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Keywords: Hydrogen, Creep, OFP copper.

Abstract

Creep testing of OFP copper subjected to continuous and simultaneous hydrogen charging was performed on specimens with various degrees of strain hardening. The test method was developed with the primary goal to reproduce results published by a Finnish research group (Yagodzinskyy et al. 2012). When the test temperature, creep stress and other conditions were held similar to the tests performed by the Finnish research group, no intergranular cracks were found in the OFP copper. The creep stress of the Finnish research group was found to be too low in comparison to other creep tests (Andersson-Östling and Sandström 2009) and for this reason further testing was performed at higher and more adequate creep stress levels. When the higher creep stress was applied, the SEM examinations of cross sections of tested specimens show intergranular cracks extending from the surface of the specimens. The creep strength of the OFP copper tested in this present study is remarkably larger than the creep strength of the copper tested by Yagodzinskyy et al. The results show that hydrogen was successfully introduced into the copper.

Sammanfattning

Krypprovning av OFP-koppar under samtidig inladdning av väte har utförts på prover med olika grader av deformationshårdnande. Provmetoden utvecklades med det primära målet att återskapa samma resultat som en finsk forskargrupp erhållit (Yagodzinskyy et al. 2012). När provningstemperatur, krypspänning och andra provförhållanden var desamma som för den finska forskargruppen, så erhölls inga korngränssprickor i OFP-kopparen. Krypspänningen som den finska forskargruppen använt befanns vara låg i förhållande till annan utförd krypprovning (Andersson-Östling och Sandström 2009) och därför utfördes provning vid högre och mer lämplig krypsspänningsnivå. När den högre krypspänningsnivån användes så visade SEM-undersökningar på tvärsnitt av provade provstavar sprickor från ytan av provstaven. Krypmotståndet hos OFP-kopparen var mycket större i denna studie än krypmotståndet hos kopparn i provningen utförd av Yagodzinskyy et al. Resultaten visar vidare att väteinladdning var framgångsrik.

Contents

1 Introduction

Swerea Kimab performed preliminary creep testing of OFP copper under simultaneous hydrogen charging on a limited amount of specimens under conditions similar to the study published by Yagodzinskyy et al. (Yagodzinskyy et al. 2012). Swerea Kimab strived to duplicate the experimental set up and experiment of Yagodzinsky and succeeded to charge large amount of hydrogen. However, neither the large reduction in creep strength nor reduction in tensile strength of OFP copper with intergranular crack failure with dimples at the fracture surfaces as reported by Yagodzinskyy et al. (2012) was attained. The creep stress that was used in the preliminary tests and in Yagodzinskyy's experiment was low (140 MPa) compared to the stresses used in standard creep tests performed on similar material where the stress levels have been in the range of 170–180 MPa (Andersson-Östling and Sandström 2009). Further testing at higher creep stress was for this reason decided upon.

The stress level was set to values above 170 MPa in order to achieve creep rates and creep testing times in the same order achieved by Yagodzinskyy et al. (2012). The tests were performed at the three temperatures of room temperature (23 °C), 50 °C and 75 °C. The highest temperature of 75 °C better represents the early conditions in the copper canister of the KBS-3 method for disposal of spent nuclear fuel rather than room temperature or 50 °C. The degree of strain hardening of the OFP copper was varied from total stress relaxation after soft annealing to strain hardened OFP copper with pre-strain of 10 % and 20 % respectively.

2 Experimental

2.1 Test setup

The experiments on OFP copper performed in this study aimed at duplication of the experiment reported by Yagodzinskyy et al. (2012). This meant that the experiment would have to achieve hydrogen charging of OFP copper in an electrolyte containing sulphuric acid and arsenic at controlled temperatures under simultaneous creep loading of the OFP copper. The handling of arsenic requires special attention regarding safety due to its toxic properties even in small doses. Swerea Kimab used a similar type of double-wall glass compartment for control of the temperature and containment of hydrogen charging chamber. The creep load was achieved on a combined slow strain rate and creep testing machine. Special attention has been given to seal up the compartment to avoid improper exposure to arsenic.

The experimental set up consists of the following machines and data processing systems:

- SSRT/creep machine for creep stress application.
- Haake C25 Circulating Bath with F6 controller for temperature control.
- Brooks 5800S Series Digital Thermal Mass Flow Meter & Mass Flow Controller for controlled nitrogen bubbling.
- Hamilton oxygen sensor Visiferm DO 120 for dissolved oxygen measurement.
- Sycopel Ministat Potentiostat for hydrogen charging potential.
- Vetek Load cell creep stress application.
- Double-wall glass compartment of Boron glass and PVDF polymer for containment of the hydrogen charging environment.

After SSRT/creep testing:

- A Leco Rhen 602 hydrogen determinator on cut out sections of the gauge section.
- A Bruker AXS X-ray diffraction test rig (XRD) for identifying different phases.

Figure 2-1a shows an overview of most of the equipment constituting the experimental set up. The SSRT/creep machine consists of a grey Bofors Frame and a Vetek Load cell, which is hidden by a black rubber cloth protecting the load cell from possible leakage of electrolyte. The double-wall glass compartment can be seen just above a grey polymer box for further leakage protection. An OFP copper specimen is mounted in the compartment and further attached to the creep machine through the load rod up to the Bofors load frame.

Figure 2-1b shows a close up on the double-wall glass compartment in the beginning of hydrogen charging. The hydrogen charging was performed in an electrolyte of 1 N H_2SO_4 solution with 10 mg $NaAsO_2$ (or 5 mg As_2O_3) per litre at a controlled potential of –1.1 $V_{Hg/Hg2SO4}$. The addition of arsenic to the electrolyte will impede the reaction of 2 adhered hydrogen atoms to recombine to H_2 and it will hence facilitate the hydrogen charging.

The electrode can be seen with a blue cap immersed into Luggin-probe of Hg/Hg_2SO_4. The bubble bottle standing on the double-wall glass compartment receives the hydrogen overpressure arising from the hydrogen bubbling in the compartment. The white tubing was Norprene from Watson Marlow with very low diffusivity of hydrogen. A black bellow of butyl rubber is placed on top of the double-wall glass compartment but below the outlet of the hydrogen overpressure. A black electric cable can be seen in Figure 2-1b and it is connected to the Pt reference electrode. The red electric cable is connected to the OFP copper specimen through a specimen holder constructed of the same OFP copper as the specimen. The specimen is electrically insulated from the creep testing machine further up the load rod with a layer of ceramic as well as a layer of Bakelite. The ceramic layer is applied on a steel pin going through the load rod and it is indicated with a red arrow in Figure 2-1a. The same electric insulation is to be found below the specimen, but it is hidden by the rubber cloth for leakage protection.

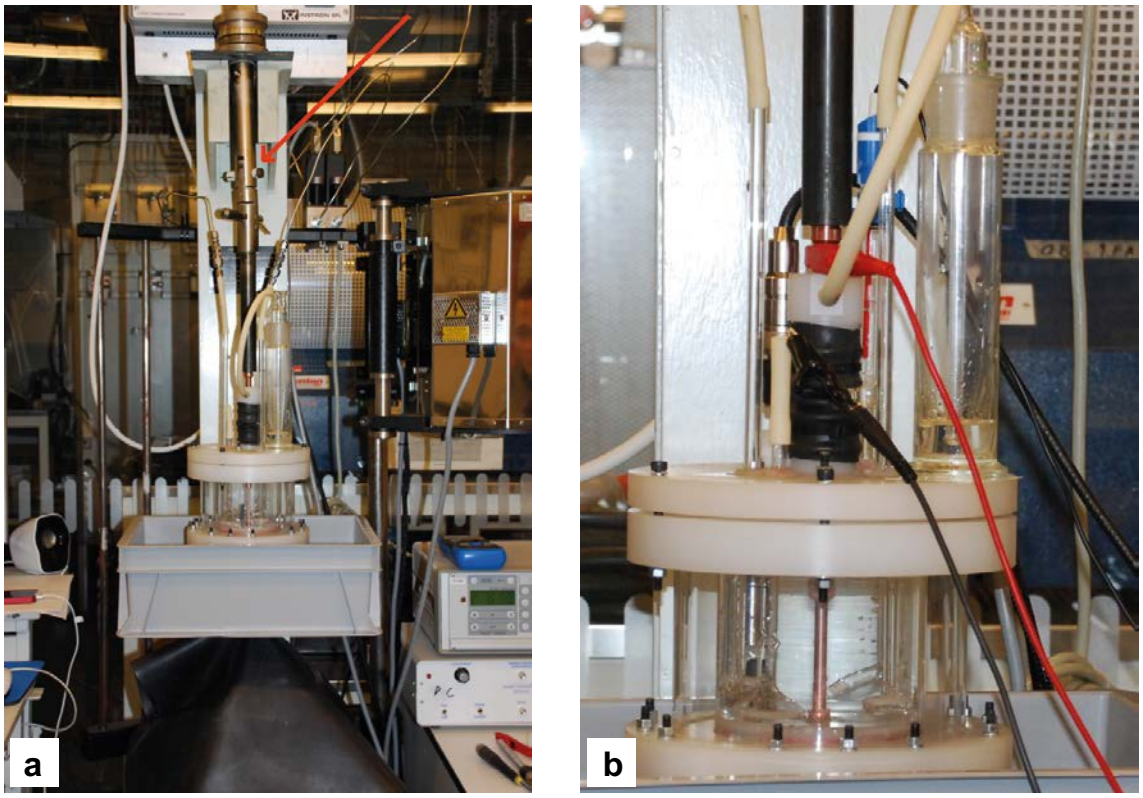


Figure 2-1. *The test setup. In a) an overview of the setup the red arrow pointing at the electrically insulated pin, b) a close-up of the reaction chamber.*

Figure 2-2 shows the drawing of the test chamber. The operator is supervising the initial phase of hydrogen charging where the potential is lowered stepwise in a controlled way to the correct level during 20 minutes. When the correct level had been attained followed the three hours of hydrogen charging and thereafter the controlled increment of tensile load to the specified creep stress. The controlled increment of load to specified creep stress lasted 7 minutes and the stress only showed a small overshot of stress close to 5 MPa and it thereafter stayed at the stipulated level.

Figure 2-3 shows a close up of the double-wall compartment under hydrogen charging. The specimen (a) in the middle is covered with bubbles over the gauge length where the hydrogen is entering the OFP copper. This is a typical sign of successful hydrogen charging since the only gas that can be released here is hydrogen. The part of the specimen outside the gauge length is protected by a layer of epoxy in order to really concentrate the hydrogen charging to the desired part of the specimen. The Luggin-probe of Hg/Hg_2SO_4 electrode (b) is directed close to the specimen gauge length. The Pt reference electrode (c) is immersed into the electrolyte through a filter tube for reversed filtration where the filter act as an obstacle for the oxygen gas arising at the Pt electrode to enter the compartment. Two filter tubes (d,e) bubbles nitrogen directly into the compartment in order to keep the dissolved oxygen level low. The dissolved oxygen level is measured with the oxygen sensor (f) Hamilton Visiferm DO 120.

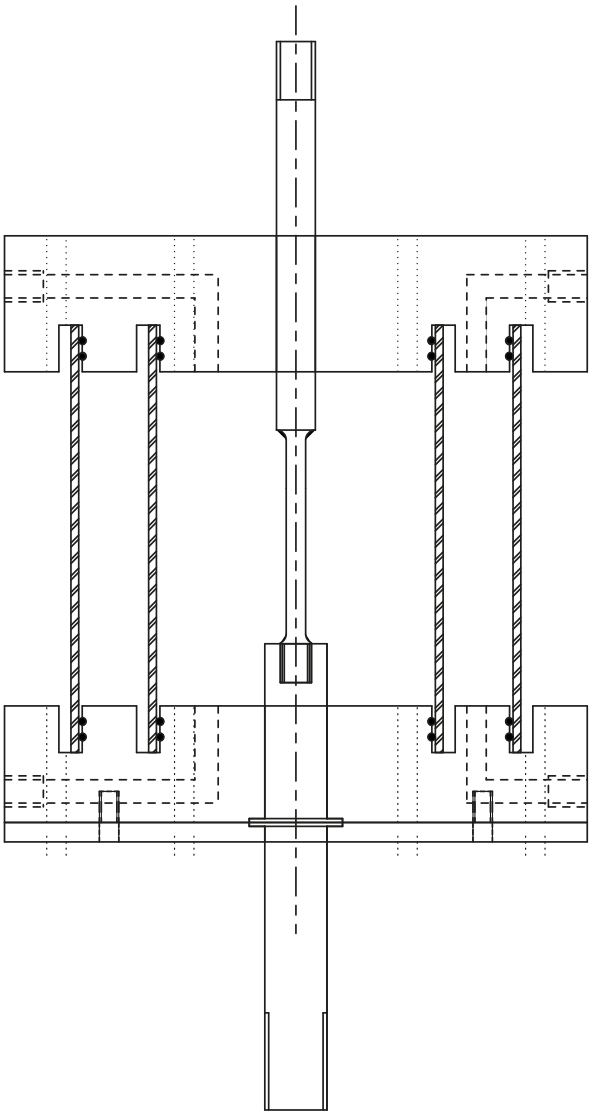


Figure 2-2. *The chamber design.*

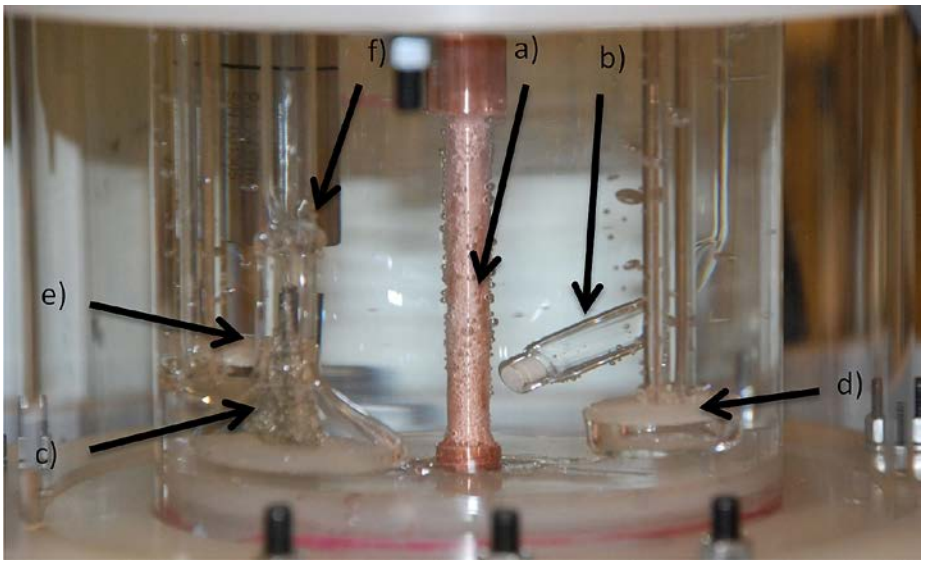


Figure 2-3. *The different parts of the reaction chamber where a) specimen, b) Luggin-probe, c) Pt reference electrode, d) e) filter tubes, f) oxygen sensor.*

2.2 Experimental details

The testing was performed in three stages, where the first preliminary stage involved the same low creep stress at 140 MPa used by Yagodzinskyy et al. (2012) and the second stage employed higher creep stress at approximately 170 MPa (see Table 2-1). The higher creep stress was choosen to obtain creep rates similar to Yagodzinskyy et al. (2012). The electolytical hydrogen charging was performed from 1 N H_2SO_4 solution with either 10 mg/l $NaAsO_2$ or 5 mg/l As_2O_2. The difference in arsenic salt is in the presence of Na in one type of the salts. Swerea Kimab has used As_2O_2 successfully previously for charging of hydrogen in OFP copper (Martinsson et al. 2013) but used the same type of salt as Yagodzinskyy with 10 mg/l $NaAsO_2$ on specimen H-creep-03 to H-creep-13 to ensure that no undesired difference would occur on behalf of the salt. The amount of arsenic is the same in both electrolytes. The surface of the specimen gauge length differed for the specimen in the degree of polishing. Specimen H-creep-01 to H-creep-03 was polished with 3 µm diamond pastes and specimen H-creep-04 to H-creep-13 was ground with P4000 silicon carbide paper. The different specimen polishing methods yield a similar surface and should for the individual specimen surface be similar. Yagodzinskyy used 3 µm diamond pastes for polishing of the specimen gauge length. The pre-strain of the specimen was 0 %, 10 % or 20 %. This is significantly below 24 %, where previous experience has showed that the necking of the specimen starts. As no recrystallization is expected at 75 °C the microstructure of the copper is unchanged during testing of the pre-strained copper in Table 2-1. (Yagodzinskyy et al. 2012) did not report on the degree of pre-straining of the OFP-copper.

The third and final stage was to repeat three of the tests from the second stage but without the hydrogen charging as a reference test (H-creep-14 to 16). The electrolyte could still have a corrosive effect not present when the charging voltage is applied, and therefore the charging voltage was set at 10 % of the voltage used for the full charging experiments. This voltage was low enough to act as a cathodic protection for the specimen but low enough to not create any hydrogen bubbles at the surface.

Table 2-1. Test matrix.

Specimen	Temperature (°C)	Creep Stress (MPa)	Pre-strain (%)	Material Designation	Arsenic salt
H-creep-01	RT	140	0	TX104-K4	5 mg/l As_2O_2
H-creep-02	RT	140	0	TX104-K4	5 mg/l As_2O_2
H-creep-03	RT	140	0	TX104-K4	10 mg/l $NaAsO_2$
H-creep-04	50	185	0	TX184-K4	10 mg/l $NaAsO_2$
H-creep-05	RT	170	0	TX184-K4	10 mg/l $NaAsO_2$
H-creep-06	50	172	0	TX184-K4	10 mg/l $NaAsO_2$
H-creep-07	RT	175	10	TX184-K4	10 mg/l $NaAsO_2$
H-creep-08	50	172	10	TX184-K4	10 mg/l $NaAsO_2$
H-creep-09	50	172	20	TX184-K4	10 mg/l $NaAsO_2$
H-creep-10	75	172	20	TX184-K4	10 mg/l $NaAsO_2$
H-creep-11	75	176	10	TX184-K4	10 mg/l $NaAsO_2$
H-creep-12	RT	176	20	TX184-K4	10 mg/l $NaAsO_2$
H-creep-13	75	176	0	TX184-K4	10 mg/l $NaAsO_2$
H-creep-14	50	172	10	TX184-K4	10 mg/l $NaAsO_2$
H-creep-15	50	172	0	TX184-K4	10 mg/l $NaAsO_2$
H-creep-16	75	172	20	TX184-K4	10 mg/l $NaAsO_2$

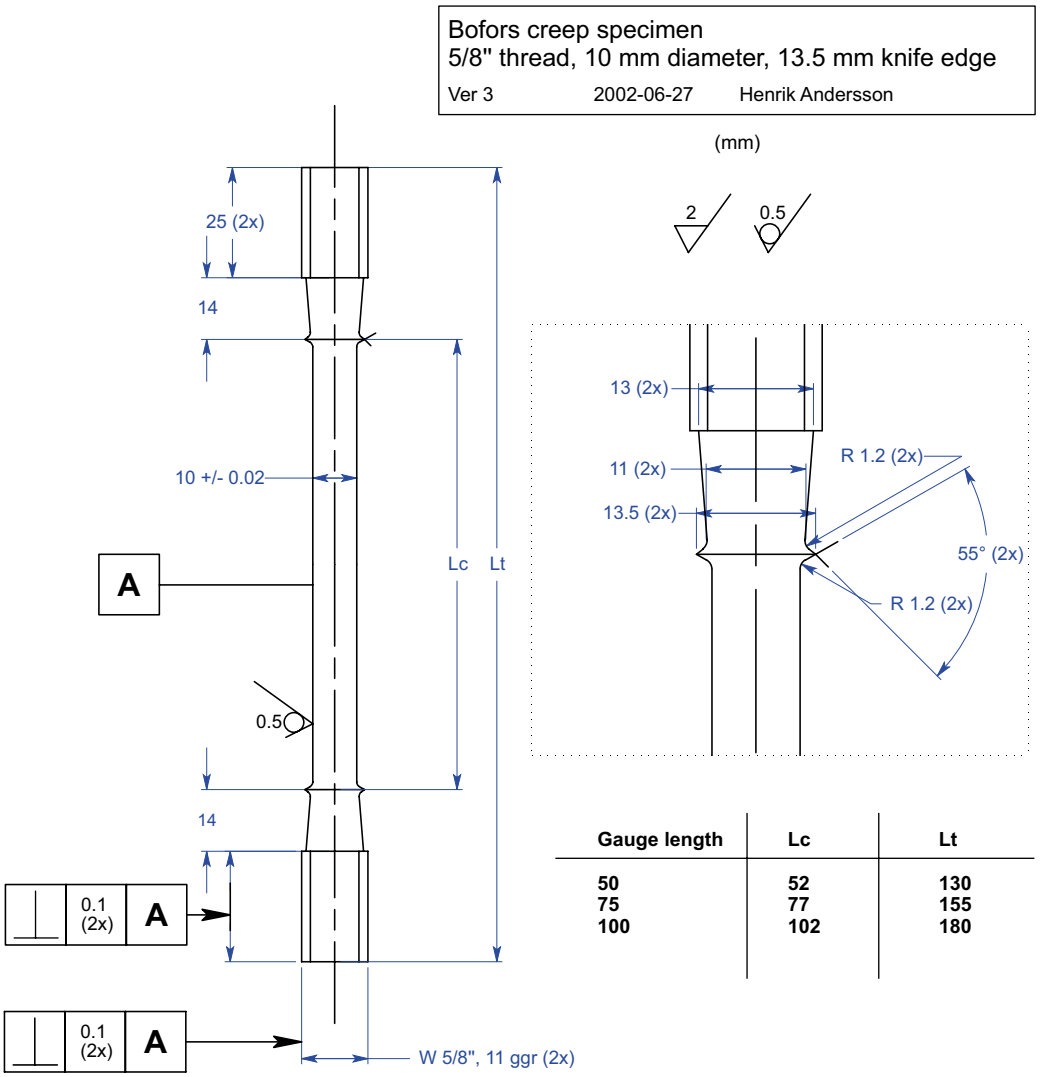
One aim of the study after the three first preliminary tests was to increase the test temperature to at least 75 °C. The increase in temperature was unfortunately difficult to achieve in the original set up as the increase in thermal expansion of copper and PVDF (polyvinylidene difluoride) parts of the compartment made the quartz glass of the double wall compartment to crack. The double wall compartment had to be adjusted to make it function at 75 °C.

The OFP copper used for the specimens of the three first tests has the designation TX104-K4 and for the following tests the designation TX184-K4 (Leskinen and Ronnetag 2009).The degree of pre-strain of specimen H-creep-04 to H-creep-16 was achieved in the following way:

1. The copper was cut and machined into specimen according to Figure 2-4.
2. All "Bofors creep specimens" were soft annealed for 10 minutes at 600 °C in a salt bath as shown in Figure 2-5. The salt was 50 % Na_2CO_3 and 50 % KCl, which melts at approximately 450 °C and has a working temperature range between 500 to 800 °C.
3. One third of the specimens were pre-strained to 10 % strain and one third of the specimens were pre-strained to 20 % strain in tensile test machine (room temperature and laboratory air, 10^{-3} s^{-1}). One third of the specimens were left without any pre-straining.
4. From the "Bofors creep specimens" with various pre-strain the actual specimens utilized in the tests were manufactured according to Figure 2-6. The specimen is a standard 5K50 creep specimen.

Specimen H-creep-01 to H-creep-03 was made in the following way:

1. The material was cut in small parts with the approximate dimensions of 120 × 10 × 10 mm.
2. The parts were soft annealed for 10 minutes at 600 °C in an ordinary resistance oven.
3. The specimens were machined out of the soft annealed parts according to Figure 2-6.



Gauge length	Lc	Lt
50	52	130
75	77	155
100	102	180

Figure 2-4. *The Bofors Creep Specimen with Lc = 100 mm and Lt = 180 mm.*

Figure 2-5. *The salt bath used for soft annealing of the Bofors creep specimens at 600 °C for 10 minutes.*

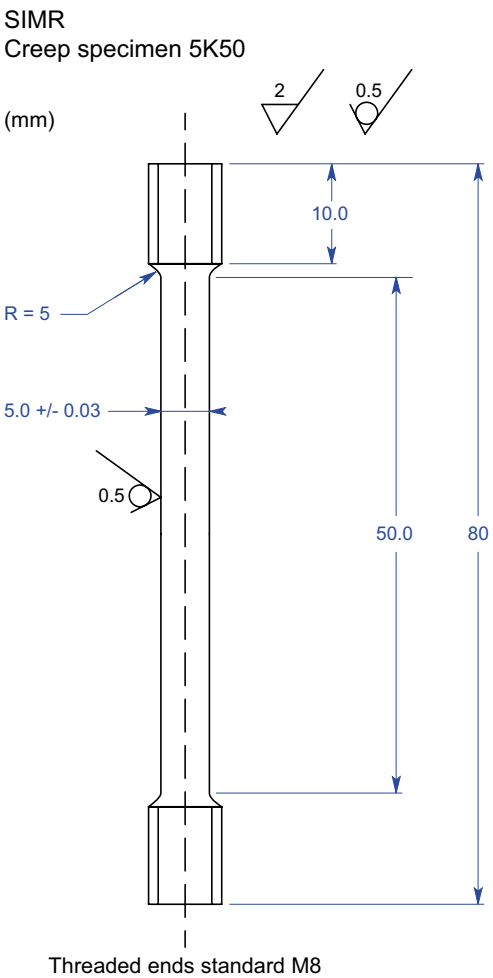


Figure 2-6. *The standard 5K50 specimen used in the testing of hydrogen charging under simultaneous creep load.*

3 Results

Swerea Kimab performed 13 tests of hydrogen charging of OFP copper under simultaneous creep loading using the experimental set up described in the previous section. The specimens were hydrogen charged for three hours before the creep stress was applied. The parameters of the tests are given in Table 3-1 together with the amount of hydrogen obtained after each test. The hydrogen content was determined on pieces cut from the gauge length approximately 5.5 mm long. Two sections were cut out for each specimen.

Yagodzinskyy reports that the tests were discontinued after 100 hours if no failure yet had occurred. Most of the tests performed in this study were discontinued after a certain time with no problems occurring during the test. On one occasion (specimen H-creep-04) did the specimen reach such large degrees of strain that large necking occurred and the creep test was discontinued without fracture, but with large local strain at the neck. The creep stress of 185 MPa applied on specimen H-creep-04 was chosen on basis of creep testing of OFP copper performed in another project at Swerea Kimab. The intention was to achieve large strain with a short creep testing time, but the short time of 200 minutes was not expected. The hydrogen charging time for this specimen was 16.7 hours including the 3 hours before the actual creep load was applied and the time of 10.2 h after creep testing until the whole test was discontinued.

One of the tests, specimen H-creep-13, ended with fracture of the specimen. The creep stress of 176 MPa applied on the specimen H-creep-13, which was not pre-strained after soft annealing, proved to be too high at 75 °C.

Table 3-1. Test matrix with test parameters and amount of charged hydrogen in wt-ppm.

Specimen	Temp. (°C)	Creep stress (MPa)	Creep time (hours)	Charge time (hours)	Pre-strain. (%)	Hydrogen amount (wt ppm)		Comment
						Measured values	Average	
H-creep-01	RT	140	92.5	95.5	0	3.7 ; 3.9	3.8	Discontinued
H-creep-02	RT	140	92	95	0	7.8 ; 8.0	7.9	Discontinued
H-creep-03	RT	140	100	103	0	7.6 ; 8.1	7.9	Discontinued
H-creep-04	50	185	3.3	16.7	0	1.8 ; 1.3	1.6	Discontinued/ Large necking
H-creep-05	RT	170	1 005.7	1 008.7	0	8.7 ; 8.2	8.5	Discontinued
H-creep-06	50	172	113.0	116.0	0	7.1 ; 8.3	7.7	Discontinued/ charge unstable
H-creep-07	RT	175	94.6	97.6	10	2.9 ; 4.7	3.8	Discontinued
H-creep-08	50	172	114.5	117.5	10	7.3 ; 8.7	8.0	Discontinued/ charge unstable
H-creep-09 *	50	172	168.5	171.5	20	4.6 ; 5.0	4.8	Discontinued
H-creep-10	75	172	168.8	171.8	20	11.8 ; 6.4	9.2	Discontinued
H-creep-11	75	176	97.9	100.9	10	10.8 ; 7.2	9.0	Discontinued
H-creep-12	RT	176	257.3	260.3	20	6.1 ; 6.0	6.1	Discontinued
H-creep-13	75	176	13.4	16.4	0	Measurement failed		Fractured
H-creep-14	50	172	120	0**	10	1.6 ; 2.5	2.0	Discontinued
H-creep-15	50	172	167	0**	0	1.6 ; 2.0	1.8	Discontinued
H-creep-16	75	172	20	0**	20	1.2 ; 0.9	1.0	Discontinued

* Specimen H-creep-09 experienced longer time (5 hours) before it was put in liquid nitrogen prior to the hydrogen measurement.
** Specimens H-creep-14 to 16 are reference samples where no hydrogen charging was taking place.

The specimens H-creep-06 and H-creep-08 were discontinued due to unstable charging conditions. Despite the assumed instability, the hydrogen charging proved out to be successful since high amounts of hydrogen were measured in both specimens. A possible reason for the unstable charging could be that the reference electrode was poor in function. The reference electrode was changed after testing of specimen H-creep-08, and the problem did not occur again. The unstable hydrogen charging manifested itself in a variation in the controlled potential of –1.1 $V_{Hg/Hg2SO4}$, but on both occasions did the bubbling of hydrogen gas close to the specimen continue with high intensity. The variation in the control potential occurred at the end of the test when it was discontinued.

The test parameters for the reference tests H-creep-14, H-creep-15 and H-creep-16 was chosen to repeat H-creep-08, H-creep-06 and H-creep-10 respectively.

The time after the test was discontinued until the specimen was cut and put into liquid nitrogen was 5 hours for specimen H-creep-09. For all other specimens this time was approximately 10 minutes. This may be the explanation for this relatively low value of the hydrogen content for specimen H-creep-09. Note that Yagodzinskyy et al. do not present any measurements on hydrogen content in the specimens (Yagodzinskyy et al. 2012).

Parts of the specimens gauge length were cut out for SEM inspection. Figure 3-1 shows two pictures of the surface of specimen H-creep-04 from close to the necking portion of the gauge length where the material had undergone a large deformation. This creep test was finished after only 200 minutes (3.3 hours) of creep testing when the necking was so large that the load drop limit triggered. The load drop trigger was set at 30 kg, which corresponds to approximately 8 % decrease in load from the initial 367 kg. The amount of charged hydrogen was very low compared to all other specimens, most probably due to the short total hydrogen charge time of 16.7 hours.

Figure 3-2 shows the surface of specimen H-creep-13 taken on the necking section of the specimen that experienced large transverse contraction, but not at the actual fracture surface. The section shown in the picture is hence from the same part as for the section of specimen H-creep-4 shown in Figure 3-1 and may be compared.

The micrographs shown in Figure 3-1 and Figure 3-2 present cracking of the surface at the necking section of specimen that experienced large transverse contraction, but not at the fracture surface (cross section). The resemblance of the surface shown in Figure 3-2 with the SEM image shown by Yagodzinskyy et al. (2012, p 933, Figure 3) is striking. One difference in appearance is that the surface shown by Yagodzinskyy et al. seems glossier than the surfaces in Figure 3-1 and Figure 3-2. The lustreless appearance in Figure 3-1 and Figure 3-2 is due to the grey CuAs layer on the specimen surface from the testing. This layer is easily detached from the surface and does not need extensive polishing to wear off. Another difference is that the many small dimples shown by Yagodzinskyy et al. at higher magnification could not be found in the surface cracks on specimen H-creep-04 or H-creep-13 at the corresponding magnifications.

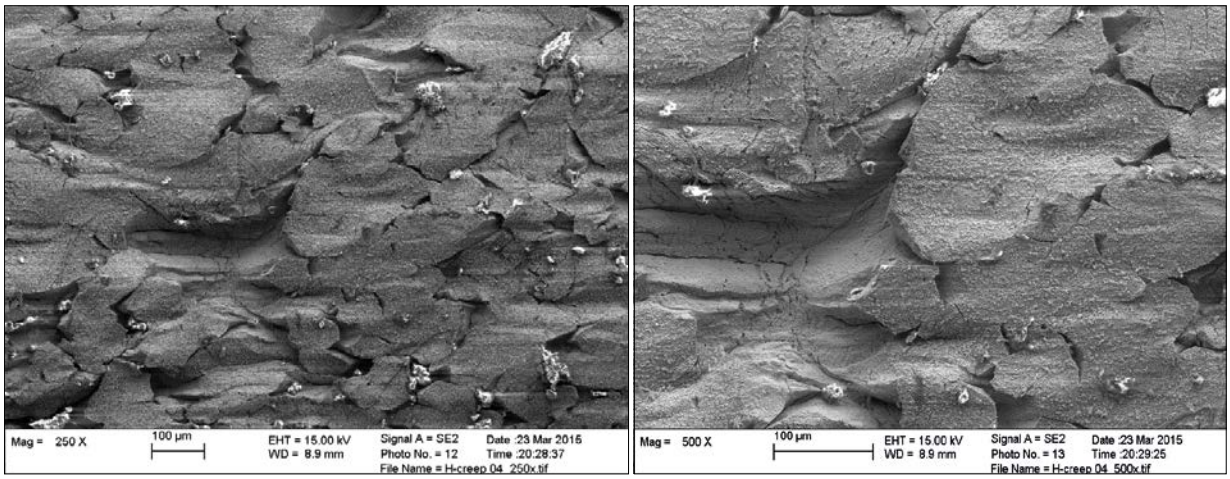


Figure 3-1. *The surface of specimen H-creep-04 at the necking section of the specimen that experienced large transverse contraction. The specimen contained 1.6 ppm of hydrogen and was creep tested at 200 minutes before the test was finished due to necking and trigger of load drop criteria.*

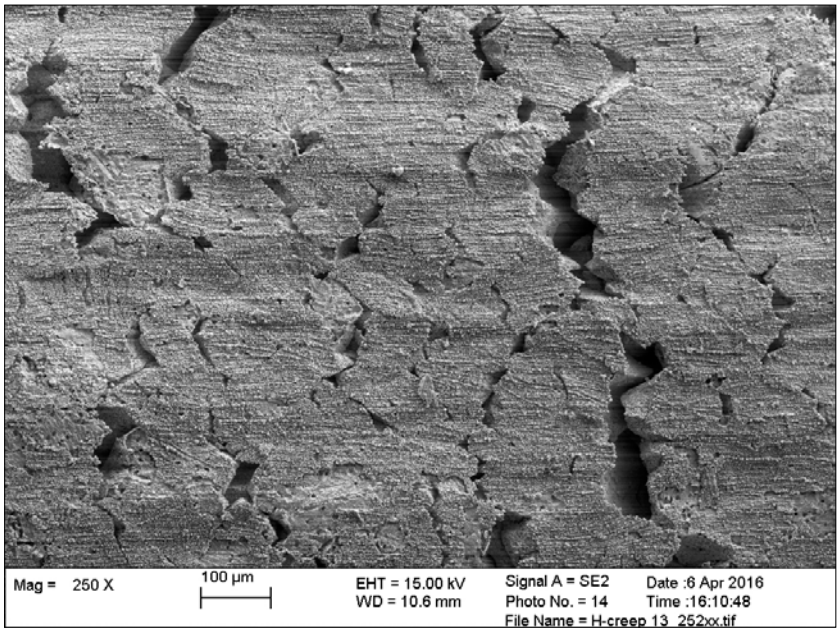


Figure 3-2. *At the neck of the specimen H-creep-13.*

Even though most of the specimens did not fail during the testing, they could still present hydrogen attack of the grain boundaries with cavities (or dimples) at or near the grain boundaries. Figure 3-3 shows a cross section of specimen H-creep-08 with a crack that extends from the surface approximately 25–30 µm into the bulk.

Figure 3-4 shows a cross section of specimen H-creep-11 creep tested at 75 °C. Note the change in direction of the crack as the crack follows the grain boundary.

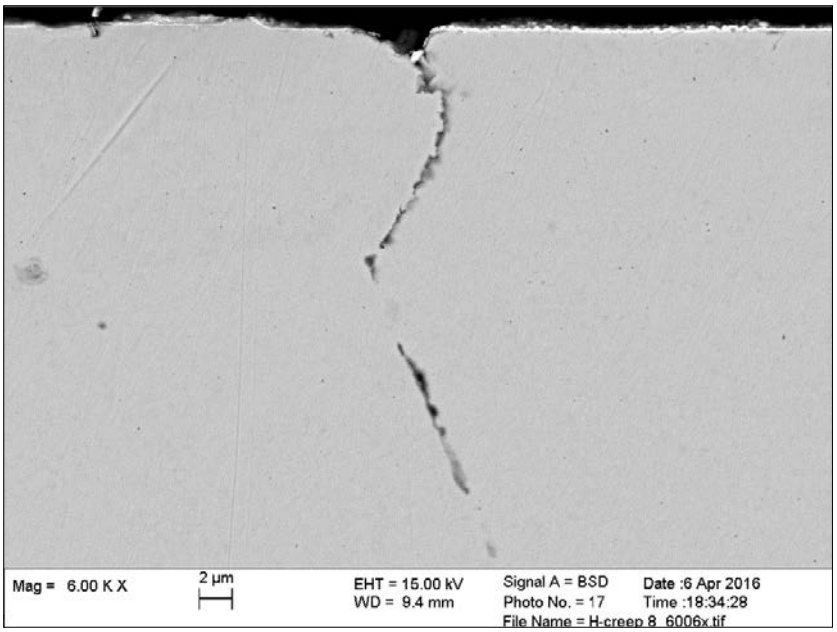


Figure 3-3. *Specimen H-creep-08 tested at 50 °C for 117.5 hours of hydrogen charging time and at 172 MPa creep stress. The picture is a cut out cross section of the specimen showing a crack extending from the surface of the specimen.*

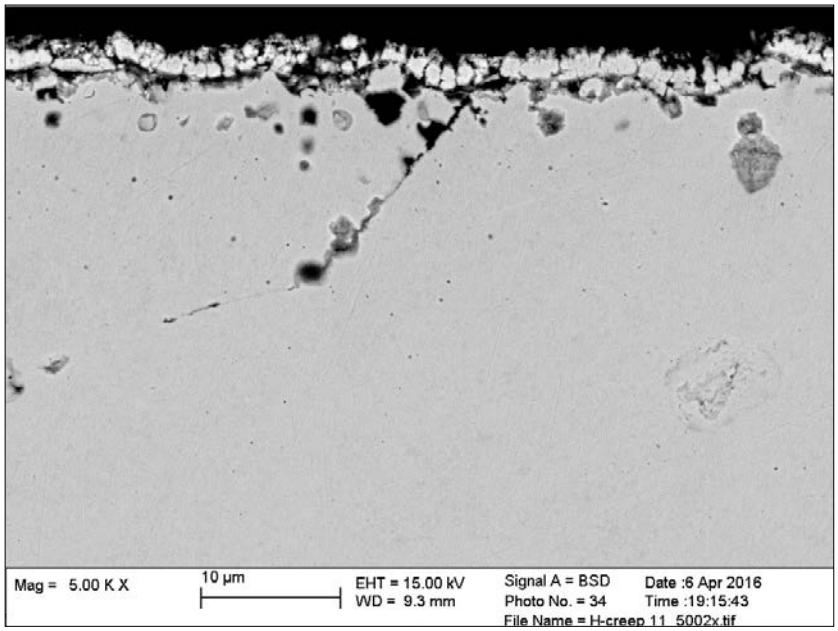


Figure 3-4. *Specimen H-creep-11 tested at 75 °C for 100.9 hours hydrogen charging time. The picture is a cut out cross section of the specimen showing a crack extending from the surface of the specimen.*

Figure 3-5 shows a cross section of specimen H-creep-12 where no cracks could be found. The specimen was tested at RT with a creep stress of 176 MPa and 260.3 hours of hydrogen charging. The total amount of hydrogen was 6.0 ppm for specimen H-creep-12 which is intermediate in comparison with the amount of hydrogen obtained for other specimens.

The displacement during creep testing with simultaneous hydrogen charging was measured successfully for some of the specimen with an analogue dial indicator with 1 µm in resolution (Figure 3-6). Figure 3-7 shows the specimen elongation for the two specimens H-creep-08 and H-creep-11.

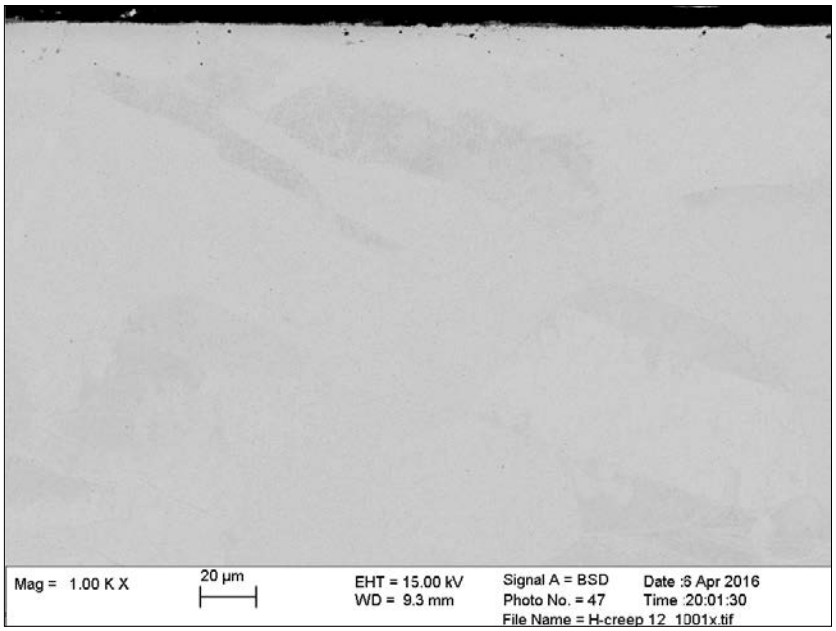


Figure 3-5. *Specimen H-creep-12 tested at RT for 260.3 hours hydrogen charging time and creep stress of 176 MPa. No cracks are seen. The specimen was pre-strained to 20 %.*

Figure 3-6. *The analogue dial indicator with 1 µm in resolution used for measurement of elongation.*

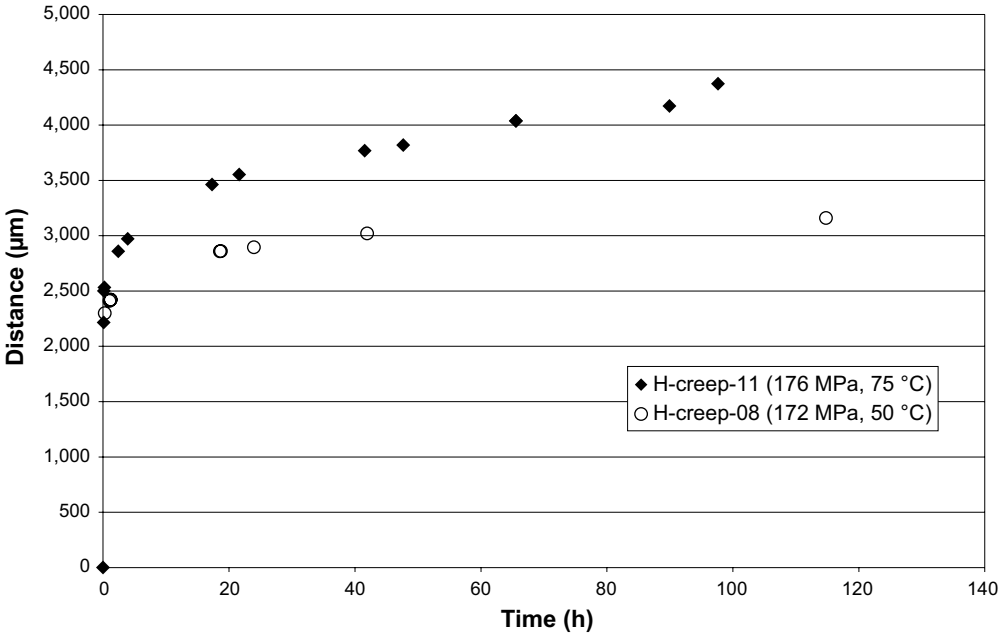


Figure 3-7. *Displacement during creep testing with simultaneous hydrogen charging for specimen H-creep-08 and H-creep-11 measured with an analogue dial indicator with 1 µm in resolution.*

Figure 3-8 shows one of the largest intergranular cracks found in this study. It was found at a cross section of specimen H-creep-05, which had been subjected to 1 005.7 hours of hydrogen charging under 170 MPa nominal creep stress. The specimen was of 0 % pre-strain, i.e. it was manufactured from soft annealed copper. Note the encircled formation of cavities following the grain boundaries where no crack has yet been established.

Figure 3-9 shows another example of cracks discovered on a cross section of specimen H-creep-05.

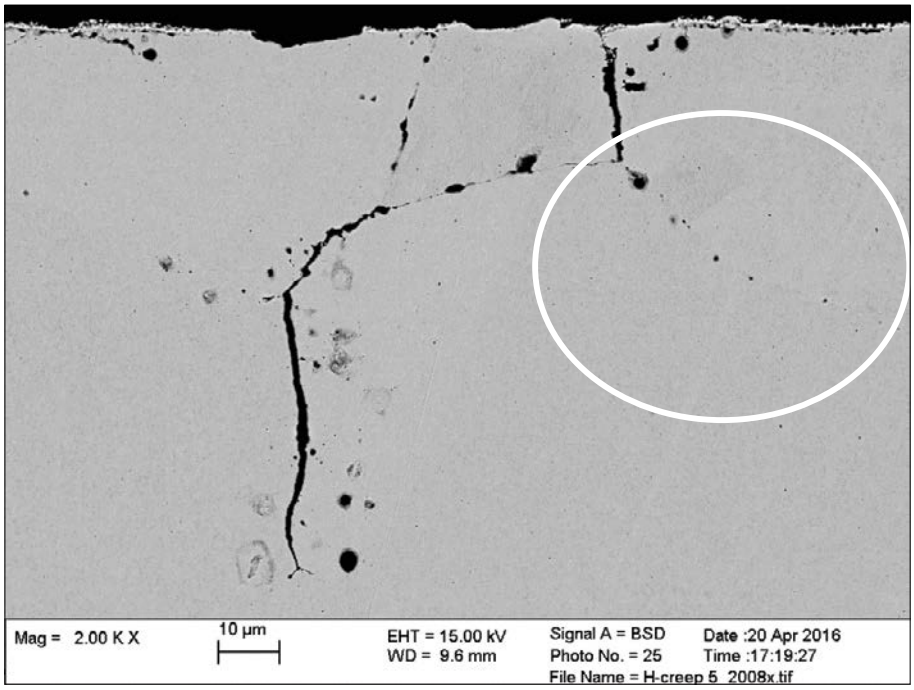


Figure 3-8. *Specimen H-creep-05 tested at RT for 1 005.7 hours hydrogen charging time and creep stress of 170 MPa. Larger cracks were discovered. The specimen was tested in soft annealed condition without any pre-strain.*

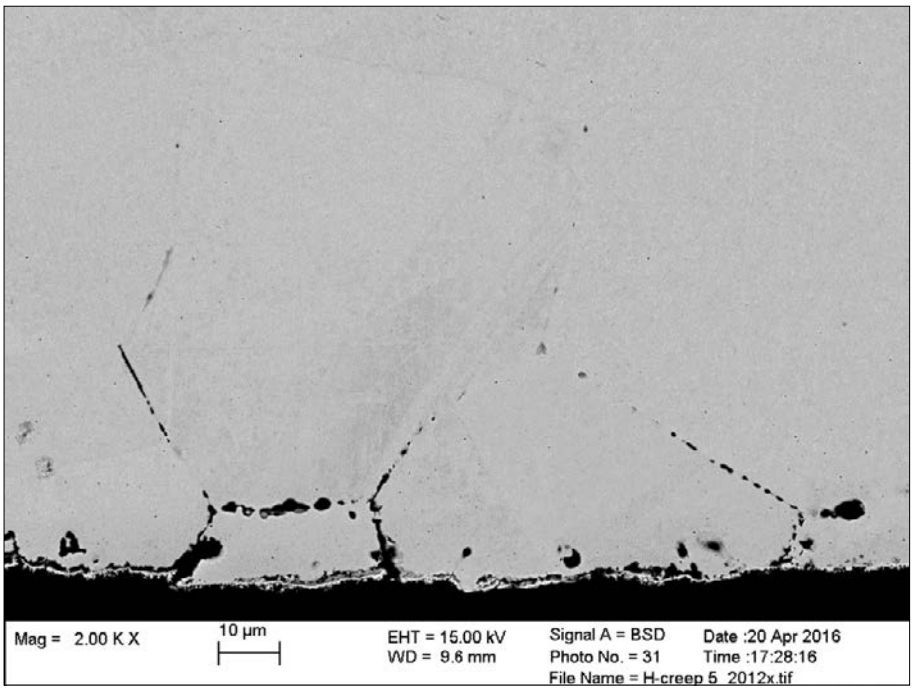


Figure 3-9. *Specimen H-creep-05 tested at RT for 1 005.7 hours hydrogen charging time and creep stress of 170 MPa. Larger cracks were discovered. The specimen was manufactured in the soft annealed condition without any pre-strain.*

Figure 3-10 shows a cross section of specimen H-creep-09 which had been hydrogen charged for 168.5 hours at 172 MPa nominal creep stress and 50 °C. Specimen H-creep-09 was pre-strained to 20 %. The crack is much smaller than the cracks found in specimen H-creep-05.

Figure 3-11 and Figure 3-12 shows another example of intergranular cracks of specimen H-creep-09. The magnification is different in Figure 3-11 and Figure 3-12.

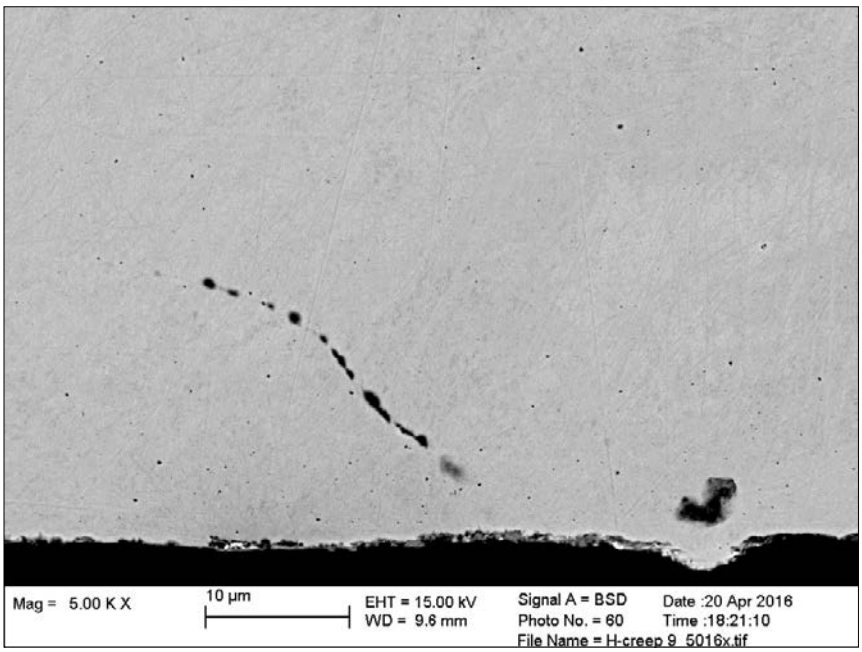


Figure 3-10. *Specimen H-creep-09 tested at 50 °C for 168.5 hours hydrogen charging time and creep stress of 172 MPa. Cracks were discovered. The specimen was manufactured with 20 % pre-strain.*

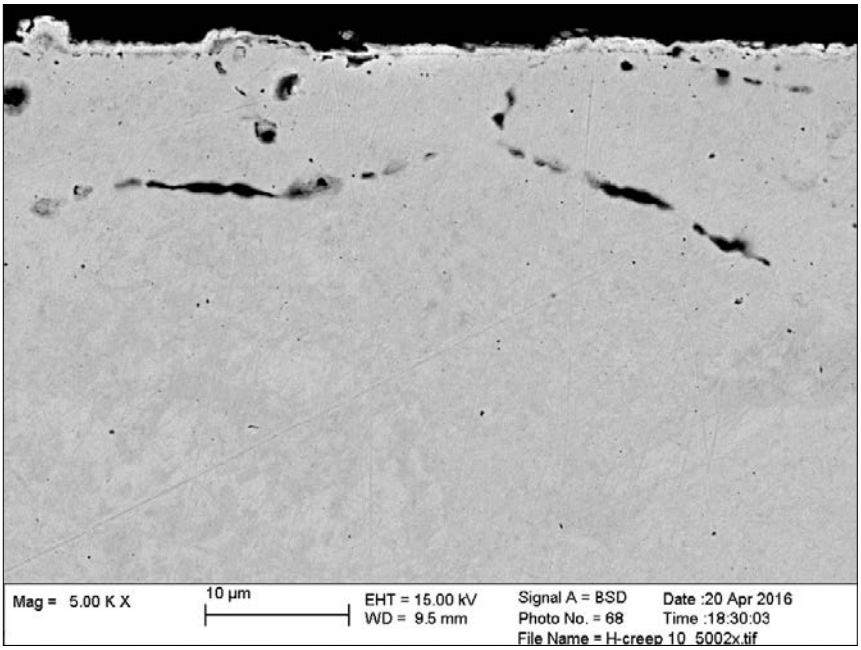


Figure 3-11. *Specimen H-creep-09 tested at 50 °C for 168.5 hours hydrogen charging time and creep stress of 172 MPa. Cracks were discovered. The specimen was manufactured with 20 % pre-strain.*

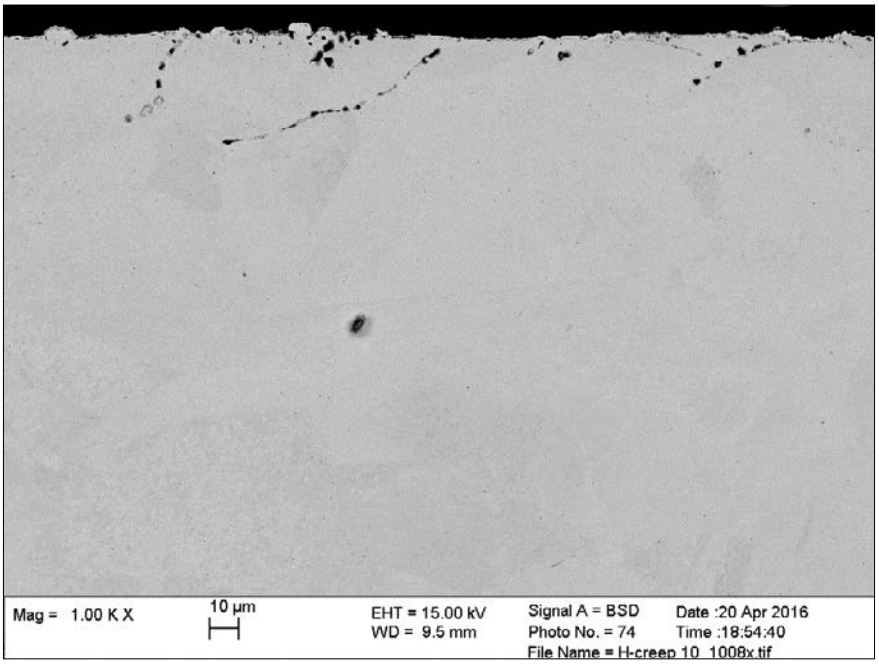


Figure 3-12. *Specimen H-creep-09 tested at 50 °C for 168.5 hours hydrogen charging time and creep stress of 172 MPa. Cracks were discovered. The specimen was manufactured with 20 % pre-strain.*

Figure 3-13 and Figure 3-14 shows two examples of the specimens tested at the lower creep stress of 140 MPa , where no cracks were found.

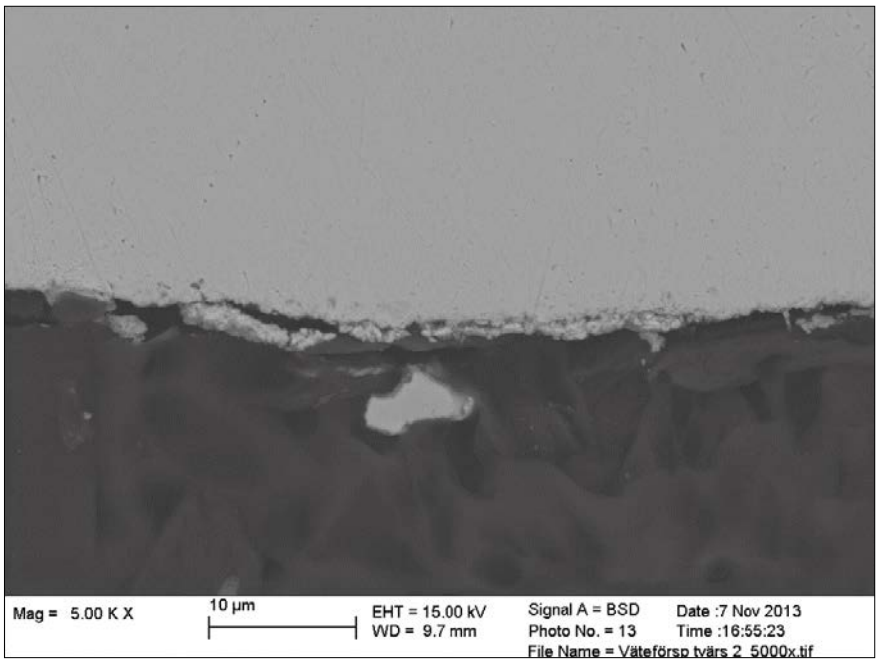


Figure 3-13. *Specimen H-creep-01 tested at room temperature for 95.5 hours hydrogen charging time and creep stress of 140 MPa. No cracks were discovered.*

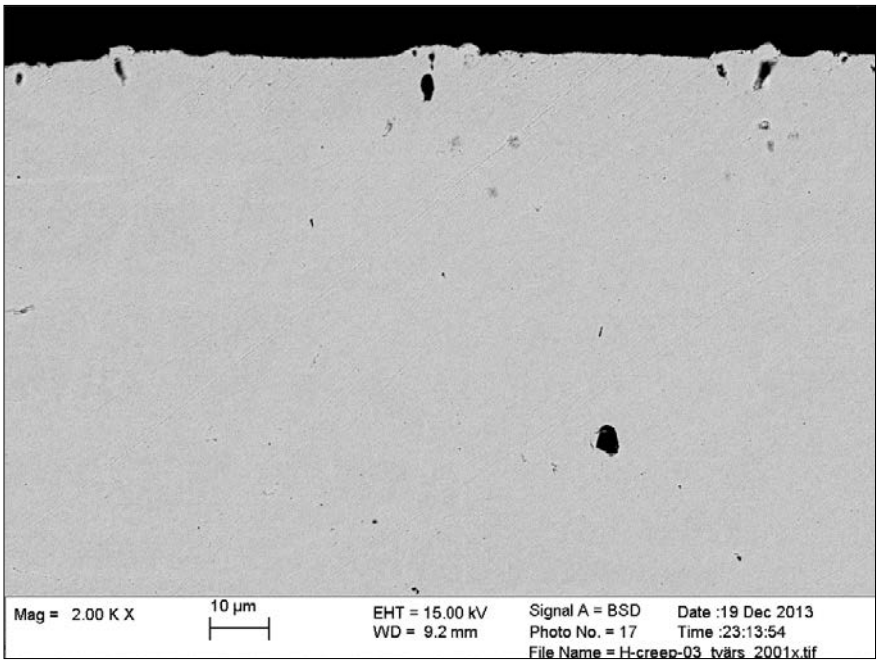


Figure 3-14. *Specimen H-creep-03 tested at room temperature for 103 hours hydrogen charging time and creep stress of 140 MPa. No cracks were discovered.*

In Figure 3-15 the surface of the specimen H-creep-03 is shown. This specimen has been tested at room temperature for 103 hours hydrogen charging time at a creep stress of 140 MPa. In this specimen no cracks were found. In the images round objects can be observed on the surface. This is a residue from the electrolyte. For subsequent specimens in stage 2 the electrolyte composition was changed to eliminate these residues.

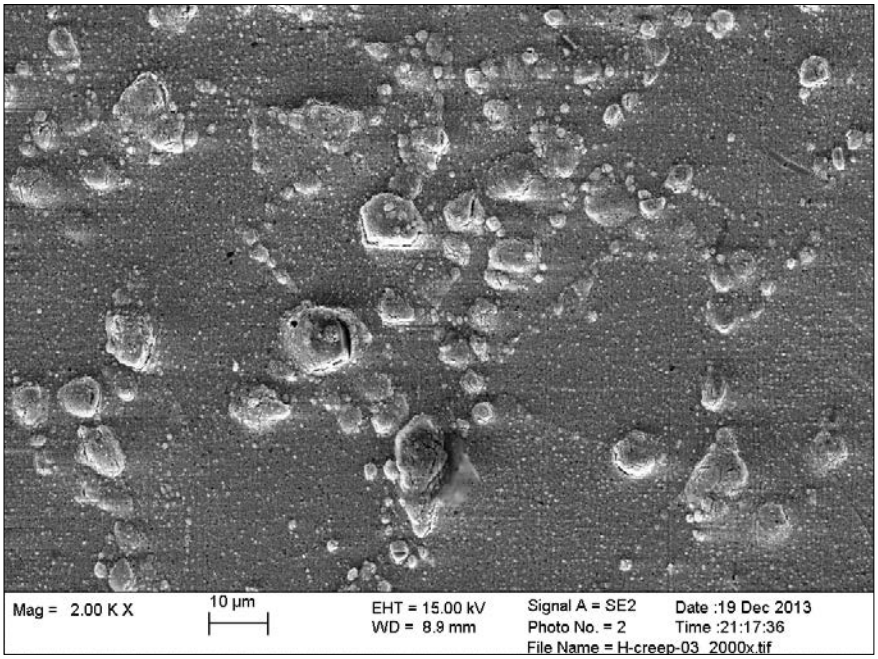


Figure 3-15. *Surface of specimen H-creep-03 tested at room temperature for 103 hours hydrogen charging time and creep stress of 140MPa. No cracks were discovered. The round objects on the surface are residue from the electrolyte. For subsequent specimens in stage 2 the electrolyte composition was changed to eliminate the residues.*

The reference specimens H-creep-14 to H-creep-16 did not show any cracks on the surface of the specimens, Figure 3-16 and Figure 3-17. The hydrogen content when studied was low and in the region of the base content in the material before testing. Hence, the conclusion is that the cracks seen in previous testing is due to the hydrogen content, not the effect of the electrolyte.

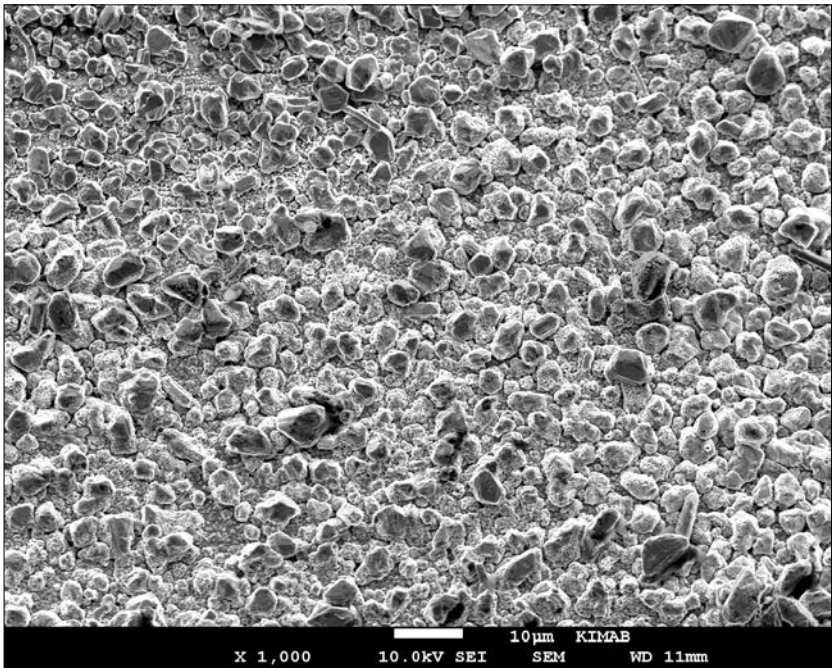


Figure 3-16. *Surface of H-creep-14 with lots of residues but no visible cracks.*

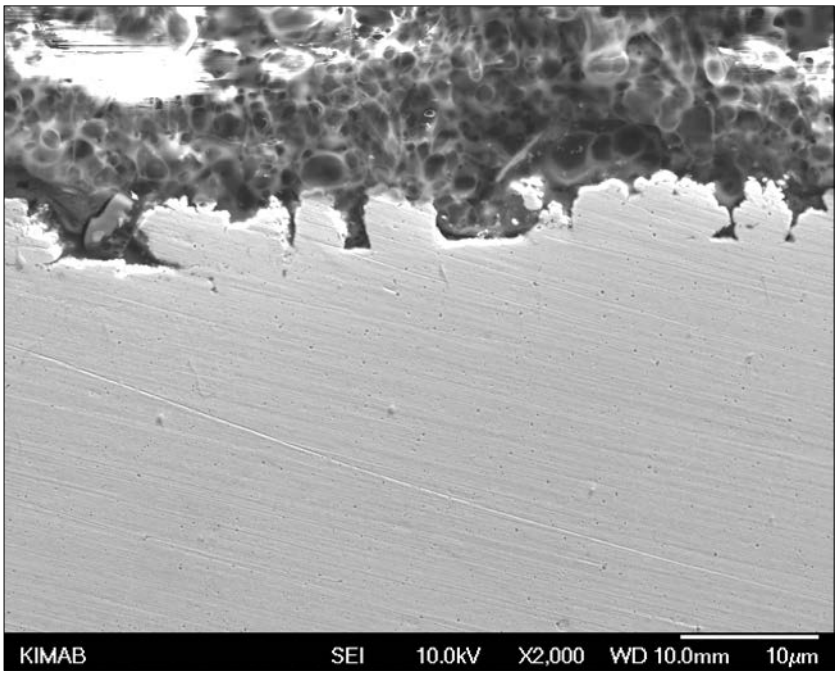


Figure 3-17. *Cross section of H-creep-15. No cracks are visible.*

4 Discussion

Based on the experimental results in this study, it is apparent that hydrogen is charged into the OFP copper. The three specimens tested in the preliminary part of the project and with a low creep stress did not present any cracks. When the creep stress was increased approximately 20 % percentage above the preliminary tests, cracks of various sizes did occur on the cross sections of the specimens. The depths of cracks are relatively small on most specimens (20 to 30 µm). On some specimens, however, larger cracks have been discovered. The largest cracks of approximately 100 µm were found on specimen H-creep-05 and H-creep-06. Specimen H-creep-05 experienced the longest times of hydrogen charging of approximately 1 000 hours. The temperature was room temperature (close to 23 °C) and the specimen was manufactured from copper with no pre-straining in the soft annealed condition. Dimples and cracks at the grain boundaries with an approximate length of 100 µm were observed on the specimen H-creep-05. Specimen H-creep-06 was hydrogen charged for 116 hours at 50 °C but did also present cracks similar to specimen H-creep-05. The cavities most likely arise from recombination of atomic hydrogen into molecular hydrogen and not from reduction of Cu_2O. The oxygen level of the OFP copper probably is too low for water formation to occur from reduction of Cu_2O.

In order to sort out the influence of the testing parameters on the occurrence of creep cracks on cross sections of the specimens, Table 4-1 summarizes the estimated crack sizes. The estimations are based on the cross cut sections of the specimen. The results are not unambiguous. Specimen 12 presented no cracks whereas specimen 05 presented the largest cracks. Both specimens were tested at room temperature and specimen 05 was tested at a somewhat lower creep stress but for 4 times longer time. Specimen 12 was made from 20 % pre-strained material compared to specimen 05 which was made from the soft annealed condition. If only the results from specimen 05 and 12 was to be considered it seems as there would be a clear effect of pre-straining of the copper, but the results from specimen 07, and 10 complicate the view on the influence of pre-straining. Specimen 13 has been cut and examined for cracks but is to be regarded as a special case, since the cross section present cracks but not of the same type as the cracks that have been found on the other specimens. Figure 4-1 shows a large crack found on specimen H-creep-13 but note the difference in appearance of the crack in comparison with the appearances of the crack of e.g. specimen H-creep-05. There are no clear cavities in front of the cracks on specimen H-creep-13, but there are large cracks. Some small cavities can be perceived at adjacent grain boundaries from the crack, but they are less clear. The creep stress of 176 MPa has been too large at 75 °C for the soft annealed OFP copper and the specimen fractured before the hydrogen present could have any effect on the copper. Specimen H-creep-10 and H-creep-11 do present cracks with cavities advancing ahead of the crack along the grain boundaries and they were tested at the same creep stress of 176 MPa and temperature of 75 °C with the only difference that they were manufactured from pre-strained copper of 10 % and 20 % pre-strain respectively. The pre-strain does hence influence the creep strength of the material, but it does not necessarily influence the hydrogen cavity formation.

When the total number of cracks found in all specimens exhibiting cracks is studied one phenomena stands out. There is a higher density of cracks on the surface of the specimens in areas of the gauge length that has experienced large plastic deformation, for example close to the necking section. Only a few cracks have been found on the sections of the gauge length where the plastic strain is negligible. A conclusion is that during simultaneous creep testing and hydrogen charging, plastic deformation is often needed to form cracks. Only a few tests where this was not true were found in this study.

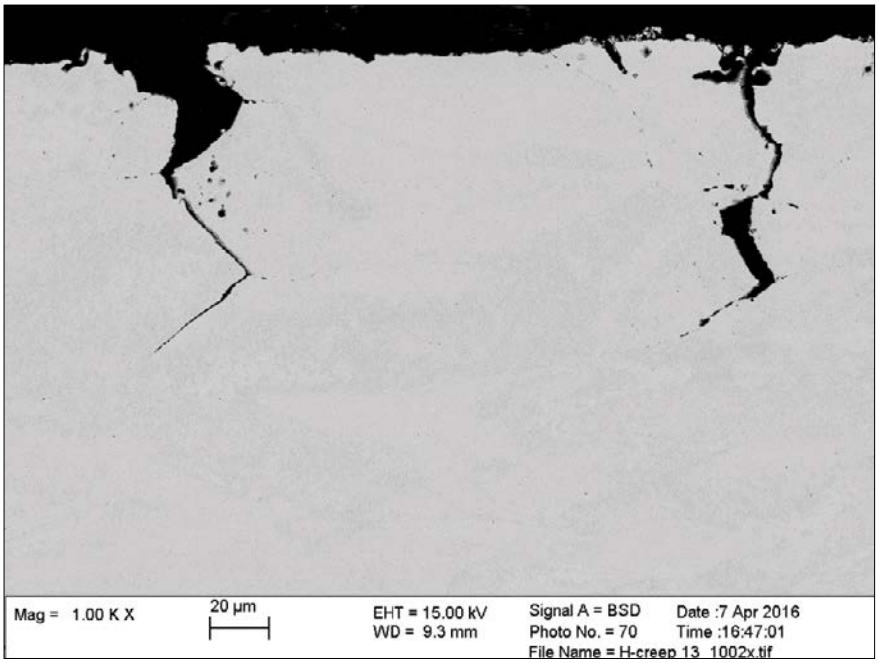


Figure 4-1. *Specimen H-creep-13 tested at 75 °C for 13 hours of simultaneous hydrogen charging and at creep stress 172 MPa. Large cracks were discovered, but no or very small amount of cavities in front of the crack. The specimen was manufactured from soft annealed condition without pre-strain.*

Table 4-1. Test results, hydrogen content and crack size.

Specimen nr.	Temperature (°C)	Creep stress (MPa)	Creep time (h)	Hydrogen charging time (h)	Pre-strain (%)	Average hydrogen amount (wt ppm)	Approximate crack size (µm)
H-creep-01	RT	140	92.5	95.5	0	3.8	0
H-creep-02	RT	140	92	95	0	7.9	0
H-creep-03	RT	140	100	103	0	7.9	0
H-creep-04	50	185	3.3	16.7	0	1.6	0
H-creep-05	RT	170	1 005.7	1 008.7	0	8.5	100
H-creep-06	50	172	113.0	116.0	0	7.7	100
H-creep-07	RT	175	94.6	97.6	10	3.8	0
H-creep-08	50	172	114.5	117.5	10	8.0	30
H-creep-09	50	172	168.5	171.5	20	4.8	20
H-creep-10	75	172	168.8	171.8	20	9.2	20
H-creep-11	75	176	97.9	100.9	10	9.0	30
H-creep-12	RT	176	257.3	260.3	20	6.1	0
H-creep-13	75	176	13.4	16.4	0	Measurement failed	0
H-creep-14	50	172	120	0	10	2.0	0
H-creep-15	50	172	167	0	0	1.8	0
H-creep-16	75	172	20	0	20	1.0	0

Figure 4-2 shows the amount of charged hydrogen as a function of creep testing time. The specimens which presented cracks are encircled.

The amount of hydrogen was measured with Leco Rhen 602 hydrogen determinator on sections cut out of the gauge section of the specimens with approximately a weight of 1 g. For each specimen, two such sections were cut out and the amount of hydrogen was determined. It should be noted that the amount of hydrogen could vary significantly on the two parts cut out from the same specimen.

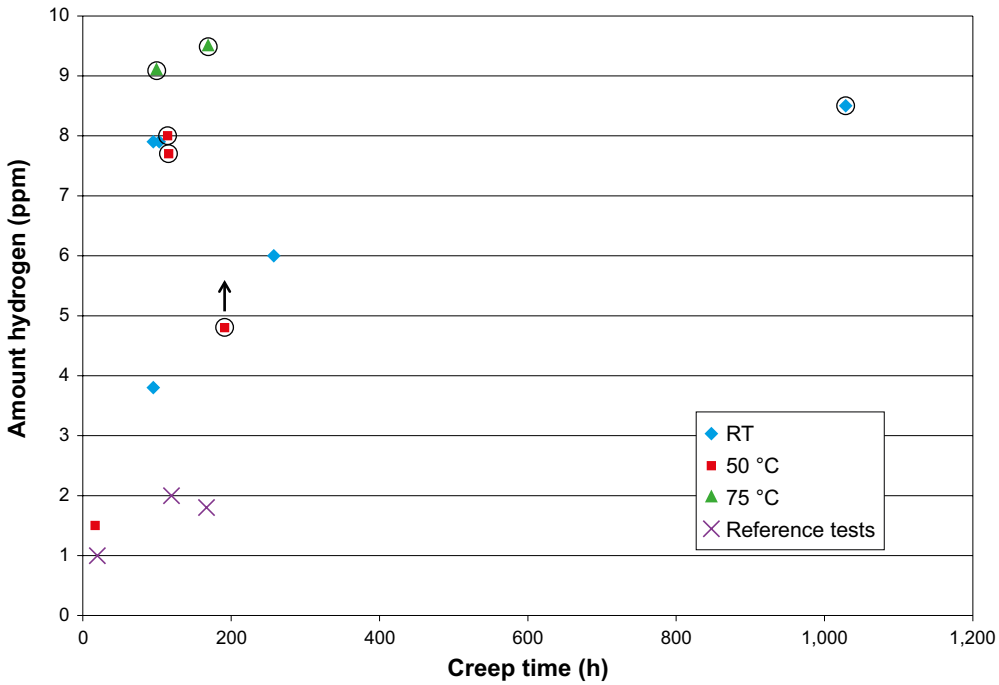


Figure 4-2. *The amount of charged hydrogen versus creep testing time. The specimens which presented cracks are encircled. Specimen H-creep-09 presented 4.8 ppm hydrogen, but there was a delay in the analysis of the hydrogen content and an arrow is therefore pointing towards the assumed higher hydrogen amounts for this specimen.*

The reason for this is most likely that the hydrogen concentration is high at the surface and that a significant amount hydrogen is to be found just below the CuAs layer or even perhaps in the layer of CuAs itself. If some of the CuAs layer is unintentionally removed in the actual handling of the specimen which contain a significant amount of hydrogen it could explain the variation in measured hydrogen content obtained on the same specimen. The CuAs layer that has a dark grey and black colour is easily removed just by pulling a finger along the surface with a small pressure. Some of the layer will come off and the CuAs layer will be discernible on the finger instead. Figure 4-3 shows the diffraction spectrum of low angle X-ray photoelectron spectroscopy performed on the surface of specimen H-creep-03. The spectrum presented the presence of two phases namely FCC-copper and the intermetallic hexagonal Cu-As phase. The identification of the two phases was performed with matching with "EVA" from Bruker AXS. Note that no sulphides, oxides or hydroxides can be found in the diffraction spectrum.

It is of interest to note that the creep stress applied on the OFP copper in this study needed to be as high as 172 MPa to obtain creep rates high enough to make the specimen fracture or achieve necking of the specimen. Yagodzinskyy et al. report that this was achieved at creep stresses ranging from 120 to 140 MPa. Specimen H-creep-05 was tested at 170 MPa creep stress and at room temperature under simultaneous hydrogen charging for 1 005.7 hours without fracture or necking of the specimen, whereas Yagodzinskyy reports of fracture under the same hydrogen charging conditions after 66.7 hours at 140 MPa. Remember that specimen H-creep-05 was soft annealed and that the hydrogen charging was successful. The discrepancy in creep results under hydrogen charging between what Yagodzinskyy reports and what Swerea Kimab has attained is difficult to understand. Table 4-2 presents the numbers and outcome of the two very different results. The most plausible explanation for this discrepancy is that Swerea Kimab and Yagodzinskyy et al. have tested different materials.

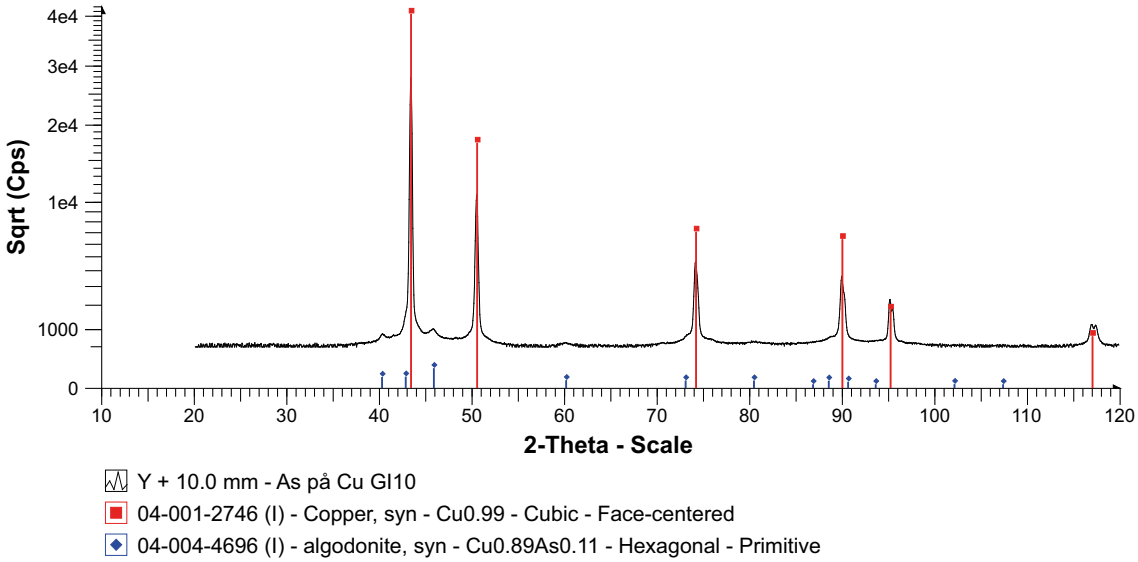


Figure 4-3. *The diffraction spectrum of low angle X-ray photoelectron spectroscopy of the surface of specimen H-creep-03.*

Table 4-2. Comparison test results at different labs and at different creep stresses.

	Creep stress (MPa)	Creep time (minutes)	Temperature (°C)	Amount hydrogen (wt ppm)	Result	Study
Swerea Kimab	170	1 005.7	RT	8.5	No fracture	Present
Swerea Kimab	140	100	RT	3.8	No fracture	Present
Aalto University	140	66.7	RT	?	Fracture	*

* Yagodzinskyy et al. 2012.

The formation of intergranular creep cracks under the formation of hydrogen cavities in front of the cracks is not understood. An increase in temperature and hydrogen charging time seem to have an expected effect on the amount of charged hydrogen of the copper. The formation of hydrogen cavities in front of the crack is probably an effect of all the varied parameters in this study together with possible other parameters. One such parameter that should be of interest is of course the actual creep stress of the specimen and not only the nominal creep stress. It would also be of interest to achieve better displacement curves to get proper stress strain curves. In this study it was only accomplished twice to get the complete displacement curve of the test with an analogue dial indicator. If further testing is to be performed, the displacement should be recorded by a suitable length sensor coupled to the creep stress program of the test set up in the HT-lab. This could be done but it has not been the focus in this study.

Figure 4-4 shows crack size versus pre-strain with the stress values and creep testing time shown near the symbols. Low stress or short creep testing time seem to reduce cracking. The amount of pre-straining also seem to influence cracking in the way that larger pre-straining gives less cracking. It can further be seen that higher temperature seem to give more cracking compared to room temperature.

The reference test performed without hydrogen charging all show no cracks. All cracks found in the specimens with hydrogen charging as detailed above must therefore be due to the hydrogen charging.

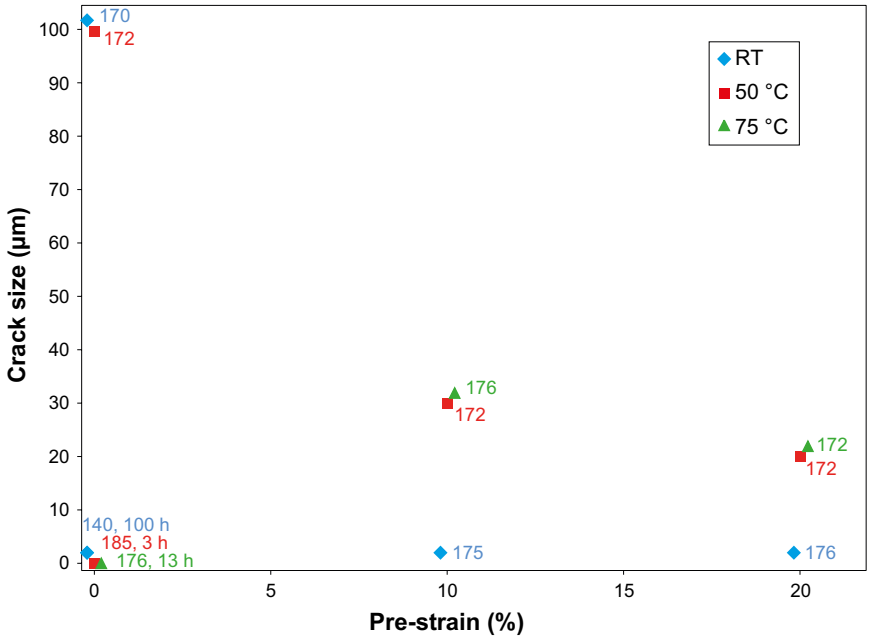


Figure 4-4. *Crack size versus pre-strain is plotted with the creep stress values and creep testing times values presented beside the symbols.*

5 Conclusions

Further testing using a similar experimental set up as the one presented by Yagodzinskyy et al. (2012) for hydrogen charging of OFP copper under simultaneous tensile testing (SSRT) or creep testing has been performed at Swerea Kimab. The tests have been performed at higher creep stresses compared to the testing performed by Yagodzinskyy et al. The temperature was elevated to 75 °C for three specimens. The effect of degree of strain hardening has been studied. The specimen copper material was either of no pre-strain (soft annealed at 600 °C for 10 minutes) or pre-strained to 10 % or 20 % respectively.

The following conclusions can be made based on this study:

- The hydrogen charging was successful with high levels of hydrogen in the specimens after testing.
- Specimens tested at Swerea Kimab presented cracks starting at the surface and following the grain boundaries. The size of these cracks ranged from 20 to 100 µm. The grain boundaries in front of the cracks presented cavities arising from hydrogen charging.
- Most, but not all, cracks were formed in areas of the specimen where large plastic deformation had occurred.
- The size and number of surface cracks seems to increase with increasing time and temperature. The role of creep stress and pre-strain is unclear, but higher pre-strain and lower creep stress seem to reduce cracking.
- No cracks occur at low creep stresses of 140 MPa or short creep testing times with high creep stress.
- No cracks occur in the reference test performed without hydrogen charging.
- The difference in creep rate between the study performed by Yagodzinskyy et al. and Swerea Kimab is large.
- There is a large discrepancy between the results obtained at Aalto University and Swerea Kimab regarding creep strength.

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Arkitektkopia AB, Bromma, 2018

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