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ARTICLE



Sulphide-induced stress corrosion cracking and hydrogen absorption of copper in deoxygenated water at 90°C

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Abstract

Stress corrosion cracking (SCC) of oxygen-free phosphorous-alloyed copper was investigated in sulphide- and chloride-containing deoxygenated water at 90°C with sulphide concentrations of 0.001 and 0.00001 M. Several intergranular defects were found in the specimen exposed to the high sulphide environment. Similar defects were not found in the low sulphide environment, where only slight corrosion on grain boundaries and slip lines occurred. Hydrogen content measurements show an increase in hydrogen uptake of the plastically deformed specimens, which is dependent on the sulphide concentration and on plastic deformation of copper. However, the highest hydrogen content was measured in friction stir welds, welded in air without shielding gas, and tested in the high sulphide environment. The embedded oxide particles in the weld metal act as local hydrogen trapping sites and selectively react with the sulphide solution. A relatively thick air-formed oxide film covers the copper canisters when deposited, which transforms into a sulphide film in the repository conditions. Thus, some of the coupon specimens were preoxidised. The conversion of the pre-existing Cu₂O film into Cu₂S film occurs quickly and the transformation is almost 100% efficient. The structure and properties of the Cu₂S films, susceptibility of copper to sulphide-induced SCC and hydrogen uptake of copper in reducing, anoxic repository conditions are discussed.

KEYWORDS

copper, hydrogen absorption, stress corrosion cracking, sulphide corrosion

1 INTRODUCTION

Sulphide-induced stress corrosion cracking (SCC) of copper is a possible degradation mechanism in the final disposal conditions of spent nuclear fuel.^[1] It is known that some key agents, such as ammonia, acetate and nitrite cause SCC of copper, but they are not expected to be present in sufficient amounts. However, during the long

anaerobic phase of disposal, sulphide anions (SH⁻) are present in groundwater and they are transported to the canister surface by diffusion through the saturated bentonite. This causes general corrosion of the copper canister surface; the corrosion rate being limited by the mass transport of sulphide anions through the bentonite buffer.^[1] Before full saturation of the bentonite, transportation of the sulphide anions to the canister surface

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is less limited, and conditions for sulphide-producing microbial activity in the buffer are more favourable.

Sulphide-induced SCC of copper has been reported to occur at sulphide concentration of 0.01 M,^[2] which is considerably higher than typically expected in the repository conditions. However, a recent collaboration study of Studsvik Nuclear AB, Sweden, and Aalto University, Finland, involving slow strain rate tensile testing (SSRT) of phosphorous-alloyed oxygen-free copper (Cu-OFP) showed that cracking can occur at sulphide concentration of 0.001 M,^[3,4] which is an order of magnitude lower than reported in Taniguchi and Kawasaki,^[2] but still higher than the highest measured sulphide concentration in the planned Swedish final repository site in Forsmark, which is 0.00012 M.^[5] In all studied conditions, surface defects, not positively attributed to SCC (except for the 0.001 M sulphide concentration) were also found.^[3,4] In addition, the hydrogen content of copper increased from 0.5 to 1.2 wt ppm during short-term SSRT of 2 weeks.^[4] In comparison, the maximum allowed hydrogen content of copper in the KBS-3 concept is 0.6 wt ppm.^[6]

The hydrogen absorption may be related to the SCC susceptibility of copper, since cracking of grain boundaries and hydrogen-enhanced creep of Cu-OFP are known to occur, for example, in tensile testing coupled with electrochemical hydrogen charging.^[7] Hydrogen charging causes micro-void formation on the grain boundaries resulting in intergranular cracking. However, this mechanism requires a very high fugacity of hydrogen, which is not present in the repository conditions. On the other hand, a recent simulation study on hydrogen effects on void nucleation in copper shows that hydrogen stabilises di-vacancies in copper and promotes vacancy cluster formation by preventing the collapse of vacancy clusters.^[8] This may as well contribute to plastic deformation of copper and possibly to SCC. Thus, the risk of SCC in the repository conditions should be evaluated in more detail.

Two additional exposures (#8 and #9) were conducted at Studsvik Nuclear AB. The aim was to study, in addition to SCC of Cu-OFP, the oxide/sulphide film (Cu_2O/Cu_2S) transformation, structure and properties of the films, and effects of the mechanical loading on hydrogen uptake of copper in reducing, anoxic, simulated repository conditions. A comprehensive report of the whole testing programme can be found in Becker et al.^[9]

2 | MATERIALS AND METHODS

2.1 | Test materials and specimens

The two SSRT specimens were manufactured from Cu-OFP, cut from top part of a canister lid.^[3] The chemical composition is shown in Table 1. The geometry of the SSRT specimens, previously determined by finiteelement method (FEM) calculations to obtain a desired strain in the narrowest part of the gauge section by the end of the SSRT,^[3] is shown in Figure 1a. The lower half (Figure 1b) shows the two SSRT specimens after exposure together with the locations and naming of samples cut for the hydrogen content measurements.

In addition, 12 coupon specimens of size $20 \times$ 20×2 mm were simultaneously exposed to each of the test environments together with the SSRT specimens. These coupons were cut from the base material (same as the SSRT specimens) and two different copper canister friction stir welds (FSW) provided by the Swedish Nuclear Fuel and Waste Management Co. (SKB), Sweden, and by Posiva Oy, Finland. The first canister weld was welded in air (weld designation FSWL69) and the second one was welded in argon shielding gas (weld designation FSWL109). These are named 1W (welded in air) and 2W (welded in argon), respectively, when discussing the results. The FSW coupon specimens were cut from the weld nugget from the location where most of the oxide particles^[10] are located, and exposed to the test environment to reveal possible Cu₂O particle sulphidation and penetration of the corrosion attack along the oxide particle stringers into the weld metal, as well as hydrogen trapping by the Cu₂O particles. Some of the unloaded coupon specimens were also pre-oxidised using the method of Aaltonen et al.^[11] to simulate a thick copper oxide film expected to be present on the canister surfaces at the time of disposal. Naming of the specimens is presented in Table 2. More detailed information on the specimens and the exposures can be found in Becker et al.^[9]

2.2 | Autoclave exposures

The two exposures (#8 and #9) were conducted at Studsvik AB, Sweden, with the strain rate being halved from the previous testing.^[3,4] This resulted in test time of 4 weeks to reach a strain of 9% in the narrow part of the

 TABLE 1
 Specification of chemical composition of Cu-OFP in wt ppm (unless otherwise stated)^[3]

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Cu	0	Р	Pb	Bi	As	Sb	Sn	Zn	Mn	Cr	Со	Cd	Fe	Ni	Ag	Se	Те	S
99.99 wt%	1–2	43-60	<1	<1	<1	1	< 0.5	<1	< 0.5	<1	<1	<1	<1	2	12	<1	<1	6

FIGURE 1 (a) Schematic illustration of the SSRT specimen geometry. (b) SSRT specimens #8 and #9 after exposure. Locations and naming of the hydrogen TDS samples are marked with red rectangles and yellow text^[9] (reprinted with permission from SSM). SSRT, slow strain rate tensile testing; TDS, thermal desorption spectroscopy [Color figure can be viewed at wileyonlinelibrary.com]





gauge section. The repository conditions were simulated by controlling the test solution temperature at 90°C, which is the expected maximum surface temperature of the copper canisters in the repository, and by controlling the solution chemistry by addition of dosage solution of 0.1 M NaCl and 0.001–0.00001 M Na₂S to the main flow, simulating the groundwater chemistry in the repository. A second dosage flow was used to control the pH at 7.2 by addition of Na₂HPO₄ and NaH₂PO₄.^[3] The average electrochemical corrosion potentials (ECP) of the SSRT specimens were –720 and –370 mV versus standard hydrogen electrode (SHE) for exposures #8 and #9, respectively. More detailed information on the exposures can be found in Becker et al.^[9]

2.3 | Specimen examination

The specimens were primarily observed by scanning electron microscopy (SEM) for the structure of the films and defects on the specimen surfaces. The SEM is a Zeiss Merlin VP Compact field-emission gun SEM (FEG-SEM) equipped with Bruker xFlash 6|30 energy-dispersive spectrometry (EDS) detector. Additionally, electron backscatter diffraction (EBSD) was performed for crosssections of the defects with a Zeiss Ultra 55 FEG-SEM equipped with HKL Nordlys II EBSD detector.

The SSRT specimens were cleaned by rinsing with ethanol to avoid removal of the copper sulphide films. After initial observations, additional ultrasonic cleaning in ethanol was applied, which removed the films easily and revealed the copper surface underneath. The cross-sections for EBSD were prepared by cutting the tensile specimen in half by electrical discharge machining (EDM), by mounting the cut sample in conductive resin, and polishing down to $^{1}\!/_{4}\,\mu$ m diamond paste, followed by vibratory polishing in colloidal silica for at least 48 hr to remove deformation from the surfaces.

2.4 | Hydrogen thermal desorption spectroscopy

Hydrogen thermal desorption spectroscopy (TDS) was performed to measure hydrogen contents in the SSRT and coupon specimens. The TDS apparatus is based on a precise mass-spectrometry measurement of gas partial pressure in ultra-high vacuum (UHV) chamber, equipped with a vacuum-friendly internal furnace. It allows the measurement of hydrogen desorption at a temperature range of 20–1,200°C with controlled heating rate between 1 and 10°C/min. Normal vacuum in the UHV chamber is about 5×10^{-9} mbar, providing the possibility to monitor hydrogen in copper with concentration down to about 0.02 wt ppm. After conversion of the measured partial pressure of hydrogen to desorption rate, the hydrogen content is calculated as area under the TDS curve.

Samples for TDS were cut with EDM from the SSRT specimens from locations shown in Figure 1 to measure hydrogen absorption in different parts of the tensile specimens. The TDS samples of the coupon specimens were cut mechanically before and after exposure to the sulphide-containing environments. To remove the cutting-affected surface layer, the samples were mechanically ground to size

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Specimen name	Specimen type/testing environment	Notes
B_AS1	TDS sample, as-supplied	Base material of the SSRT specimens (lid material)
69_AS1	TDS sample, as-supplied	Weld metal of FSWL69
109_AS_L	TDS sample, as-supplied	Lid material of FSWL109
109_AS_W	TDS sample, as-supplied	Weld metal of FSWL109
B1_ox_HS B2_ox_HS B3_HS B4_HS 1W1_ox_HS 1W2_HS 1W4_HS 2W1_ox_HS 2W2_HS 2W3_HS 2W4_HS	Unloaded coupon specimens exposed in 10 ⁻³ M sulphide	Base material, pre-oxidised Base material, pre-oxidised Base material Base material FSW weld metal welded in air, pre-oxidised FSW weld metal welded in air FSW weld metal welded in air FSW weld metal welded in argon, pre-oxidised FSW weld metal welded in argon FSW weld metal welded in argon FSW weld metal welded in argon
B1_ox	Non-exposed coupon specimen	Base material, pre-oxidised, used only for XRD measurements of the oxide film
B2_ox_LS B3_LS B4_LS B5_LS 1W1_ox_LS 1W2_LS 1W3_LS 2W1_ox_LS 2W2_LS 2W3_LS 2W4_LS	Unloaded coupon specimens exposed in 10 ⁻⁵ M sulphide	Base material, pre-oxidised Base material Base material Base material FSW weld metal welded in air, pre-oxidised FSW weld metal welded in air FSW weld metal welded in argon, pre-oxidised FSW weld metal welded in argon FSW weld metal welded in argon FSW weld metal welded in argon

TABLE 2 Naming of the coupon specimens

Abbreviations: FSW, friction stir weld; SSRT, slow strain rate tensile testing; TDS, thermal desorption spectroscopy; XRD, X-ray diffraction.

of about $0.9 \times 3.8 \times 10.0$ mm, finishing with 2,000 grit silicon carbide paper. Just before TDS measurements, the samples were cleaned in acetone in an ultrasonic bath for 1 min and dried in pure helium gas flow.

2.5 | X-ray diffraction

The structure of the copper oxide and copper sulphide films was studied with X-ray diffraction (XRD) analysis with PANalytical X'Pert Pro MPD in grazing incidence geometry (GIXRD) using X-ray mirror and parallel plate collimator for the parallel beam optics and 1° constant incident angle. The film was also removed from the copper substrate, ground to fine powder, and then measured in Bragg–Brentano geometry using programmable incident and anti-scatter slits and PIXcel 1D detector.

3 | RESULTS

3.1 | SSRT specimens

The SSRT specimens from both exposures were observed with SEM before and after removal of the sulphide film. SSRT specimen #8, which was tested in the high sulphide concentration of 0.001 M, is shown in Figure 2. A thick, multi-layer sulphide film was formed, where the multiple layers consist of single layers of sulphide crystals. This is

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due to repeated detachment of the film from the specimen surface caused by contraction of the specimen by plastic deformation. The films have a wavy appearance for the same reason, not observed on the coupon specimens. The films are also very brittle and crack easily already during testing perpendicular to the loading direction.

There were at least three film layers formed on SSRT specimen #8, and the different layers had different crystal morphologies (shown in Figure 3). The crystals were confirmed by EDS to contain only Cu and S implying that they were Cu₂S crystals, later confirmed by XRD measurements. The surface underneath the crystals was confirmed by EDS to be Cu. Side view of the inner, but still detached copper sulphide film is shown in Figure 4. Cracking of the film occurred intergranularly. The crystals are most likely held, at least partially, in place by mechanical locking as evidenced by the brittleness of the films.

Observations of the copper surface underneath the copper sulphide films revealed several surface defects, resembling the defects found in References [3,4]. These surface defects, some of them shown in Figure 5, form underneath the copper sulphide film, and thus they are difficult to find without removal of the film. In many locations, small pitting-like corrosion was also found on

the grain boundaries (Figure 5e). These later possibly form larger defects by joining together (Figure 5f). Similar defects were not found in the coupon specimens.

The depth of the surface defects was examined by cutting specimen #8 in half by EDM from the location of the largest defects and examined in SEM with EBSD. Several surface defects were found in the same crosssection. Two of them are shown in Figure 6. The EBSD analysis confirms that the defects grow preferably on random high-angle grain boundaries. However, in one instance, shown in Figure 6a,b, the defect formed on a thin-twinned grain, growing between the two parallel twin grain boundaries, which are generally considered more resistant to corrosion and deformation than random grain boundaries.

The defects found in specimen #8 were rather small with penetration depths of $10-15 \,\mu$ m, when compared with cracks found in References [3,4]. where the penetration of the largest defect was up to $70 \,\mu$ m in the specimen tested in the same conditions (except for the strain rate). The lower strain rate utilised in this study may have affected the crack propagation rate.

SSRT specimen #9 was tested in the low sulphide concentration of 0.00001 M, which is an order of magnitude lower than that measured in Forsmark groundwater.^[5] Figure 7 shows the general appearance



FIGURE 2 (a) General view of SSRT specimen #8. (b) Several copper sulphide films formed in 0.001 M sulphide. (c) The films detached from the copper surface due to plastic deformation of the copper substrate. (d) The crystals grow directly from the copper surface. SSRT, slow strain rate tensile testing



FIGURE 3 (a,b) The copper sulphide films crack perpendicular to the loading direction. (c) The inner (but still detached) film consists of larger crystals and their size does not vary much. (d) The outer film consists of smaller crystals and their size varies more

of the specimen and the thin film after exposure to the sulphide solution. Similar to specimen #8, the film was wavy, caused by the plastic deformation of the copper substrate, but otherwise the appearance is markedly different. Only a single layer of thin film formed, again very brittle and easily removed by mechanical contact or ultrasonic cleaning utilised after the initial observations. No cracking of grain boundaries or any other form of clear surface defects were found in this specimen, but many grain boundaries and slip lines were slightly corroded (Figure 7b-d).

3.2 | Coupon specimens

The coupon specimens of the two exposures were examined by SEM for sulphide film structure and appearance. The general appearance of the sulphide films is shown in Figures 8 and 9. A thick, multi-layer film is formed in high sulphide conditions, while a thin singlelayer film is formed in low sulphide conditions. The sulphide crystals formed in different environments are markedly different. Large plate-like crystals are formed on the top-layer in high sulphide conditions, whereas



FIGURE 4 Side view of the inner detached copper sulphide film



FIGURE 5 (a,b) Surface defects form underneath the copper sulphide film. (c) More defects were found after film removal, (d) the largest defects being about 80 μ m in length along the surface. (e) Small pitting-like corrosion forms on the grain boundaries, (f) which may later join and form larger defects^[9] (reprinted with permission from SSM)

small cellular crystals are formed in low sulphide conditions. EDS analyses of the films show that the corrosion deposits consist of only Cu and S.

The thickness of single-layer film formed in low sulphide conditions was about 200–400 nm and the films were often porous. A much thicker multi-layer film of $10-30 \,\mu\text{m}$ in thickness was formed in high sulphide conditions and the films were more compact, but still often contained free volume in them. Cross-sections of the two different films are shown in Figure 9.

Three distinct types of Cu_2S films have been reported in the literature.^[12] Type I is a thin single layer, porous film forming in low sulphide conditions and with low sulphide fluxes. Type II is a porous, dual-layer film forming with intermediate and high sulphide fluxes. Type III is a passive or at least partially

passive film forming in high sulphide conditions and with high transportation fluxes. According to this classification, the low sulphide conditions produced a Type I film and the high sulphide conditions produced a Type II film.

As the copper sulphide crystals grow from the copper surface, a markedly roughened copper surface is formed once the film is removed or detached. The crystallographic marks left on the surface match well with the size of the copper sulphide crystals. No intergranular corrosion was found in any of the coupon specimens, though grain boundaries were often visible. This is consistent with the presence of uniformly distributed porous film and confirms that localised anodic dissolution did not occur including locations where large pores were present in the film.



FIGURE 6 (a-d) EBSD maps (on the left) and secondary electron images (on the right) of surface defects found in specimen #8. In the EBSD maps, white is nonindexed data points, black lines represent random high-angle grain boundaries, and red lines represent Σ 3 twin boundaries. The length of the black scale bar in EBSD maps is $20 \,\mu\text{m}$. (e) The orientation of the copper grains may be interpreted by using the IPF colour key shown in the zdirection^[9] (reprinted with permission from SSM). EBSD, electron backscatter diffraction; IPF, inverse pole figure [Color figure can be viewed at wileyonlinelibrary.com

Growth of the coherent Cu_2S crystals at the Cu/Cu_2S interphase may be limited by the build-up of interfacial stress leading to film fracture. The Pilling–Bedworth (P–B) ratio for Cu_2S on Cu is 2.00, whereas the ratio for Cu₂O on Cu is 1.68. In general, if the P–B ratio is greater than 1, compressive stresses form in the film, and if the ratio is greater than 2 the surface film is non-protective and may crack and flake off, continuously exposing the metal surface.^[13] Film growth at the Cu₂S/solution interphase does not cause build-up of interfacial stresses, and growth of the outer Cu₂S layer may continue unimpeded at a rate, at least partially controlled by sulphide ion (SH⁻) diffusion to the Cu₂S/solution interface, and partially by Cu⁺ diffusion in the film. The film growth process may also be partially controlled by CuCl₂⁻ diffusion in the spaces between the Cu₂S plates.^[14]

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Some of the films formed in low sulphide conditions are shown in Figure 10. The films were porous and large openings in the films were often present. The copper surface showed very little roughness when compared with high sulphide conditions when the films were removed, or in locations of openings in the films. Before exposure to the sulphide solutions, some coupon specimens where pre-oxidised to study the conversion of the Cu_2O film into a Cu_2S film in the aqueous sulphide solutions. Appearance of the oxide film before exposure to the sulphide solution is shown in Figure 11a. After exposure to the solutions, the sulphide films formed on the pre-oxidised specimens were similar to the other specimens tested in the same environment. In some locations, debris of the oxide film was preserved locally under the film (Figure 11b), but for the most part the Cu_2O films were converted almost entirely into Cu_2S films. Thus, the pre-existing oxide film did not affect markedly the Cu_2S film formation.

Coupons of FSW metals, representing both welding in air and welding in argon shielding gas, were simultaneously exposed to the simulated repository conditions as the other specimens. In general, the Cu_2S films formed on the weld metal specimens were, in both environments, similar to the films formed on the base material. However, the weld metal specimens revealed some interesting features that were not present in the reference state.



FIGURE 7 (a) General view of specimen #9 before ultrasonic cleaning^[9] (reprinted with permission from SSM). (b–d) The copper surface underneath the sulphide film shows slight corrosion on grain boundaries and slip lines

Figure 12 shows the corroded 1W-weld metal surface formed underneath the Cu₂S film. The penetrations on the surface are caused by local corrosion of oxide particle stringers embedded in the weld metal welded in air. The oxide particles are very small ($\leq 1 \mu m$) in diameter and they are consumed by the sulphide corrosion process. Cross-sections of the defects (Figures 13 and 14) show that they are located on grain boundaries of copper, where most of the oxide particles are located,^[10] and locally attacked by the sulphide solution. Thus, the Cu₂O particles embedded in the weld metal are also destabilised by the sulphide solution similar to the pre-existing oxide films. Similar defects were not found in the weld metal welded in shielding gas.

Another common feature in both weld metal types was that the Cu₂S film was not continuous and there were openings in the film. In the middle of these openings, there were corroded particles always containing iron (Fe) and nickel (Ni) oxides and sulphides, especially in the high sulphide conditions, as analysed by EDS. These Fe-/Ni-rich particles are most likely debris of tool wear, which were embedded in the weld metal during the FSW process. More information on these specimens may be found in Becker et al.^[9]



FIGURE 8 (a) Thin cellular Cu₂S crystal film formed in 0.00001 M sulphide solution at 90°C (coupon specimen 1W4-LS). (b) Thick plate-like Cu₂S crystal film formed in 0.001 M sulphide solution at 90°C (coupon specimen B3-HS)



FIGURE 9 (a) Cross-section of thin copper sulphide film formed in 0.0001 M sulphide solution at 90°C (coupon specimen 1W3-LS). (b) Cross-section of thick copper sulphide film formed in 0.001 M sulphide solution at 90°C (coupon specimen 1W3-HS) [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 10 Thin crystalline copper sulphide film formed in 0.00001 M sulphide solution at 90°C. (a) Coupon specimen 2W1-LS. (b) Coupon specimen B5-LS

3.3 | Sulphide and oxide film characterisation by XRD

The phase composition of the pre-oxidised surface and the sulphide films was analysed by XRD. The measurement of the unexposed pre-oxidised specimen reveals cuprite (Cu_2O) as the only oxide species in the electrochemically deposited surface film. Tenorite (CuO) was not found. The XRD measurements of three base material coupon specimens, two exposed to high sulphide environment and one to low sulphide environment, are shown in Figure 15. The major phase in all specimens is monoclinic Cu₂S (ICDD PDF card 33-490). While the peak locations coincide well for all the specimens (with the exception of the copper substrate being clearly visible for the thin film formed



FIGURE 11 (a) Pre-oxidised copper surface before exposure to sulphide solution. (b) Debris of the oxide film may be found underneath the copper sulphide film (coupon specimen B2-ox-HS)^[9] (reprinted with permission from SSM)



FIGURE 12 Corrosion attack underneath the sulphide film on the air-welded coupon specimen tested in 0.001 M sulphide solution at 90°C (coupon specimen 1W1-ox-HS)

on the specimen exposed to the low sulphide environment), there are large variations in intensities. This is most likely due to the very large crystallites and non-random orientation of the crystallites, which causes preferred orientation effects and poor particle statistics. CuS does not seem to be present at all, according to these measurements. When compared with the other two specimens, there are noticeable reflections from residual Cu_2O phase in the pre-oxidised B2-ox-HS specimen. These are marked with solid dots (ICDD PDF card 5-667) in Figure 15.

To reduce the effect of orientation and poor particle statistics, and thus obtain more accurate compositional analysis, the Cu_2S film was removed from coupon specimen B3-HS, ground to fine powder and then measured in Bragg–Brentano geometry. The results of the Rietveld refinement to the data match well with monoclinic Cu_2S phase, although addition of few atomic percentages of hexagonal Cu_2S (ICDD PDF card 26-1116) slightly improves the fitting. However, the hexagonal phase is not stable at room temperature. Adding CuS did not improve the fit and therefore most likely is not present.

3.4 | Hydrogen uptake measured by TDS

The hydrogen desorption rates were measured for the SSRT specimens and for the different types of coupons exposed in the high and low sulphide environments. For further analysis, the hydrogen contents of each specimen were calculated. The measurements for high sulphide environment (abbreviated here as HS) are shown in Figure 16. The distinctive hydrogen desorption peaks are observed in the temperature range of 550-850 K. The peaks consist of at least two overlapping (Gaussian) components most visible in the as-supplied state. The hydrogen content in all TDS samples cut from SSRT specimen #8 increased when compared with the assupplied state and when compared with the coupons exposed in the same environment (except for the airwelded coupons). Hydrogen content in sample S1-G1-HS, which was cut from the narrow part of the gauge section, increased the most, up to 1.08 wt ppm when compared with 0.66 wt ppm of the as-supplied state. This is possibly because it experienced the highest plastic strain.

An important finding is that significant hydrogen uptake did not occur in the unloaded coupon specimens,



FIGURE 13 Cross-section of a defect formed on an oxide particle stringer (coupon specimen 1W1-ox-HS)



FIGURE 14 (a–f) EBSD maps (on the left) and secondary electron images (on the right) of some of the attacked oxide particle stringers in coupon specimen 1W1-ox-HS. In the EBSD maps, white is non-indexed data points, black lines represent random high-angle grain boundaries, and red lines represent twin boundaries. The length of the black scale bar is (a) $20 \,\mu$ m, (c) $50 \,\mu$ m, and (e) $100 \,\mu$ m. EBSD, electron backscatter diffraction [Color figure can be viewed at wileyonlinelibrary.com]



FIGURE 15 XRD measurement of Cu_2S films formed on two high sulphide coupon specimens (B3-HS and B2-ox-HS) and one low sulphide coupon specimen (B2-ox-LS)^[9] (reprinted with permission from SSM). XRD, X-ray diffraction

except for the FSW weld metal welded in air (Figure 16b). The specimen welded in air (1W3-HS, green curve) manifests almost three times higher hydrogen content (2.05 wt ppm) than the material welded in protective atmosphere (2W3-HS, blue curve) (0.76 wt ppm). This indicates that the Cu₂O particles embedded in the weld metal act as strong trapping sites for hydrogen. Moreover, a great number of hydrogen partial pressure spikes is observed at the low-temperature side of the TDS peak, evidencing that hydrogen forms gas-filled voids at the Cu₂O particles, some of which are located close to the specimen surface and open suddenly due to increasing gas pressure with increasing temperature.

The TDS measurements for the specimens exposed to low sulphide environment (abbreviated here as LS) are shown in Figure 17. The hydrogen desorption curves of SSRT specimen #9 show, similarly to specimen #8, an increase in hydrogen content when compared with the coupons exposed to the same environment. However, it should be noted that the hydrogen content of the coupons



FIGURE 16 (a) Hydrogen desorption rates for samples cut from specimen #8 after SSRT in 0.001 M sulphide environment. (b) Hydrogen desorption rates for coupons of base copper (B2-ox-HS), FSW weld metal welded in air (1W3-HS), and FSW welded in protective atmosphere (2W3-HS) after exposure to 0.001 M sulphide environment, as well as for the non-exposed as-supplied state^[9] (reprinted with permission from SSM). SSRT, slow strain rate tensile testing [Color figure can be viewed at wileyonlinelibrary.com]

was reduced from the as-supplied state, which indicates that hydrogen outgassing occurred during the exposure in the test environment. In the samples exposed to the low sulphide environment, no spikes were observed on the low-temperature side of the TDS curves of FSW weld metal welded in air. However, hydrogen content in this sample (1W4-LS2) (0.30 wt ppm) was still somewhat higher than that in the coupon of the FSW weld metal welded under protective shielding gas (2W4-LS2) (0.22 wt ppm).

A summary of the hydrogen contents is shown in Figure 18. Coupons of base material are marked with B(n),

coupons of FSW made in air are marked with 1W(n), coupons of FSW produced in protective atmosphere are marked with 2W(n) and SSRT specimens are marked with S(n), where (n) represents the numbering of the specimen. Several TDS samples were cut from some of the coupons. In addition, the as-supplied base materials were measured for hydrogen content. The highest value for these unexposed samples was measured in the as-supplied weld metal of the argon shielded weld (1.02 wt ppm). The hydrogen content in the lid material of the same mock-up canister weld was lower (0.72 wt ppm), being closer to the hydrogen content of the base material of the SSRT specimens in the as-supplied



FIGURE 17 (a) Hydrogen desorption rates for samples cut from specimen #9 after SSRT in 0.00001 M sulphide environment. (b) Hydrogen desorption rates for coupons of base copper (B4-LS2), FSW weld metal welded in air (1W4-LS2), and FSW welded under shielding gas (2W4-LS2) after exposure in 0.00001 M sulphide environment, as well as for the non-exposed as-supplied state^[9] (reprinted with permission from SSM). SSRT, slow strain rate tensile testing [Color figure can be viewed at wileyonlinelibrary.com]

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state (0.66 wt ppm), which was also cut from a canister lid. The hydrogen content in the air-welded weld metal was also slightly higher than in the lid materials (0.79 wt ppm). A possible source of hydrogen in the weld metal may be the shielding gas, if hydrogen–argon mixture is used, but according to Björck et al.^[15] the shielding gas for outside of weld FSWL109 was pure argon, and for the inside of the canister nitrogen was used. For one reason or another, all the measured as-supplied values are slightly higher than the threshold limit of the KBS-3 concept of 0.6 wt ppm.

When compared with the samples exposed to the sulphide environments, the samples exposed to high sulphide environment show, in general, higher hydrogen contents than the samples exposed to low sulphide environment. In addition, the TDS samples cut from the SSRT specimens in both high and low sulphide conditions, show the highest hydrogen contents in the narrow part of the gauge section; 1.08 wt ppm in high sulphide and 0.67 wt ppm in low sulphide conditions. The values are slightly lower in the thick section (0.88 wt ppm in HS and 0.65 wt ppm in LS) than in the narrow part, and even slightly lower in the threaded ends (0.84 wt ppm in HS and 0.62 wt ppm in LS). Although the differences in low sulphide conditions are within the resolution limit of the

measurement technique, the measurements in general suggest that the hydrogen uptake is increased by plastic deformation.

4 | DISCUSSION

Sulphide anions are the main corroding agent of copper in the expected repository conditions.^[16–18] However, as the conditions will initially be oxidising due to the presence of oxygen trapped in the repository upon closing and the presence of oxidants produced by radiolysis of groundwater, localised corrosion is initially possible. The extent of general corrosion due to this oxygen and due to the radiolytic corrosion is expected to be minimal at $80-90 \,\mu\text{m}$.^[19] A requirement for pitting and SCC to occur is that the copper surface must be passive, and the conditions are required to support the separation of anodes and cathodes. Whether or not pitting or SCC occurs is a balance between factors that promote passivation and factors that lead to film breakdown and the establishment of general corrosion.

Based on well-known thermodynamic data, Cu_2S is more stable in sulphide solutions than Cu_2O .



FIGURE 18 Hydrogen contents of base materials, and coupon specimens and SSRT specimens tested in the two different sulphidecontaining environments at 90°C. SSRT, slow strain rate tensile testing [Color figure can be viewed at wileyonlinelibrary.com]

Therefore, conversion of the pre-existing copper oxide film on the copper canister surface leads to Cu₂S formation in sulphide solutions. Once anaerobic conditions have been established the major corrosion mechanism is, thus, corrosion by sulphide-induced reactions. Corrosion studies in aqueous solutions containing sulphide anions (SH⁻) have shown that sulphide corrosion is a two-step process where adsorption on copper surface occurs first to form the chemisorbed species Cu(SH)_{ads}.^[14,20-24] This chemisorbed species then reacts with Cu and SH⁻ leading to deposition of Cu₂S on the surface. Hydrogen evolution under anoxic conditions is the viable cathodic reaction. This leads to hydrogen gas (H₂) formation, which occurs initially at the Cu/electrolyte interface, but probably shifts to the Cu₂S/electrolyte interface on the conducting film once the film has grown.^[20–23] Whether or not this reaction occurs partially at the copper surface at the base of the pores, when porous films are present, is not known. However, the cathodic reaction provides hydrogen near or at the copper surface and some of the hydrogen may enter the metal as H⁺.

Similar hydrogen uptake as initially found in Forsström et al.^[4] was confirmed to occur in the SSRT specimens in this study. Based on the results, the amount of hydrogen uptake depends on, at least two factors; the sulphide concentration of the test solution and amount of plastic deformation of the copper specimen. The sulphide concentration affects the fugacity of hydrogen; higher fugacity providing more hydrogen on the surface, and thus making absorption into the copper lattice more likely. Plastic deformation, on the other hand, provides lattice defects, such as dislocations and vacancies for the hydrogen to be trapped in. Since hydrogen affinity to vacancies is higher than affinity to, for example, dislocations or grain boundaries in copper,^[8] hydrogen is most likely trapped in vacancies, which form in plastic deformation. Furthermore, hydrogen stabilises the vacancies and vacancy clusters,^[8] possibly enhancing the hydrogen absorption. Positron annihilation spectroscopy measurements confirm that vacancies and vacancy complexes are effective trapping sites of hydrogen in copper.^[25] It seems that their generation in plastic deformation and consequent stabilisation by hydrogen explains the observed hydrogen uptake in copper in sulphide solutions initially observed in Forsström et al.^[4]

Intergranular defects were found in the specimen tested in the high sulphide conditions, but the defects penetrated less deep than the largest defects found in Becker and Öijerholm^[3] and Forsström et al.^[4] (10–15 μ m vs. 70 μ m). Only minor intergranular corrosion and corrosion of slip lines was found in the SSRT specimen tested in low sulphide conditions. However, the intergranular defects found in mechanically unloaded

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FSW coupons, welded in air and tested in high sulphide conditions, penetrated much deeper to up to $100 \,\mu$ m. In principle, the oxide particle stringers extend through the whole thickness of the weld and thus may enable penetration of corrosion deep into the weld metal. As hydrogen is generated in the corrosion reactions, some of it is trapped by the oxide particle interphases that have not reacted with the solution, yet. Similar hydrogen uptake in the oxide particle zone of FSW welded copper, welded in air, was also observed to occur in thermal hydrogen charging of the weld metal.^[26] Neither defects nor hydrogen uptake were observed in coupons of FSW copper, welded in protective shielding gas.

Hydrogen of high fugacity is known to result in cracking of grain boundaries of Cu-OFP in tensile loading.^[7] However, the fugacity of hydrogen in the current SSRT was much lower. Thus, the surface defect formation on the grain boundaries is most likely related to localised intergranular sulphide corrosion rather than hydrogen embrittlement of the grain boundaries. An intergranular corrosion/cracking mechanism as proposed in Taxen et al.^[27] is possible. However, as the cracking required tensile loading and no similar cracking occurred in the unloaded coupons, it may be attributed to some form of SCC. Whether or not the intergranular defects are able to propagate further, given more time, is an open question. In Taxen et al.^[27] where the specimens were deformed until final fracture, the surface defects, which were found especially near stress concentration sites at the ends of the tensile specimens, did not propagate deeper than $20-30 \,\mu\text{m}$. It would be interesting to test, whether or not the defects would continue to grow in constant load conditions, where the deformation mechanisms will be different than in continuously increasing load conditions.

5 | CONCLUSIONS

Intergranular SCC of Cu-OFP in sulphide- and chloridecontaining deoxygenated water at 90°C in reducing anoxic neutral pH conditions occurring at a sulphide concentration of 0.001 M, which is an order of magnitude lower than found in Taniguchi and Kawasaki,^[2] and similar results were reported in References [3,4,27]. The EBSD cross-section analysis of the surface defects shows that they grow preferably on random high-angle grain boundaries. The defects are filled by the corrosion product, making visual detection of the defects difficult without removal of the sulphide film. No similar intergranular cracking was found in low sulphide concentration of 0.00001 M, but the specimen surface was slightly corroded on grain boundaries and slip lines.

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Defects on grain boundaries were also found in mechanically unloaded coupons of FSW copper welded in air and tested in the high sulphide conditions. These defects are attributed to localised sulphidation of oxide particle stringers embedded in the weld metal during the welding process. Similar defects were not found in FSW copper welded in protective shielding gas.

A thin, single-layer sulphide film formed in 0.00001 M sulphide solution and a thick, multi-layer film formed in 0.001 M sulphide solution. The films in both conditions were porous and very brittle. Thus, they are not expected to be protective. The sulphide crystals were confirmed to be Cu_2S .

The hydrogen content in the plastically deformed SSRT specimens was increased when compared with unloaded coupons tested in the same environments (except when compared with weld specimens welded in air). The hydrogen uptake in the SSRT specimens in the sulphide environments is most likely related to interaction of hydrogen, forming in the corrosion reactions, and vacancies, forming in plastic deformation of copper. The markedly increased hydrogen uptake in the FSW weld metal, welded in air, is explained by localised sulphidation of copper oxide particles embedded in the weld metal during the welding process, and trapping of hydrogen, most likely by the oxide particle interphases.

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