Hydrogen absorption in copper as a result of corrosion reactions in sulphide and chloride containing deoxygenated water at 90 °C in simulated spent nuclear fuel repository conditions

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Abstract

Recently, copper corrosion in anoxic conditions in pure water has been claimed to take place by hydrogen evolution. Part of this hydrogen is expected to absorb in copper. However, the most important source of hydrogen in copper is sulphide corrosion, which is the main form of copper corrosion during the long-term deposition of spent nuclear fuel. In this study stress corrosion cracking of copper in sulphide and chloride containing deoxygenated water was studied at 90 °C at sulphide concentrations from 0.001 to 0.00001 M using a slow strain rate testing (SSRT) method up to 9% strain. Intergranular cracks were detected in specimens exposed at 0.001 M sulphide concentration. Hydrogen is generated due to sulphide corrosion reactions and therefore the hydrogen content of SCC specimens was measured. A noticeable increase of hydrogen content in the copper specimens was observed even at the lowest sulphide level in the test. The occurrence of sulphide-induced SCC of copper in deoxygenated water is discussed based on hydrogen-enhanced intergranular cracking mechanism.

Introduction

Stress Corrosion Cracking (SCC) of copper in conditions relevant to final repository of spent nuclear fuel is considered possible, but not plausible [1]. The key agents known to induce SCC of copper (ammonia, acetate, nitrite) are expected to be present during the aerobic phase, but not in sufficient amounts to induce stress corrosion cracking. During the long anaerobic phase sulphide in groundwater will be transported to the canister surface by diffusion through the saturated bentonite, which causes general corrosion at the canister surface. The corrosion rate will be limited by the mass transportation of sulphide ions through the buffer [1]. However, before full saturation of bentonite, the mass transportation of sulphide is less limited, and conditions for sulphide producing microbial activity in the buffer material are more favourable.

Indication of sulphide-induced SCC of copper has been reported at a sulphide concentration of 0.01M [2], which is higher than those typically expected in repository conditions. However, recent studies of Studsvik [3] have shown that cracking can occur at sulphide concentration of 0.001 M, which is one tenth lower than the value reported before, but still higher than the highest measured sulphide concentration in the Swedish planned site for final repository in Forsmark (0.00012 M) [4]. The fact that SCC occurred at sulphide concentrations close to the expected Forsmark-values makes studying sulphide-induced SCC of copper in reducing, anoxic repository conditions important.

The mechanism of sulphide-induced SCC of pure copper in the above-mentioned conditions is still unknown. Studies should thus tentatively be directed to the mechanisms of oxide/sulphide film formation in both oxidizing and reducing environments. In addition, the role of hydrogen in sulphide-induced SCC of copper should be studied because hydrogen is generated in the corrosion reactions. In anoxic conditions hydrogen is generated at the surface of copper according to corrosion reactions (1)-(7) [5].

Cathodic reaction:
$$2\ H_2O + 2\ e^- \leftrightarrow 2\ OH^- + H_2 \tag{1}$$

Sulphide ion hydrogenation:
$$S^{2-} + H_2O \leftrightarrow HS^- + OH^- \tag{2}$$

Anodic dissolution of copper:
$$Cu + HS^- \rightarrow Cu(HS) + e^- \tag{3}$$

Dissociation and recombination:
$$Cu(HS) \rightarrow Cu^+ + HS^- \tag{4}$$
$$2\ Cu^+ + HS^- + OH^- \rightarrow Cu_2S + H_2O \tag{5}$$

Hydrogen evolution at electrode surface:
$$HS^- + e^- \rightarrow H_{ads} + S^{2-} \tag{6}$$
$$H_{ads} + H_{ads} \rightarrow H_2 \tag{7}$$

Studsvik [3] has made several slow strain rate tests (SSRT) of copper in a 0.1 M NaCl containing solution with varying concentration of S^{2-} (Na_2S) from 0.001 M to 0.00001 M. Sulphide-induced

SCC was positively identified only for specimens exposed at 0.001 M sulphide concentration. Surface defects were present in specimens exposed at 0.0001 M sulphide concentration, but they were not positively attributed to SCC. The specimens were further studied at Aalto University for crack initiation and hydrogen uptake. The results are presented here.

Experimental Methods

Test material and specimens

The material used in the tests was phosphorous-alloyed oxygen-free copper (Cu-OFP) provided by The Swedish Radiation Safety Authority (SSM). The copper was cut from the top part of a canister lid [3]. The chemical composition is presented in Table 1.

Table 1. Chemical composition of Cu-OFP used in the tests. (wt.ppm)

Cu+P	O_2	P	Pb	Bi	As	Sb	Sn	Zn	Mn	Cr	Co	Cd	Fe	Ni	Ag	Se	Te	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

The geometry of the SSRT specimens was determined by FEM calculations to achieve a desired strain along the gauge section. The maximum strain was 9 % in the narrowest section allowing a 1.3 mm elongation. The main dimensions were ø 4.2 mm in the narrowest section, ø 8.0 mm in the thick section, and 35 mm length of the tapered section [3]. One tested SSRT specimen is presented in Figure 1 together with the location of samples for Thermal Desorption Spectroscopy (TDS) cut from the SSRT specimens after testing.
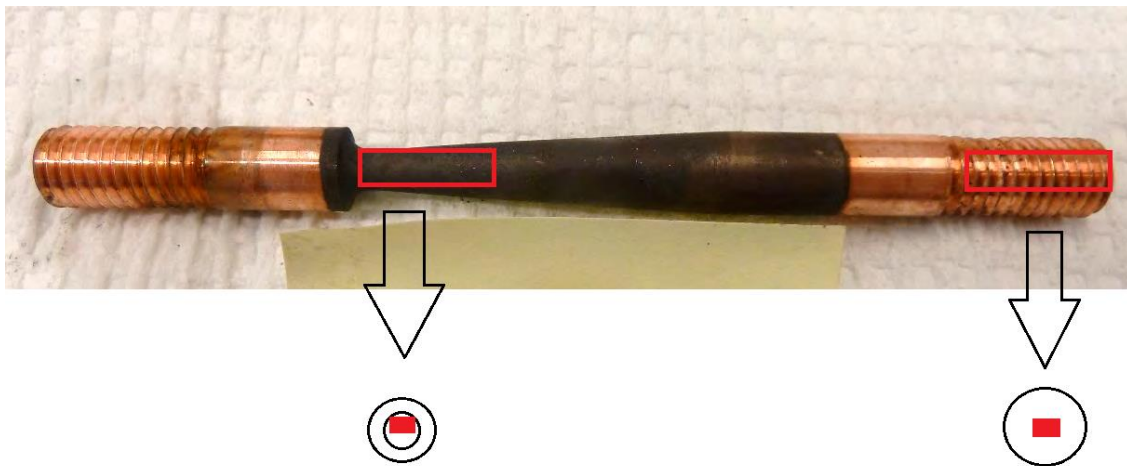

Figure 1. Location of samples for TDS, cut from the SSRT specimens. The samples for TDS were cut from the narrow section of the SSRT specimens and the threaded part of the specimens outside of the Cu_2S covered zone.

SSRT and test environment

The SSRT testing was performed in a controlled deoxygenated environment, in which the only variable was the sulphide concentration [3].   An autoclave loop was used to control the

temperature and test solution. Several experiments were performed with different sulphide concentrations. Target test parameters and measured sulphide concentrations for three of the specimens, which were also TDS tested, are presented in Table 2. In addition, several parameters were monitored during testing, including Electrochemical Corrosion Potential (ECP) of the specimens, to maintain a stable deoxygenated environment. ECPs of Specimens #3, #5, and #7 were -736, -580, and -387 mV vs SHE, respectively. The repository environment was simulated by adding NaCl and Na_2S to the test solution. Addition of Na_2HPO_4 and NaH_2PO_4 was used to control the pH of the solution at 7.2.

The Specimens #3 and #5 were cleaned after exposure in HCl to remove the formed copper sulphide layer and to reveal the eventual cracks. Specimen #7 was cleaned in an ultrasonic bath without cleaning in HCl. This was to preserve the formed sulphide film as much as possible. Crack initiation and propagation was observed with electron microscopy. The location of the cracks was defined by measuring the distance from the narrowest part of the specimen to the crack. The respective true stresses and strains were estimated according to equations based on the specimen dimensions, material properties, and FEM calculations [3].

Table 2. Target and measured test parameters.

Parameter		Target value	Measured value
Temperature		90 °C	90 °C
Cl^- (as NaCl)		0.1 M	-
S^{2-} (as Na_2S)	Specimen #3	1×10^{-3} M	0.9×10^{-3} M
	Specimen #5	1×10^{-4} M	0.7×10^{-4} M
	Specimen #7	1×10^{-5} M	0.3×10^{-5} M
Autoclave flow rate		1 l/h	1 l/h
Strain rate at the narrowest section		-	0.7×10^{-7} s^{-1}
Maximum strain		9 %	9 %
Test time		2 weeks	-

Hydrogen thermal desorption spectroscopy

Hydrogen uptake in the SSRT specimens was studied by using Thermal Desorption Spectroscopy (TDS). The TDS method is based on a mass-spectrometric measurement of hydrogen partial pressure change in an Ultra High Vacuum (UHV) chamber due to heating of the specimen under controlled heating rate.

Samples for TDS measurements were cut with Electro Discharge Machining (EDM) from different parts of the tapered SSRT specimens after their respective exposures to the sulphide containing environment. Samples were taken from the threaded part subjected to minimum load and from the part with maximum load, see Figure 1. Two reference specimens were cut from the copper alloy in as-supplied state. All the samples for TDS were mechanically polished to size of about 0.8 x 3.8 x 10.0 mm finishing with No. 2000 emery paper. Just before TDS measurement,

the samples were cleaned in acetone in an ultrasonic bath for 1 min and dried in pure He gas flow.

TDS curves for the copper specimens were obtained with a calibrated TDS apparatus designed and assembled at Aalto University (Finland). The apparatus allows measurement of hydrogen desorption rate in the temperature range of 20 to 1200 $^{\circ}$C with a controlled heating rate between 1 and 10 $^{\circ}$C/min. Vacuum in the UHV chamber of the apparatus is close to 7×10^{-9} mbar providing a possibility to monitor the hydrogen in copper at concentration level of about 0.02 wt.ppm. After conversion of the measured partial pressure of hydrogen to desorption rate (in wt.ppm per second), the hydrogen concentration in the studied copper was calculated as the area under the measured TDS curve.

Results

SSRT results

Specimen #3 was tested under the highest sulphide concentration. Several surface defects, as shown in Figure 2, were observed. The defects were expected to be possible SCC initiation sites. Cross-section analysis revealed several large SCC cracks on both sides of the narrow section of the specimen. The largest is presented in Figure 3. All of the confirmed SCC cracks were within a few millimetres from the narrowest gauge section of the specimen. The true stresses and strains at the end of test in those areas were estimated to be 154-162 MPa and 7.5-8.9 %, respectively [3].
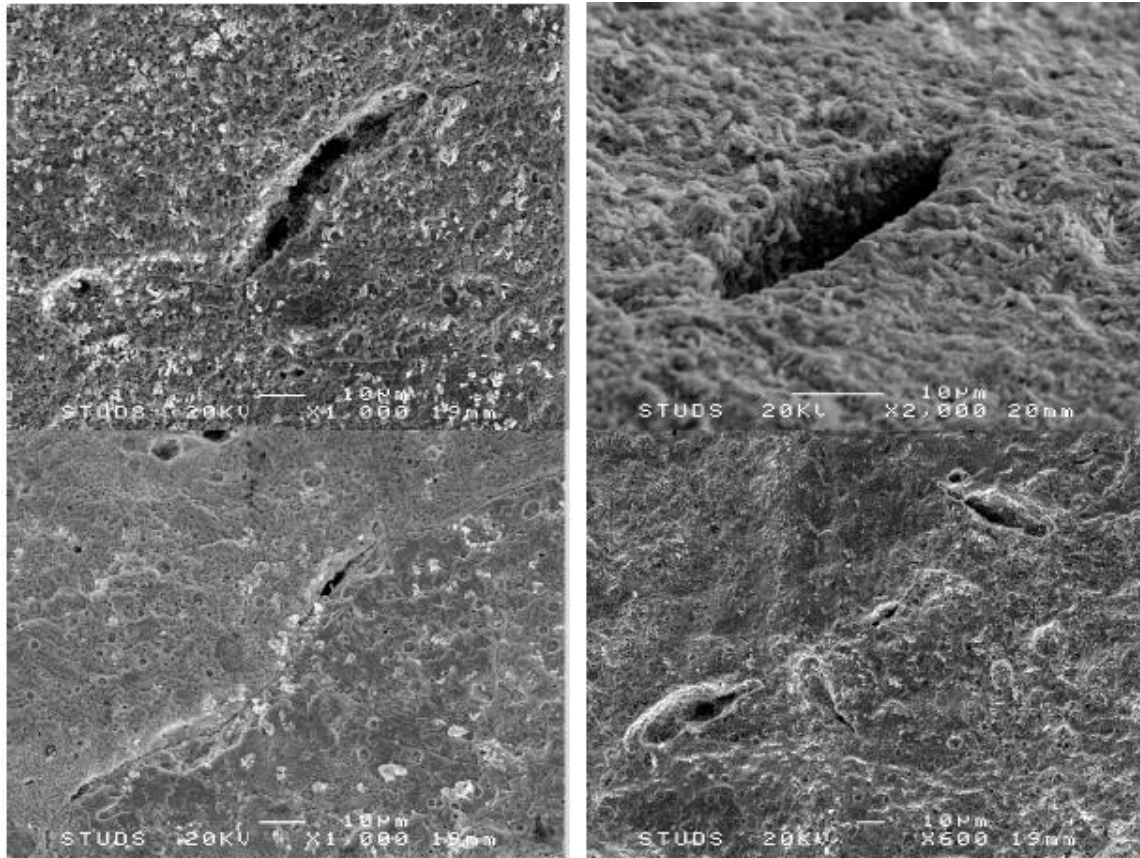
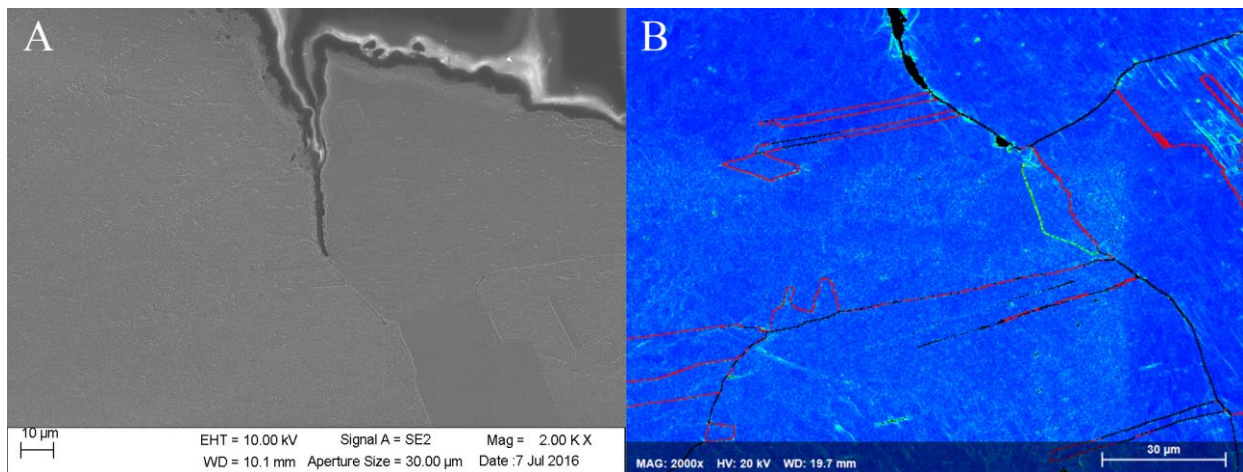*Figure 2. Surface defects near the narrowest part of Specimen #3 after SSRT testing. [3]*

Figure 3. Cross-section images of a SCC crack in the narrow section of Specimen #3. A) SEM image after etching. B) EBSD image showing crack propagation along a random grain boundary. Twin boundaries are marked in red and local misorientation in shades of green.

Specimen #5 was subjected to an environment containing less sulphide than Specimen #3. No obvious SCC cracks were observed after SSRT testing, but surface defects could be observed. Some of the surface defects are presented in Figure 4. Locations of the defects varied greatly along the tapered section of the specimen and similar defects were also found inside the material [3]. Near the waist of the specimen, defects were found deep inside the material as a chain of voids, presented in Figure 5. Such defects deep in the material cannot directly be formed due to interaction with the sulphide-containing aqueous environment. However, they could possibly be attributed to hydrogen uptake, as it diffuses deep into the material. The nature of these small defects has not been further evaluated.
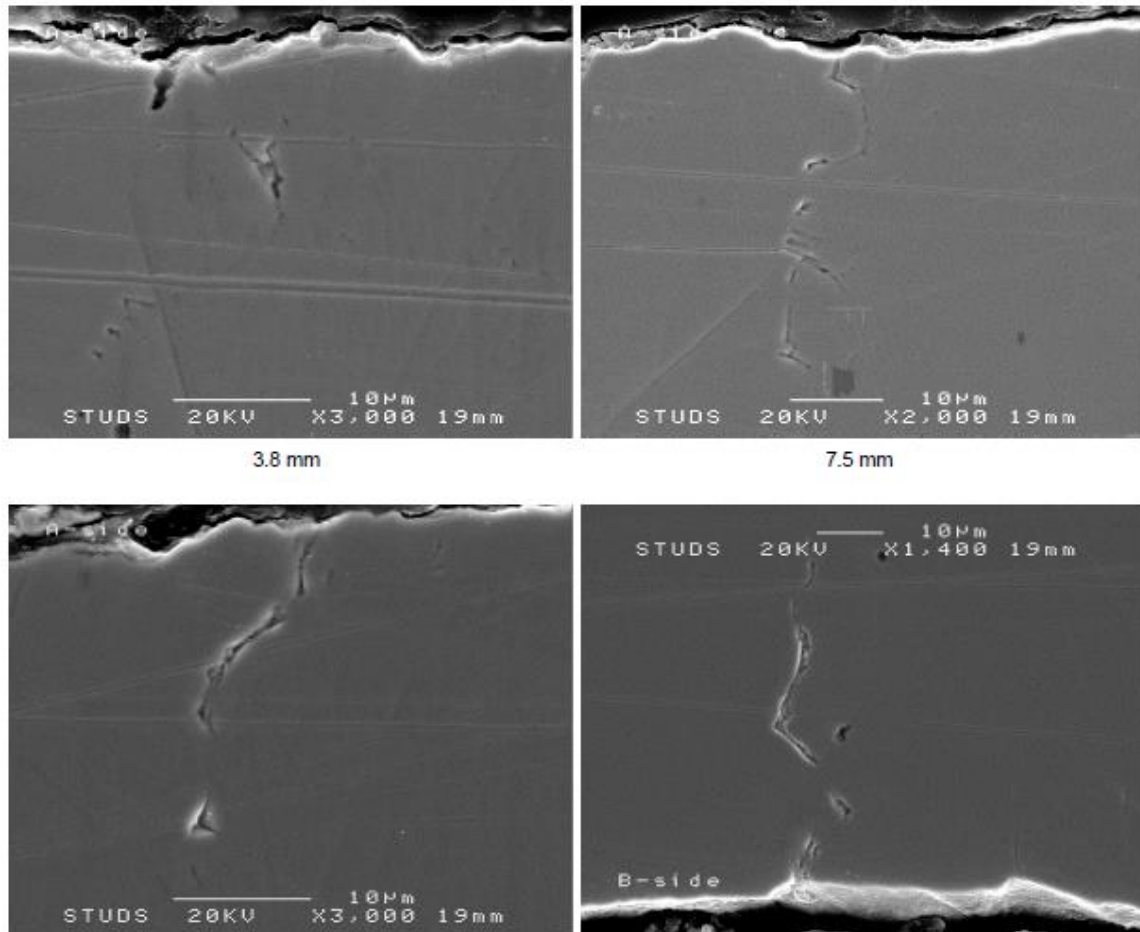

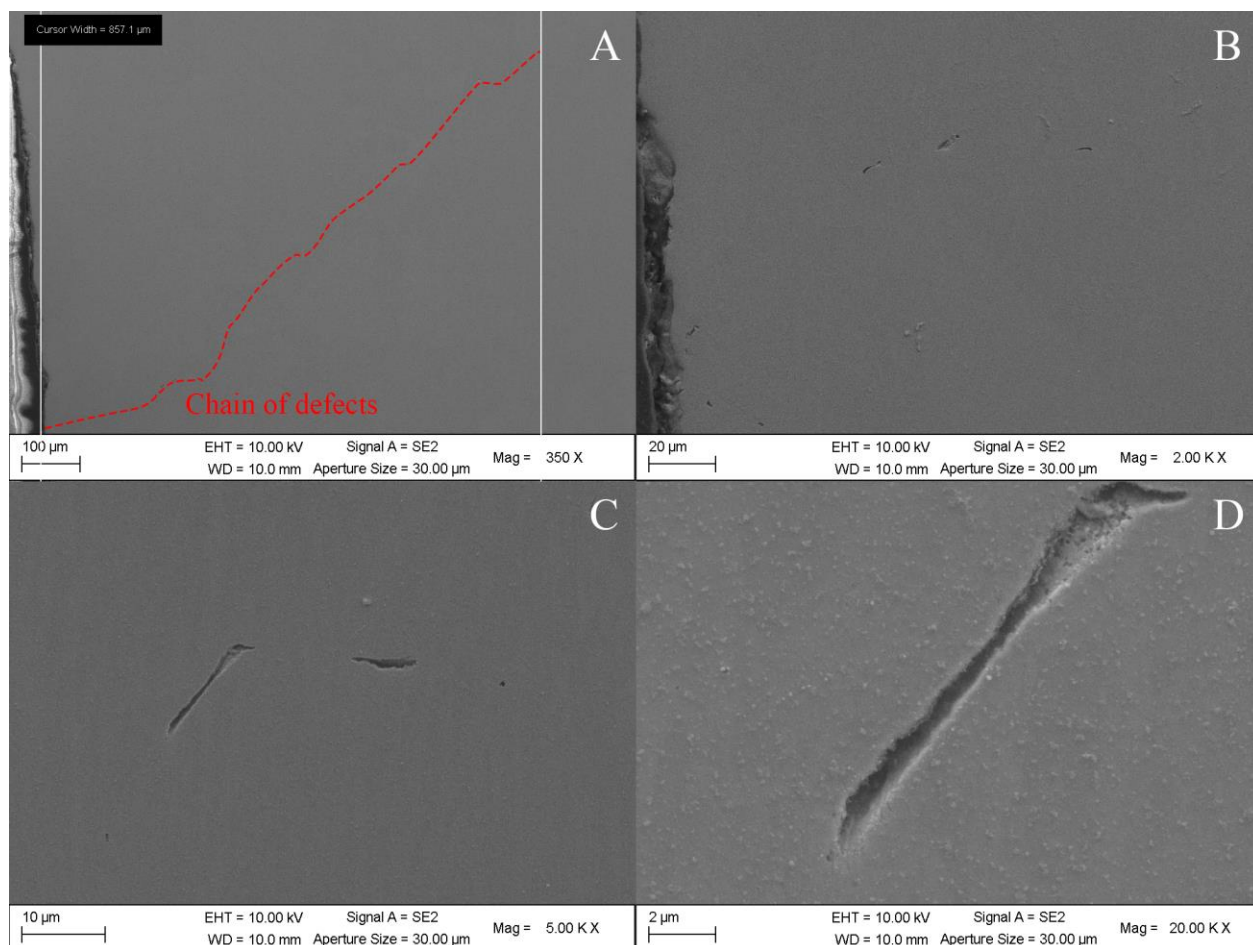*Figure 4. Cross-section images of surface defects in Specimen #5. [3]*

Figure 5. Cross-section of a chain of defects in the narrowest section of Specimen #5. A) Chain of defects propagating 0.85 mm deep into the material. B) The beginning of the chain of defects. C-D) High magnification images of the defects most likely on grain boundaries.

Specimen #7 was subjected to the lowest sulphide content when compared to the previous specimens. The formed copper sulphide film was accordingly thinner and it was partly removed by the ultrasonic cleaning. No clear SCC cracks were found, but similar surface defects were observed as in Specimen #5 and #3, albeit in less quantities. Figure 6 presents some of the surface defects. Most of the defects were located close to the narrowest section of the specimen.
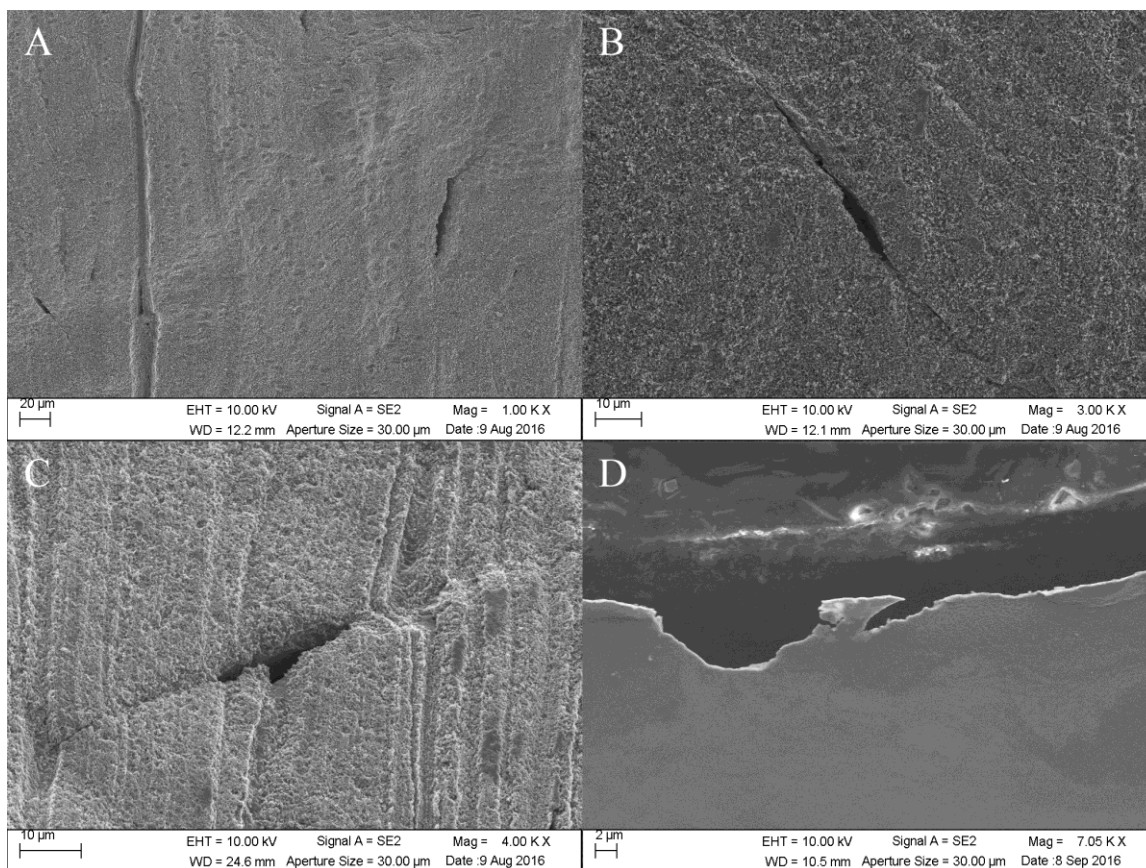
Figure 6. Surface defects in Specimen #7. A) Several small defects. The long vertical groove is most likely from manufacturing of the specimen. B-C) Small surface defects. D) Cross-section of the surface with a possible surface defect.

Results of hydrogen thermal desorption spectroscopy

Temperature dependencies of hydrogen desorption rate measured for Cu-OFP after SSRT and in the as-supplied state (red curves) are shown in Figures 7-9. The dependencies manifest a distinctive and complex peak of hydrogen desorption in the temperature range of 550 to 850 K. The peak consists of, at least, two components, which are more defined in the case of the as-supplied state of copper specimens.

The main finding of the TDS measurements is remarkable; about two times increase of hydrogen content in the copper specimens subjected to SSRT in deoxygenated sulphide environment, when compared to hydrogen content in the as-supplied state of copper. Hydrogen concentrations calculated from the TDS curves in Figures 7-9 are shown in Table 3. It can be concluded that SSRT in deoxygenated sulphide containing environment results in a rather comparable hydrogen uptake, independent of the sulphide content, which is close to 1 wt.ppm for all the tests. An exception is Specimen #5 manifesting about 10 % lower hydrogen content.

The exact origin of the observed complex TDS peak in copper is still unclear. It originated probably from hydrogen de-trapping from energetically deep trapping sites in the copper crystal

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lattice, such as vacancies and vacancy complexes. It is interesting to notice that, in general, SSRT in deoxygenated sulphide containing environment results in an increase of the high-temperature component of the TDS peak. It indicates that SSRT enhanced generation of not only the excessive hydrogen, but also the corresponding crystal lattice defects. A verification of the above hypothesis needs, however, additional studies.
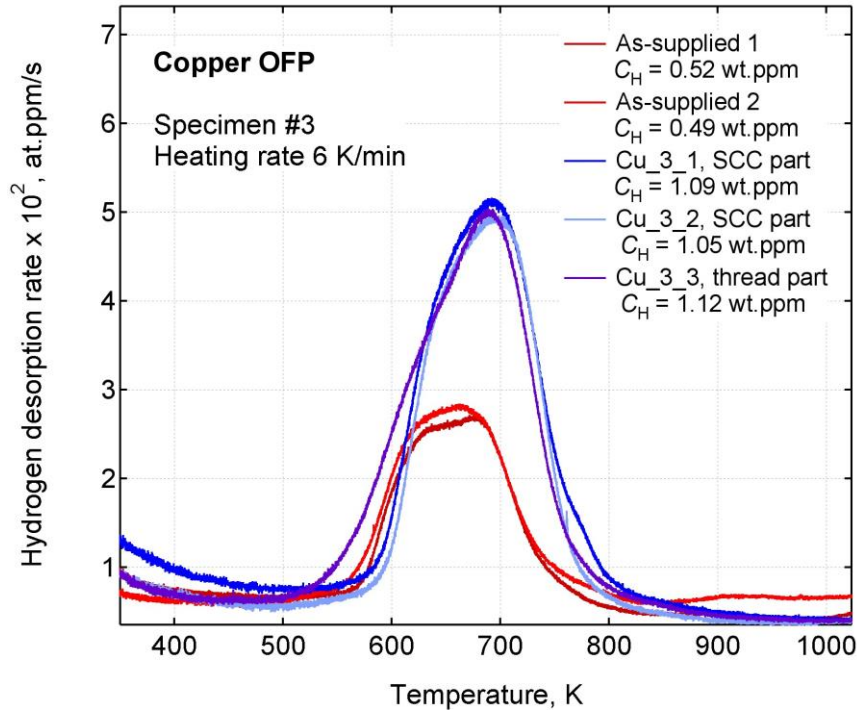

Figure 7. Temperature dependency of hydrogen desorption rate in samples cut from Specimen #3 after SSRT (blue curves) and reference samples in as-supplied state (red curves).
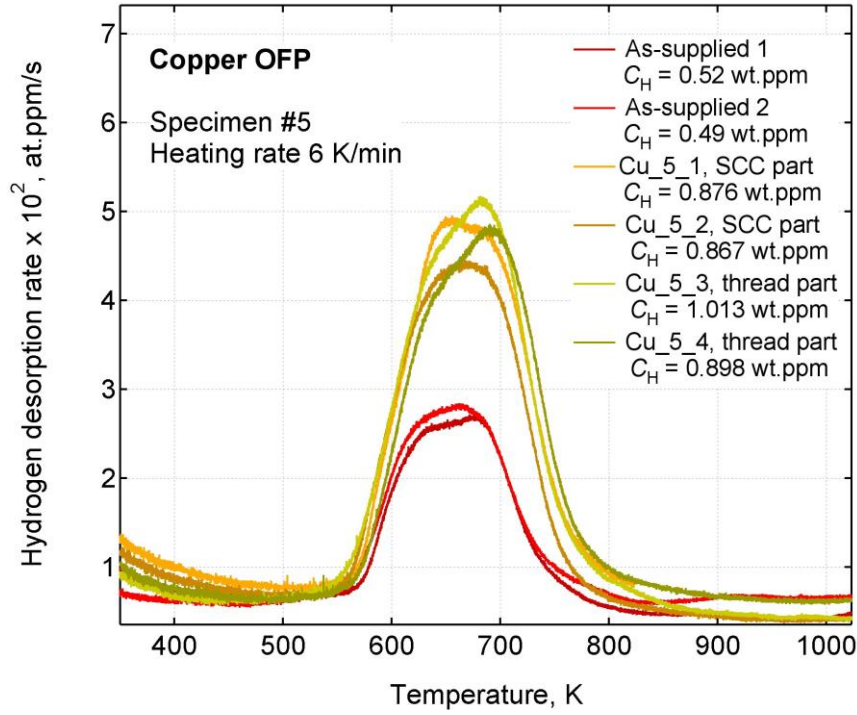
Figure 8. Temperature dependency of hydrogen desorption rate in samples cut from Specimen #5 after SSRT (blue curves) and reference samples in as-supplied state (red curves).
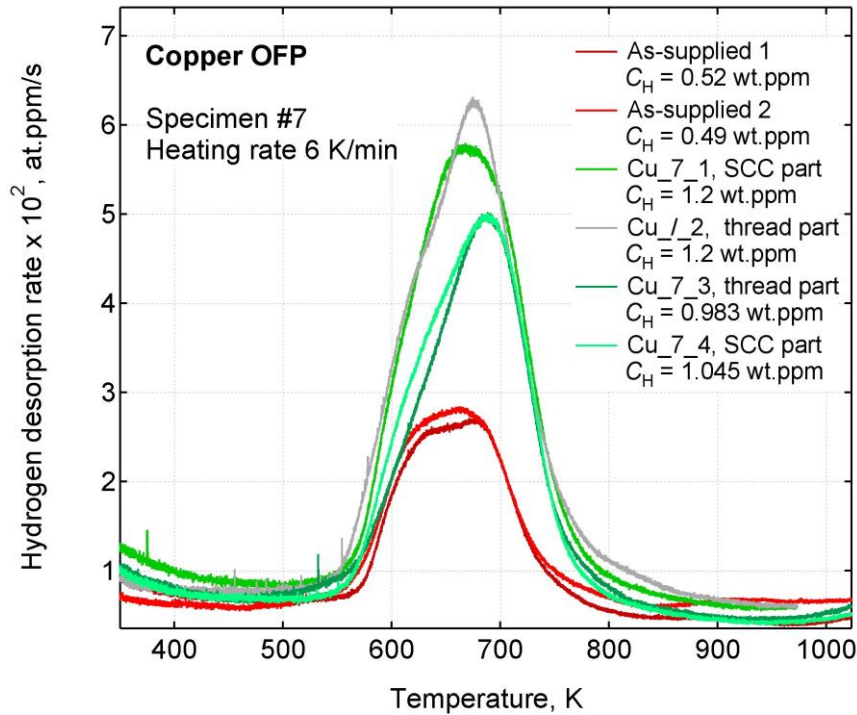

Figure 9. Temperature dependency of hydrogen desorption rate in samples cut from Specimen #7 after SSRT (blue curves) and reference samples in as-supplied state (red curves).

Table 3. Hydrogen concentrations measured with TDS from samples cut from Specimens #3, #5, and #7, as well as, copper in the as-supplied state.

Specimen	Mass (g)	C_H (wt.ppm)	Location
Cu #3 (1)	0.2425	1.10	SCC
Cu #3 (2)	0.2423	1.05	SCC
Cu #3 (3)	0.2659	1.11	Thread
Cu #5 (1)	0.2328	0.88	SCC
Cu #5 (2)	0.2311	0.88	SCC
Cu #5 (3)	0.2568	1.01	Thread
Cu #5 (4)	0.2395	0.90	Thread
Cu #7 (1)	0.2344	1.2	SCC
Cu #7 (2)	0.2677	1.2	Thread
Cu #7 (3)	0.2585	0.98	Thread
Cu #7 (4)	0.2689	1.05	SCC
As-supplied (1)	0.3834	0.52	NA
As-supplied (2)	0.3692	0.49	NA

Discussion

Several slow strain rate tests (SSRT) of Cu-OFP in 0.1 M NaCl containing solution with varying content of S^{2-} (Na_2S) from 0.001 M to 0.00001 M were conducted. The studies show that SCC cracking can occur at sulphide concentration of 0.001 M which is one tenth lower than previously reported in [2], but still higher than the highest measured sulphide content in Forsmark (0.00012 M) [4]. In all studied conditions, surface defects, not positively attributed to SCC, were also present.

The specimens were studied for hydrogen uptake during testing and the hydrogen content of copper increased from 0.5 wt.ppm to 1.2 wt.ppm during the short time SSRT testing of two weeks. This can be compared to the maximum allowed hydrogen content of copper in the KBS-3 concept, which is 0.6 wt.ppm [6]. The current study suggests that the SCC cracking mechanism of copper in reducing anoxic sulphide environment is possibly related to hydrogen uptake in copper and hydrogen-enhanced opening of grain boundaries.

The opening of grain boundaries in the current study is similar to previously observed hydrogen-enhanced creep of Cu-OFP [7]. Micro-voids formed on grain boundaries, which were positioned along maximum shear, indicating a process of accommodating the shear stress component e.g. by grain boundary sliding [7]. It is likely that a similar mechanism is operational in the current SSRT as well, due to hydrogen uptake of the specimens during SCC testing. On the other hand, a simulation study on hydrogen effects on void nucleation in copper showed that hydrogen stabilizes divacancies and promotes vacancy cluster formation [8]. Hydrogen prevents the collapse of large vacancy clusters. Impurities and alloying elements such as O, P, S, and Ag contribute to void formation by capturing vacancies.

The implications of SCC occurring at values close to the expected Forsmark sulphide levels could be severe, so studying sulphide-induced SCC of copper in reducing, anoxic repository conditions is of great importance. The SCC mechanism of Cu-OFP in the studied conditions is still unknown. Additional exposures should be conducted to study especially the mechanisms of oxide/sulphide film formation and hydrogen uptake in the metal, both under oxidizing and reducing conditions. The outcome will deepen the understanding of sulphide-induced SCC mechanism of copper in reducing anoxic conditions, which prevail in the repository conditions for centuries after the short aerobic phase in the beginning of the spent nuclear fuel disposal.

Conclusions

Intergranular SCC of copper in sulphide and chloride containing deoxygenated water at 90 °C in reducing anoxic conditions occurred at sulphide concentration of 0.001 M, which is one tenth lower than 0.01 M reported before [2]. Additional testing was performed at sulphide concentrations down to 0.00001 M, and surface defects, not positively attributed to SCC, were found on the specimen surfaces.

After the SSRT, the specimens were measured for hydrogen content with TDS. They were found to contain 0.8-1.2 wt.ppm hydrogen throughout the whole specimen, which is up to twice the allowed 0.6 wt.ppm according to design specifications [6]. The as-supplied base material contained 0.5 wt.ppm hydrogen. The increased hydrogen content indicates that corrosion reactions in sulphide and chloride containing anoxic conditions result in hydrogen absorption in copper even with a sulphide concentration of 0.00001 M. Similar hydrogen content in all the specimens, regardless of the environment, suggests rapid diffusion and saturation of copper with hydrogen.

Acknowledgements

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