent of plastic deformation increases.

The same procedure for analysing the number and length of microcracks was performed on three SEM-pictures taken on a lower magnification (200X) of the surface of the specimen tested in air to fracture. With this magnification the smallest reliably identified microcrack length was 5 µm. Figure shows the total number of microcracks identified and Figure the number of microcracks with a length longer than 15 µm. It is clear that a larger number of microcracks longer than 15 µm could be identified with the lower magnification of 200X than with a magnification of 1000X, having an analysed area of about 0.22 mm² (25 times larger than with the magnification of 1000X). Within the three areas analysed, on average, the number of microcracks longer than 15 µm was 67 per mm². Based on the higher magnification (1000X) pictures the number of microcracks longer than 15 µm was estimated at 194 per mm². These numbers are roughly equal to the number of grains per mm², estimated at 75. One could thus hypothesize that the longer than 15 µm microcracks form at grain boundaries. However, the majority of the microcracks are found within the grains and thus are associated with some internal structures of the grains, probably related to the arrangement of dislocations.

The surface of the specimen tested to fracture in water with 80 mg/l HS⁻, after removing the sulphide film with the procedure described above, is shown in Figure . The main observation is that there are very few details that resemble the microcracks identified on the surface of the air tested specimens (see Figure to Figure). A few features were detected which were suspected to be traces of earlier surface microcracks (see the red circles in Figure C), partially consumed by the sulphide film formation process. In this line of thinking, the plastic deformation does produce microcracks also when the specimen is exposed to water with sulphides, but in most cases their depth is so small that when the sulphide film forms with thickness of a few µm [13], they are consumed and not present on the surface anymore.

The surface of the specimen tested in water with 80 mg/l sulphide showed a major part of areas named as “decoration”, and also some areas which still show the polishing marks, see Figure . A detail of the “decoration” area with a larger magnification (10kX) is shown in Figure . It appears there are still Cu_xS - particles residing in the structure. Table 3 shows the compositions (a-%) of the three EDS spots analysed. The large particle targeted in Spot 1 is definitely Cu_xS . Note that for the acceleration voltage used, the spot size in EDS has a diameter of about 1.5 μm , and thus analyses over a small detail such as here can include information from the surrounding area as well. Based on the pore-like structure of the “decoration” areas, it would appear that the sulphide film has grown “roots” into the base metal, i.e. the growth has occurred along some preferential crystallographic lines.

Table 3. The compositions (a-%) of the EDS spots in Figure .

Spot	O	S	Cu
1	7.03	29.33	63.65
2	8.54	7.35	84.12
3	8.29	0.69	91.02

Another example of the surface appearance of the specimen tested in water with 80 mg/l sulphide is shown in Figure , again showing no features positively identified as microcracks. A few details suspected to be remains of microcracks are marked with red circles in Figure C.

Figure shows the surface of Air 2 specimen (tested to fracture in air), with five EDS -spots marked. The EDS analyses of these spots showed 100% Cu.

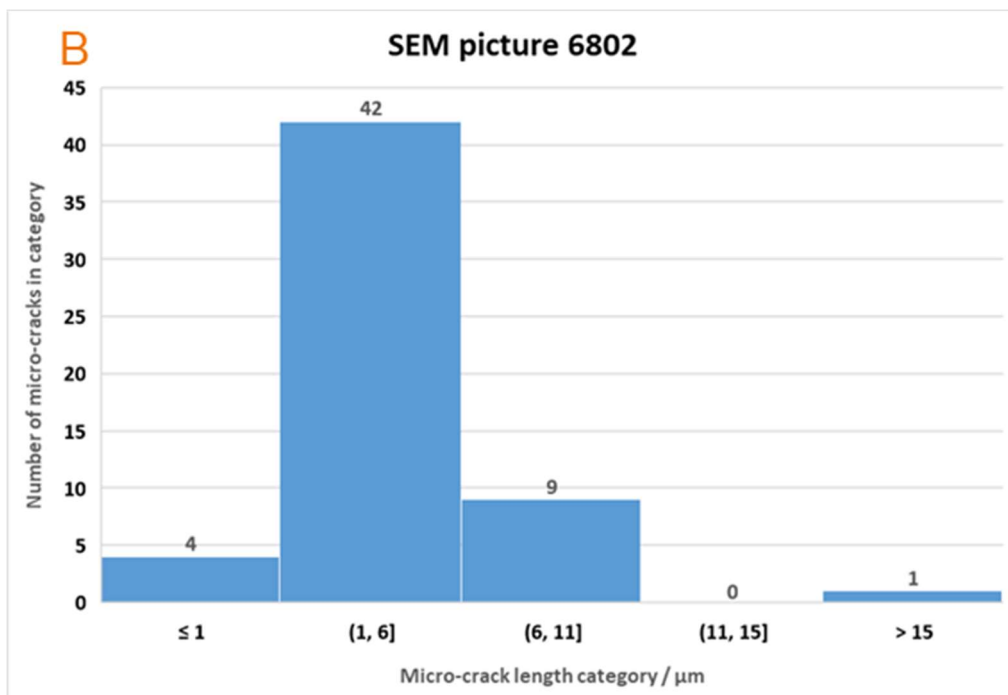
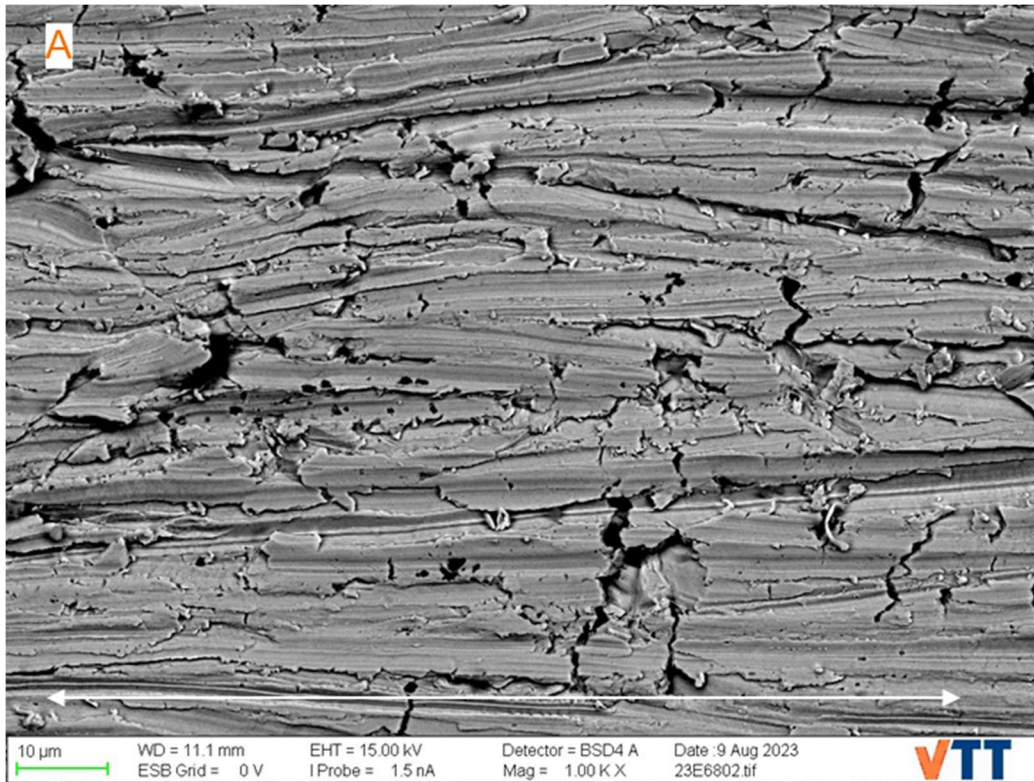


Figure 7. Example of the surface of the tensile specimen Air 2 tested in air to fracture (a) and the number of microcracks identified as categorized by their size (b). The white arrow shows the direction of the tensile loading as well as the direction of the final polishing (with polishing marks clearly visible).

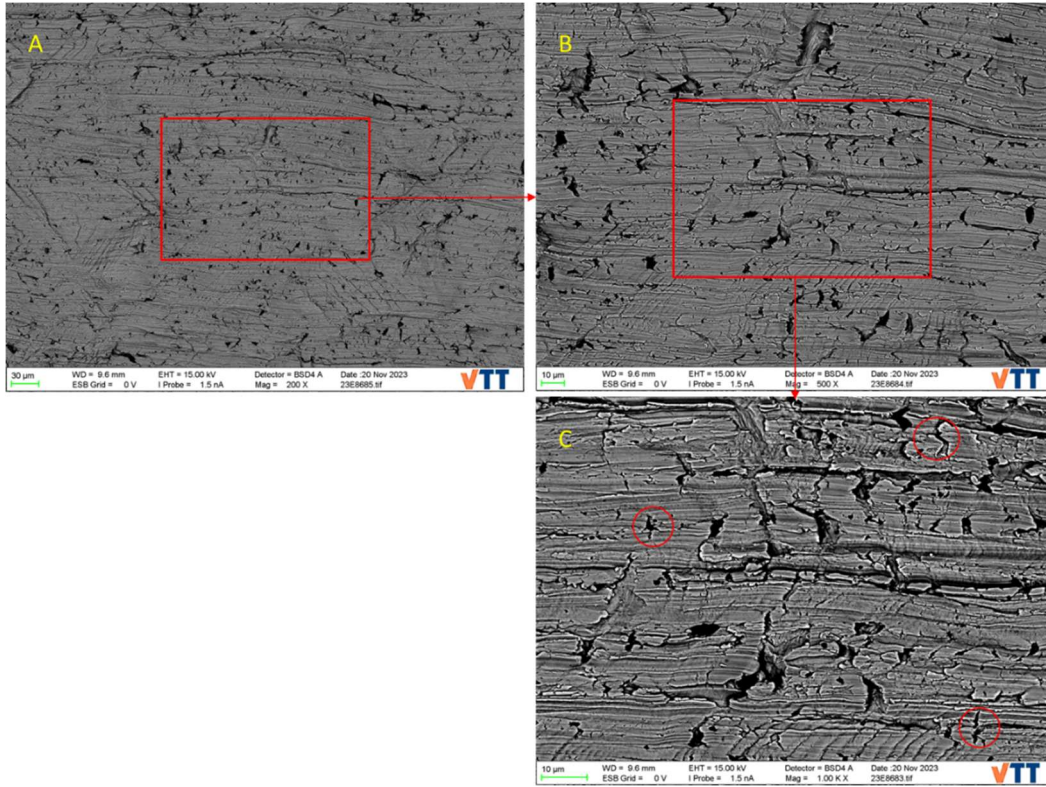


Figure 8. Specimen Air 2 (tested to fracture) after application of the sulphide film removal process. A) 200X, B) 500X and C) 1000X. Note: Red circles in C denote only a few of the microcracks, not all.

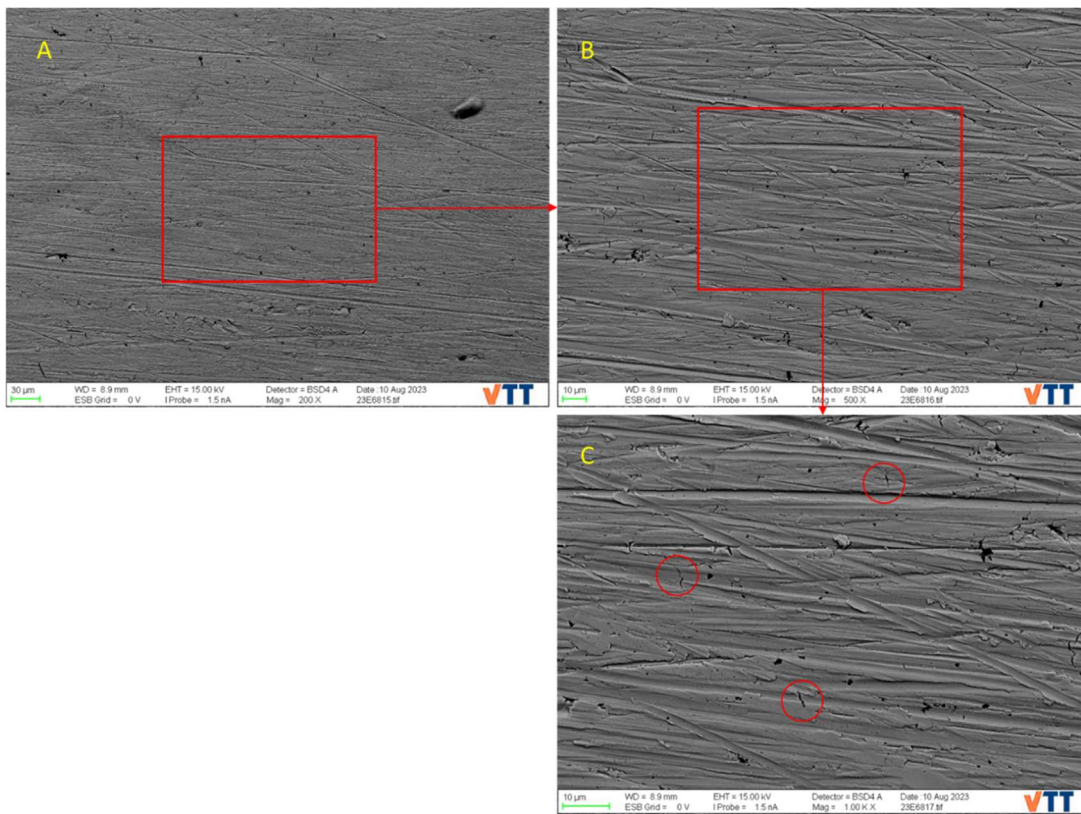


Figure 9. An example of detection of surface microcracks, specimen tested in air to 5% deformation, A) 200X, B) 500X and C) 1000X. Note: Red circles in C denote only a few of the microcracks, not all.

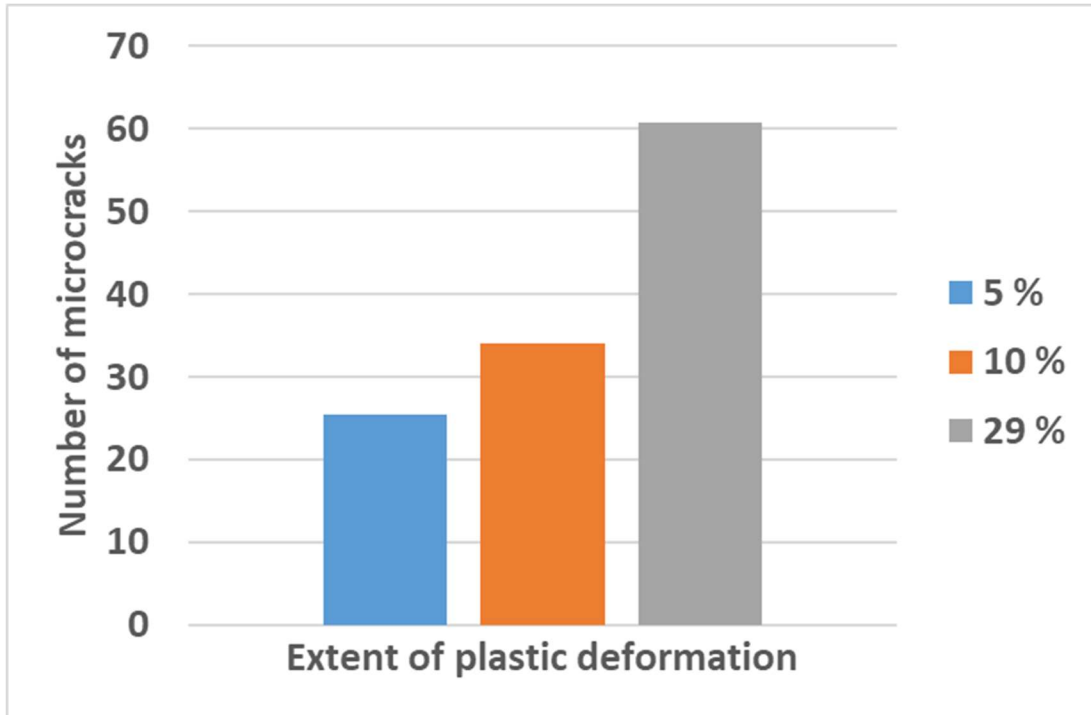


Figure 10. The total number (average of four different areas for each specimen) of microcracks longer than 1 µm in the three air-tested specimens as a function of the extent of plastic deformation. The analysed area in each SEM-picture (1000X) was 0.009 mm².

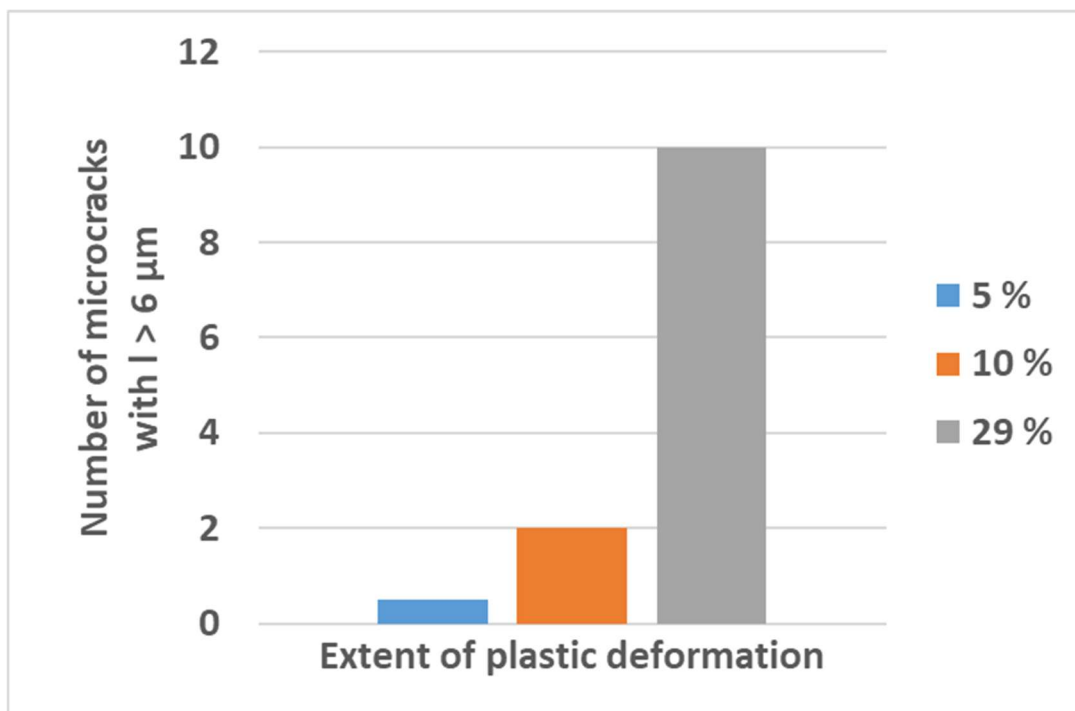


Figure 2. The number (average of four different areas for each specimen) of microcracks longer than 6 µm in the three air-tested specimens as a function of the extent of plastic deformation. The analysed area in each SEM-picture (1000X) was 0.009 mm².

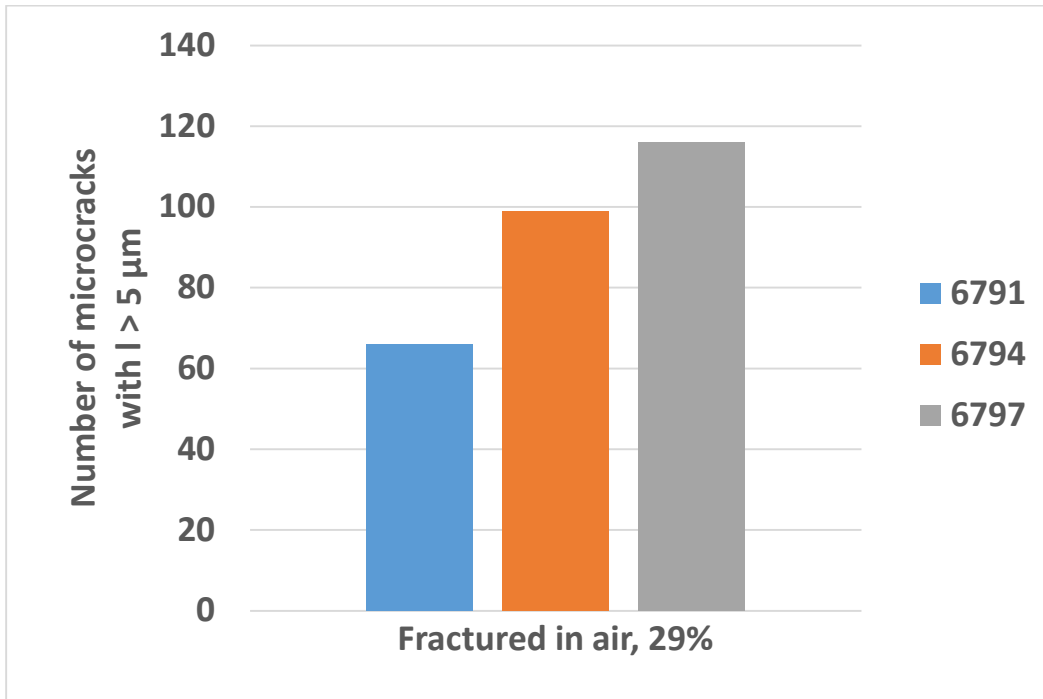


Figure 3. The number of microcracks longer than 5 μm in the specimen tested in air to fracture ($\epsilon_f = 29\%$) in three different areas. The analysed area in each SEM-picture (200X) was 0.22 mm^2 .

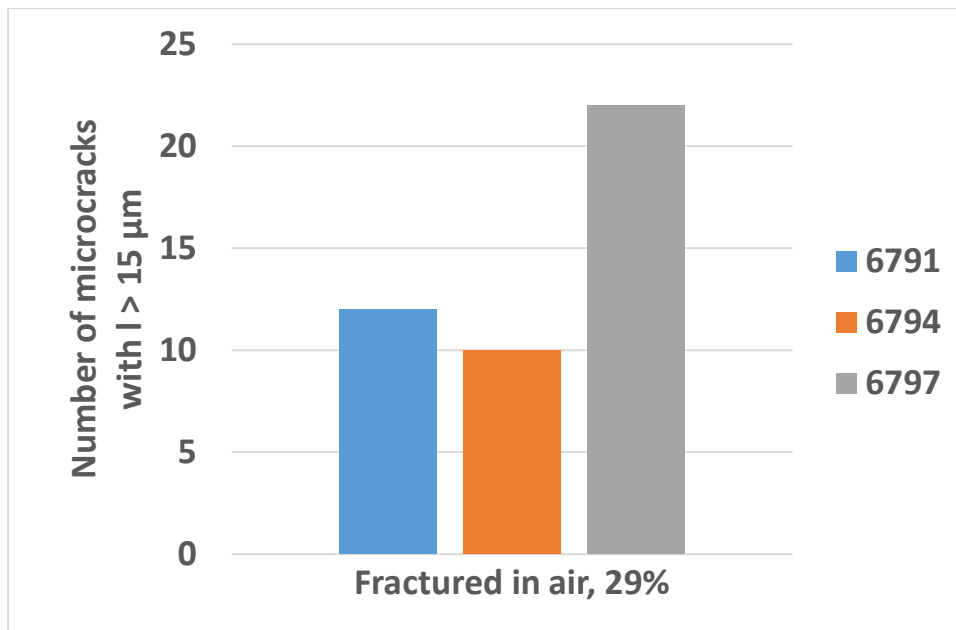


Figure 4. The number of microcracks longer than 15 μm in the specimen tested in air to fracture ($\epsilon_f = 29\%$) in three different areas. The analysed area in each SEM-picture (200X) was 0.22 mm^2 .

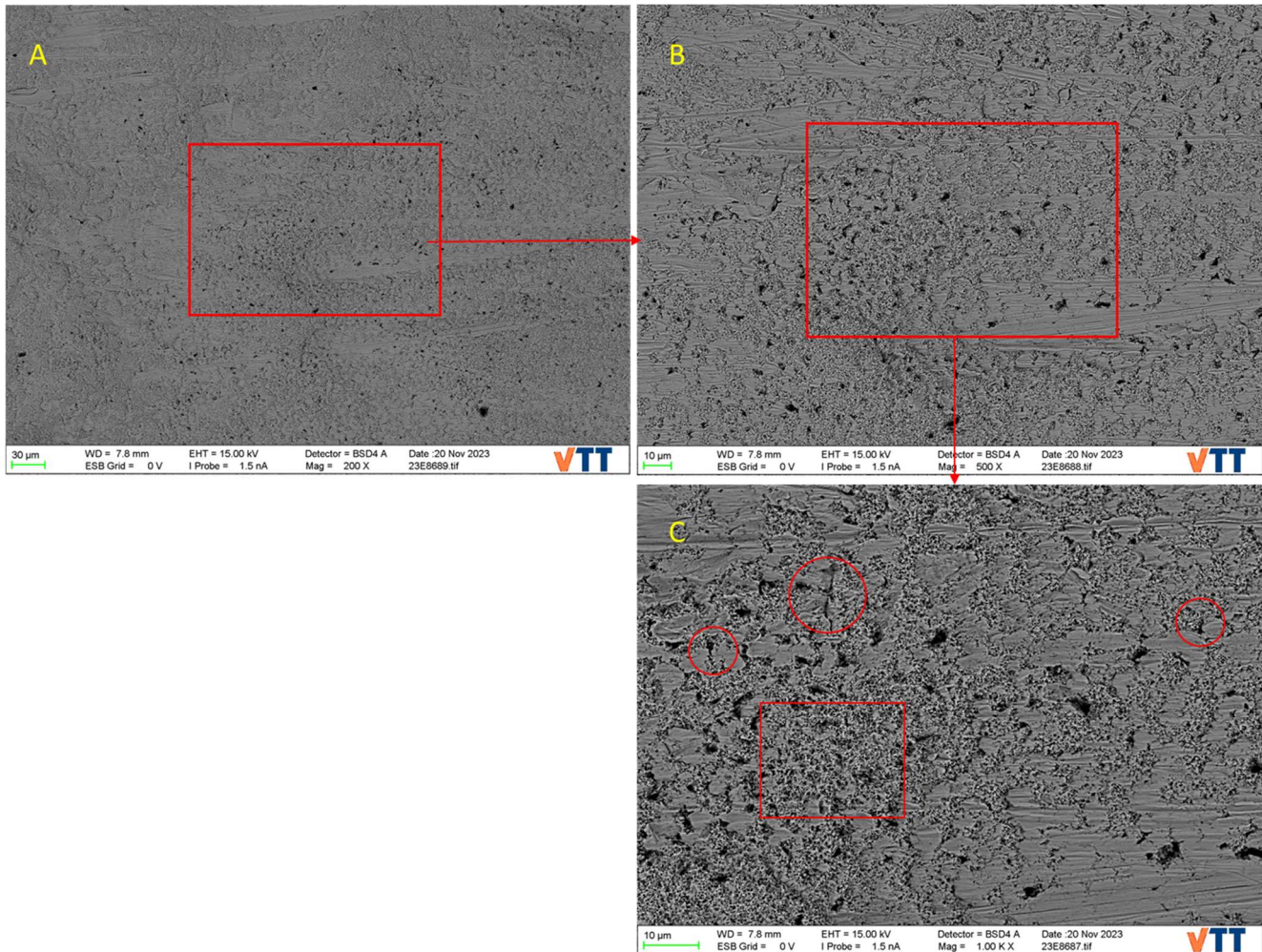


Figure 5. Surface appearance of the specimen tested to fracture in water with 80 mg/l HS^- and subjected to the sulphide film removal procedure. A) 200X, B) 500X and C) 1000X. Note: Red circles in C denote some suspected traces of earlier surface microcracks, not all. The red square denotes one area where the surface was covered with a structure named as “decoration”.

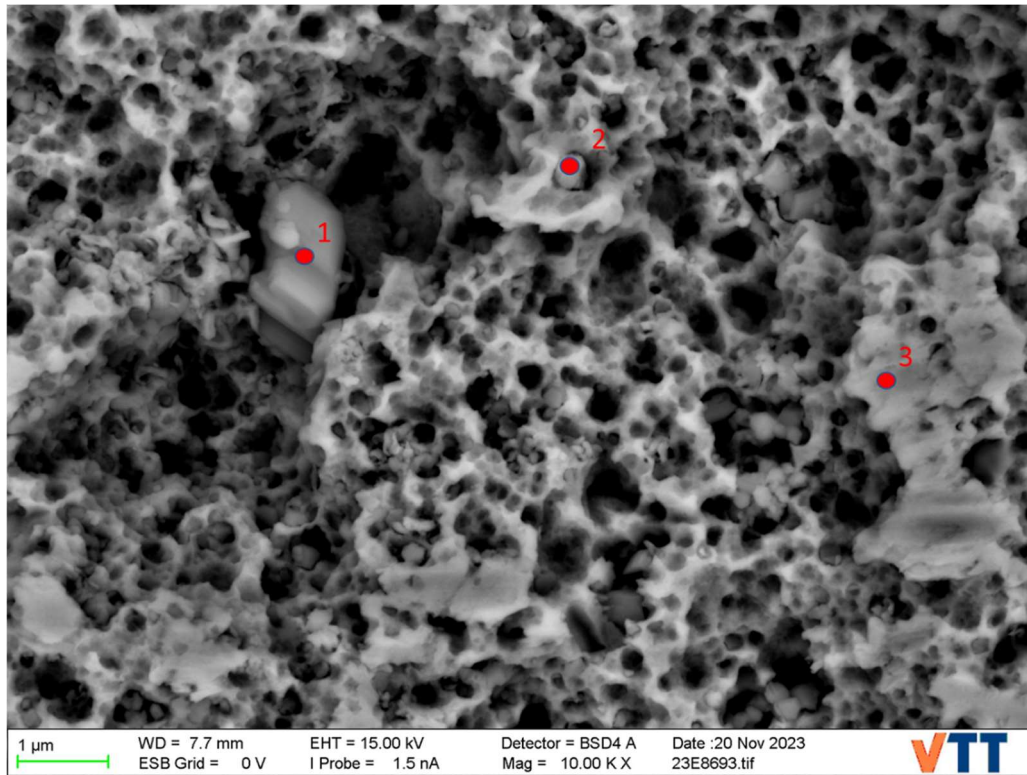


Figure 6. A detail of one area in Figure named “decoration”. The red dots denote the spots where EDS was performed. Magnification 10000X.

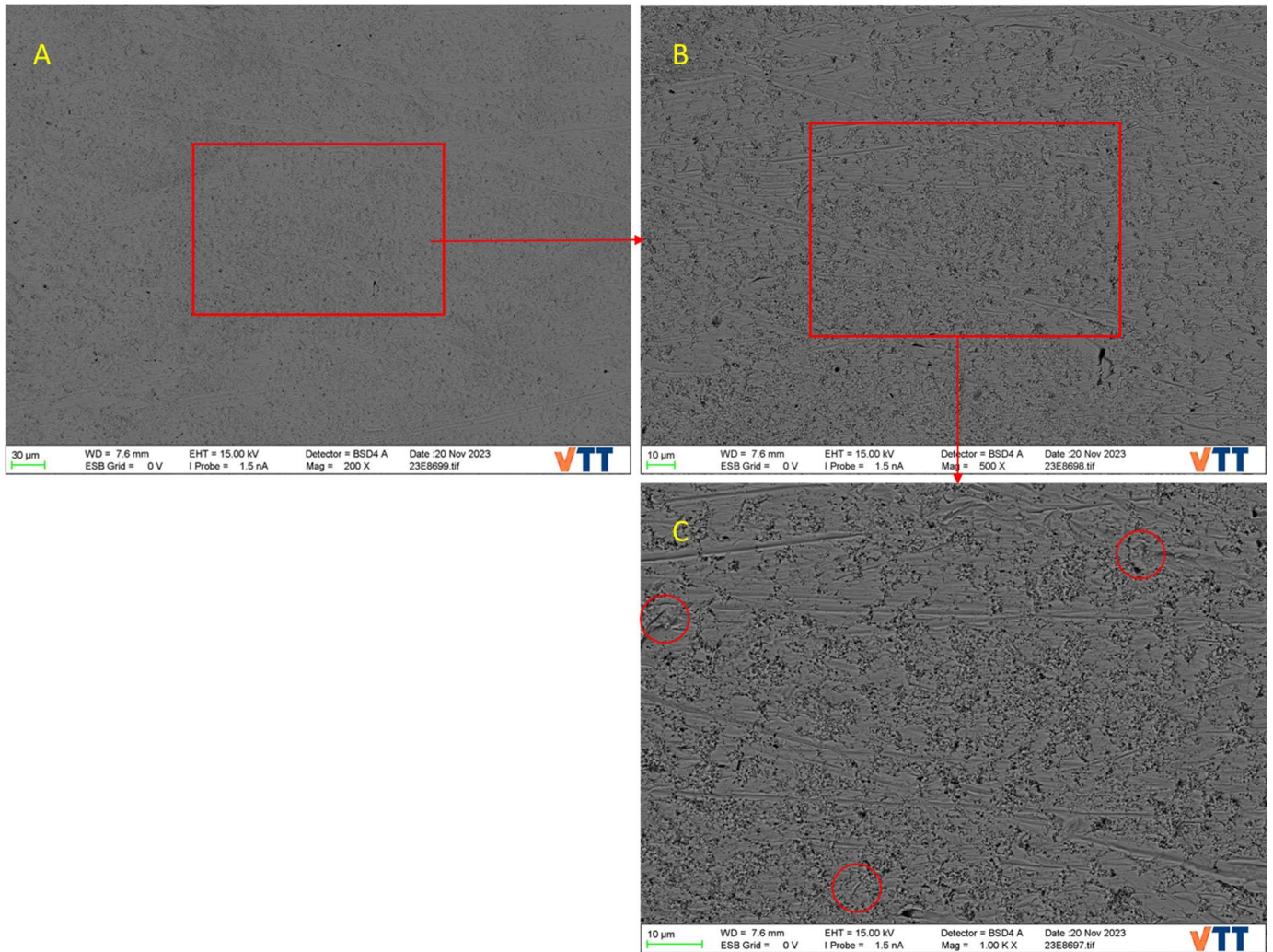


Figure 7. Another example of the surface appearance of the specimen tested to fracture in water with 80 mg/l HS⁻ and subjected to the sulphide film removal procedure. A) 200X, B) 500X and C) 1000X. Note: Red circles in C denote some suspected traces of earlier surface microcracks, not all.

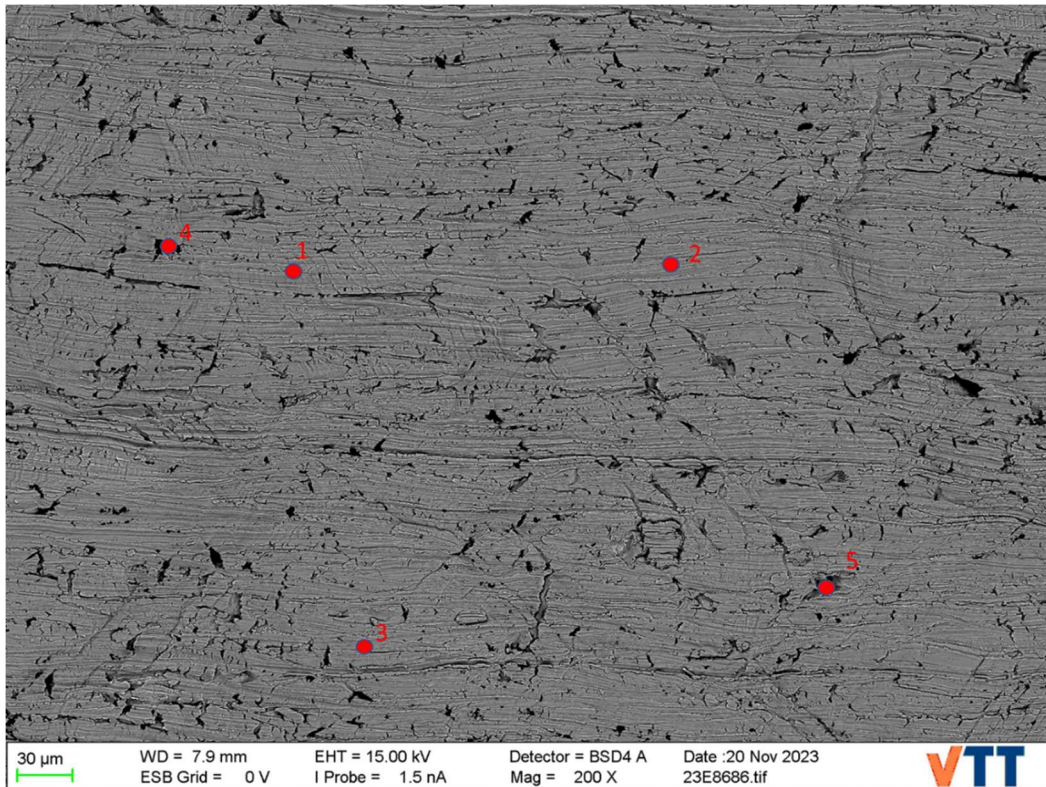


Figure 8. Surface of Air 2 -specimen (200X). The red spots mark the locations where EDS -analyses were made. All EDS spots showed only Cu.

7. Conclusions

The fracture strain of specimens tested in air to fracture was about 30%, clearly lower than the 52% reported for the same Cu-OFP batch by the manufacturer. The lower fracture strain is likely a result from several factors, including the small thickness (about 0.45 mm) of the gauge length of the specimens used in this work, and the fact that the final polishing of the gauge length was performed by hand (because of the heads of the specimen being thicker than the gauge length), which can result in some additional plastic deformation in the specimen preparation phase.

Based on the SEM-analyses of the surfaces of specimens tested in air, a large number of surface microcracks, in the range of several thousand per mm^2 , are formed as a result of plastic strain introduced by the tensile loading. The number and length of the microcracks increases as the extent of plastic deformation increases. The area in any one SEM-picture taken at 1000X magnification is about 0.009 mm^2 . Based on the high number of microcracks found, the origin of the majority of microcracks could not be opening up of the grain boundaries, and involves most probably the arrangement of dislocations within individual grains.

Very few features resembling microcracks were found on the surface of the specimen tested to fracture in water with 80 mg/l sulphide. None of them could be positively identified as microcracks. In the present hypothesis, the plastic deformation does produce microcracks also when the specimen is exposed to water with sulphides, but in most cases their depth is so small that when the sulphide film forms with thickness of a few μm , the microcracks are consumed in the process and not present on the surface anymore to be detected with SEM.

To exclude the possibility that the sulphide film removal procedure used to reveal the base material for SEM-studies (of specimen exposed to water with 80 mg/l sulphide) would remove existing microcracks, the same sulphide removal procedure was performed on a specimen tested in air. Subsequent SEM-study showed that the microcracks were not affected by the sulphide film removal process.

The main conclusion from the work is that the microcracks observed on the surface of the specimens is due to plastic straining and that exposure to water with 80 mg/l sulphide does not result in growth of such microcracks. Quite the opposite, the results indicate that the microcracks forming due to plastic deformation are shallow enough to be consumed in the sulphide film formation process and can thus not be detected by post-test SEM analyses.

In order to verify that this main conclusion is not batch-dependent, several additional batches need to be investigated. Also, to verify that the small thickness of the specimens used in the present study (of the order of 3 to 6 grain sizes of the Cu-OFP used) does not affect the formation of the microcracks, specimens with a thicker gauge section need to be studied. Another task for future work is to check the depth of the microcracks forming in specimens tested in air. This is needed to verify the applicability of the hypothesis that the microcracks are consumed in the sulphide film formation process.

8. Summary

Specimens manufactured from Cu-OFP were tested in air and in water with 80 mg/l sulphide. Post-test analysis of the surfaces of specimens tested in air by scanning electron microscope (SEM) revealed a large number of surface microcracks (in the range of 6000 per mm²) with a maximum length of not more than about 50 µm. Increasing the extent of plastic deformation resulted in an increasing number of surface microcracks.

Specimen tested in water with 80 mg/l sulphide showed no details that could be positively identified as surface microcracks. This was proposed to result from surface microcracks forming on the surface due to plastic deformation being so low in depth that they are consumed by the few µm thick sulphide film when it forms and thus were not present on the surface anymore to be detected by SEM.

The main conclusion from the work is that for the Cu-OFP batch used in the study the surface microcracks form due to plastic deformation only, and not due to the exposure to sulphide containing water. Additionally, exposure to water with 80 mg/l sulphide does not result in environmentally induced growth of the surface microcracks forming due to plastic deformation.

In order to verify that these main conclusions are not batch-dependent, several additional batches need to be investigated. Also, to verify that the small thickness of the specimens used in the present study (of the order of 3 to 6 grain sizes of the Cu-OFP used) does not affect the formation of the microcracks, specimens with a thicker gauge section need to be studied. Another task for future work is to check the depth of the microcracks forming in specimens tested in air.

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