

R-13-34

Copper corrosion experiments under anoxic conditions

Kaija Ollila
VTT Technical Research Centre of Finland

June 2013

Svensk Kärnbränslehantering AB
Swedish Nuclear Fuel
and Waste Management Co
Box 250, SE-101 24 Stockholm
Phone +46 8 459 84 00



ISSN 1402-3091

SKB R-13-34

ID 1393420

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Summary

This report gives results from the corrosion experiments with copper under anoxic conditions. The objective was to study whether hydrogen-evolving corrosion reaction could occur. Copper foil samples were exposed in deaerated deionized water in Erlenmeyer flasks in the glove box with inert atmosphere. Four corrosion experiments (Cu1, Cu2, Cu3 and Cu4) were started, as well as a reference test standing in air. Cu1 and Cu2 had gas tight seals, whereas Cu3 and Cu4 had palladium foils as hydrogen permeable enclosure. The test vessels were stored during the experiments in a closed stainless steel vessel to protect them from the trace oxygen of the gas atmosphere and light.

After the reaction time of three and a half years, there were no visible changes in the copper surfaces in any of the tests in the glove box, in contrast the Cu surfaces looked shiny and unaltered. The Cu3 test was terminated after the reaction time of 746 days. The analysis of the Pd-membrane showed the presence of H₂ in the test system. If the measured amount of $7.2 \cdot 10^{-5}$ mol H₂ was the result of formation of Cu₂O this would correspond to a 200 nm thick corrosion layer. This was not in agreement with the measured layer thickness with SIMS, which was 6 ± 1 nm. A clear weight loss observed for the Cu3 test vessel throughout the test period suggests the evaporation of water through the epoxy sealing to the closed steel vessel. If this occurred, the anaerobic corrosion of steel surface in humid oxygen-free atmosphere could be a source of hydrogen. A similar weight loss was not observed for the parallel test (Cu4). The reference test standing in air showed visible development of corrosion products.

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1 Background

Copper is generally assumed to be immune to corrosion by water itself. However, Hultquist et al. (2009) have concluded, on the basis of the results of the corrosion experiments in pure water with 15 years' exposure, that copper can corrode by water via auto-ionisation of water.

Hultquist et al. (2009) performed two experiments in closed glass containers in air atmosphere. Copper samples were exposed in deionized water at room temperature for 15 years. The glass containers were Erlenmeyer flasks (E-flasks) made of borosilicate glass. The copper was of OFHC 99.95+% quality. The initial water volume in the E-flasks was 50 ml with approximately 1 cm³ air. The exposed surface area was 85 cm² in each flask. One of the E-flasks had a 0.1 mm palladium foil as a hydrogen permeable membrane. The other had a gas tight glass stopper. The E-flasks were hermetically sealed with UHV-glue.

After 15 years, Hultquist reported that a hydrogen-containing copper corrosion product was detected by SIMS on the surface of copper in the flask with Pd membrane. Corrosion could continue in this experimental flask since hydrogen could escape from the system and the equilibrium pressure of hydrogen was not reached. An increased hydrogen concentration was also measured in the copper metal. The experiments suggested that copper could corrode via auto-ionisation of water.

The objective of this study is to conduct corrosion experiments with copper under anoxic conditions in the glove box, otherwise using a similar experimental system as Hultquist et al. (2009).

2 Experimental procedures

2.1 Copper material

Copper was purchased from Goodfellow (England) in the form of foils (100 mm × 100 mm). The thickness of the foils is 0.1 mm ($\pm 10\%$). The copper is oxygen-free high conductivity copper (OFHC, 99.95%). The temper is annealed. The phosphorous level is 0.005% maximum.

For the corrosion experiments, the foil pieces of the size of 0.85×5 cm were cut with a cutter. Ten foils of this size were used in each experiment. The resulting total surface area is 85 cm². The foils were mechanically polished with silicon carbide grinding paper. First, the foils were polished with SiC-paper (P600, Struers) in air, which was followed by cleaning with deionized water and paper. Subsequently, the foils were brought into the glove box with N₂ atmosphere. The following day, the foils were polished with SiC-paper (Grit 600/P 1200, Buehler) in the glove box, followed by cleaning with wet paper and alcohol.

2.2 Aqueous phase

The aqueous phase was anoxic deionized water (Milli-Q). The aqueous phase was prepared for the corrosion tests as follows. The deionized water (2 l, Milli-Q) was degassed purging with N₂ overnight. Highly purified nitrogen gas (N₂ 6.0) was used, see Table A1-1. The water was transferred into the glove box. The purging with N₂ continued in the glove box for an additional 12 hours. Subsequently, the water was allowed to equilibrate with the N₂ atmosphere of the glove box for three weeks with the cap of the flask loosely closed. After this, the oxygen reading of an Orbisphere oxygen analyzer showed zero for the water. The lowest oxygen reading of the analyzer is 0.00–0.01 ppb. The measurement range of the analyzer given by the manufacturer is 0.1 ppb – 20 ppm for dissolved O₂. The detection limit is not given. The oxygen content of the solution was lower than 0.1 ppb although the exact content is not known. The oxygen content of the N₂ atmosphere of the glove box is maintained low (< 1 ppm) with the help of a continuous purification cycle (Cu catalyst, molecular sieve). The box has an oxygen probe, which serves to monitor continuously the amount of residual oxygen in the N₂ atmosphere. Initially, the inert working gas of the box was N₂ 5.0. The working gas was changed to Ar 5.0 in December 2010, 357 days after the start of the tests. For gas properties, see Table A1-1.

The pH of the aqueous phase was measured to be 7.0–7.1 prior to the start of the corrosion tests. The measurement was performed with an Orion Ross pH electrode.

2.3 Temperature

The temperature in the glove box is maintained at $25 \pm 1^\circ\text{C}$ as carefully as possible by means of the air cooling of the laboratory and the water cooling of the blower of the glove box. The temperature of the box is written down daily. The average temperatures monthly and their variation are given in Table A1-2.

2.4 Starting of the corrosion experiments

Five corrosion experiments began on December 19, 2009. Four samples (Cu1, Cu2, Cu3 and Cu4) were set in a glove box in the following conditions.

Cu samples were placed in acid-washed Erlenmeyer flasks (Duran® borosilicate glass, Lenz) after weighing. Ten Cu strips were placed in each flask and 50 ml of degassed deoxidized water was added. The original size of one strip was 50 mm in length and 8.5 mm in breadth, resulting in the total surface area of 85 cm² for ten strips. The strips obviously stretched to some extent during polishing operation with SiC-paper. This was observed when the strips were immersed in water. They also bent a little when immersed in water because the material is very thin (0.1 mm).

The E-flasks used two kinds of seals. The tests Cu1 and Cu2 had gas tight seals. The E-flasks were closed with glass stoppers and hermetically sealed with steel epoxy. The tests Cu3 and Cu4 had 0.1 mm palladium foils as hydrogen permeable enclosure. A suitable-sized piece of Pd-foil was attached with epoxy glue to the mouth of the flask. The rim of the Pd-foil was sealed with epoxy glue. The gas space in the E-flasks was bigger than the one (1 cm³) in the tests by Hultquist et al. (2009). The empty space was 12 cm³ in the E-flasks with gas tight enclosure (Cu1 and Cu2), while in the E-flasks with Pd-foil it was 15 cm³.

The E-flasks are stored in the glove box in a closed stainless steel vessel with gas in- and outlets (see Figure A1-1). This is a precaution in case of the oxygen content of the N₂ atmosphere would increase for some reason. In normal conditions, the O₂ content is maintained below 1 ppm with the help of a continuous gas purification system. The samples were thus also protected from the light while in the stainless steel vessel.

The fifth corrosion experiment (Cu5) was carried out in the following conditions:

Ten Cu strips were initially placed in an E-flask in the glove box. The E-flask was brought out of the glove box. 50 ml of air-saturated deionized water (Milli-Q) was added. A piece of Pd-foil was attached with epoxy glue to the mouth of the flask and the rim of the Pd-foil was sealed with epoxy glue in the same way as above. The air space in the E-flask was 15 cm³. The E-flask was then stored in air in ordinary laboratory atmosphere and it was not protected from light.

The experimental conditions are summarized in Table 2-1.

The initial weight data for the experimental vessels are given in Table A1-3.

Table 2-1. Conditions for the Cu corrosion tests.

Test/atmosphere	Enclosure	Aqueous phase	Copper samples
Cu1 glove box (N ₂)	Gas tight	Deaerated deionized water, pH 7	Foils, OFHC 99.95+%
Cu2 glove box (N ₂)	Gas tight	"	"
Cu3 glove box (N ₂)	H ₂ permeable Pd-foil	"	"
Cu4 glove box (N ₂)	H ₂ permeable Pd-foil	"	"
Cu5 air atmosphere	H ₂ permeable Pd-foil	Deionized water, pH 5.8	"

3 Results from the first two-year period of the tests

The experiments have now continued for three and a half years (1,261 days, until May 31, 2013).

The experiments in the glove box (Cu1, Cu2, Cu3 and Cu4):

The E-flasks, with Cu strips and water, were weighed at intervals of 2–3 months (more frequently when needed) (see Table A1-3 and Figure A1-2 to A1-5). The weighing was performed in the glove box. Pressure changes due to the maintenance of overpressure, as well as static electricity caused small disturbance during weighing. This is why each E-flask was weighed several times. The average weight data are given in Table A1-3.

There was not any clear change in the weight of the test vessel Cu 1 with gas tight enclosure during 327 days from the start of the test (Figure A1-2, upper figure). In the next weighing at 335 days, the weight decreased but increased after that to the same level as at 327 days. This was apparently caused by variations in the air pressure of the outer air. The glove box adjusts its overpressure in proportion to the air pressure. An increase of 50 hPa in the air pressure causes an increase of about ~ 0.005 g in the buoyancy for the test vessel in N_2 atmosphere, and hence a decrease of ~ 0.005 g in its weight. A similar decrease and increase in the weight is observed for all test vessels in the same period of time (327–343 days). According to the data from Finnish Meteorological Institute, the air pressure was higher on 17th Nov. 2010 (335 days, 1,034.4 hPa) than on 11th Nov. 2010 (327 days, 993.9 hPa) or on 25th Nov. 2010 (343 days, 1,002.0 hPa) (see Table A1-3). This suggests that there is no significant change in the experimental conditions in Cu1 test vessel in the time period of 0 to 343 days that would be caused by the reactions of Cu surface with water.

In 357 days' time from the initiation of the experiments, the working gas of the glove box was changed from nitrogen to argon. The first Ar gas bottle was connected to the glove box on 9th Dec. 2010. The gas phase of the box is changed gradually after the change of the gas bottle depending on the gas consumption. There was a mixture of N_2 and Ar gases for approximately three weeks based on the consumption of Ar. The measured weights for the Cu1 test vessel after the change of the gas bottle (363 and 406 days from the start of the tests) are given in Figure A1-2 (the lower figure) (see also Table A1-3). At 363 days, there is a mixture of N_2 and Ar gases, and hence the measured weight is not comparable with the weights in N_2 or Ar atmospheres. At 406 days, the gas atmosphere has entirely changed to Ar. The higher density of Ar causes higher buoyancy for the test vessel in the weighing. This results in a lower weight in Ar atmosphere. The estimated weight difference for the test vessel with glass stopper in N_2 and Ar atmospheres is 0.045 g. This is based on the determination of the outer volume of the test vessel using an E-flask, which was not exactly similar with the test vessel. The difference between the measured weights of the Cu1 test vessel in pure N_2 atmosphere (343 days) and in pure Ar atmosphere (406 days), 0.038 g, is slightly smaller than the estimated effect of the different buoyancy. The corresponding differences for other test vessels in N_2 and Ar atmospheres are very similar (Cu2: 0.037 g, Cu3: 0.039 g, Cu4: 0.037 g).

In the parallel test, Cu2, the weight of the test vessel stayed at the same level until 272 days (Figure A1-3). There is a decrease of 0.0035 g in the weight between 272 days and 327 days. The reason is not known. A similar decrease and increase in the weight from 327 to 343 days is observed as in the case of Cu1, probably caused by variations in the air pressure. The reason for the weight decrease between 363 and 406 days is the changing of gas atmosphere from a mixture of N_2 and Ar gases to pure Ar gas, which causes different buoyancies at those points of times.

At 406 days, the gas atmosphere of the glove box had entirely changed from N_2 to Ar. Afterwards, there were parallel fluctuations in the weights of Cu1 and Cu2 test vessels, between 558 and 974 days, probably mainly due to strong variations in the air pressure.

The weights vs. time for the tests with palladium foils as hydrogen permeable enclosure, Cu3 and Cu4, are given in Figure A1-4 and A1-5. There is a clear decrease in the weight of Cu3 test vessel throughout the test period of 746 days. The total weight loss was 0.0279 g, with 0.0055 g during the N_2 period, and 0.0224 g after the atmosphere change from N_2 to Ar. Cu4 shows a very slight weight

loss of a few mg during 887 days. A similar decrease and increase in the weights from 327 to 343 days was observed as in the case of Cu1 and Cu2, probably caused by variations in the air pressure. After the termination of the Cu3 test, the weight fluctuates strongly between 700 and 988 days for the Cu4 test, as it did also for Cu1 and Cu2 tests.

It is possible that the weight loss of Cu3 is partly explained by curing or hardening of the steel epoxy used for sealing. On the other hand, Cu4 did not lose weight in the same way. A slow evaporation of water has apparently occurred through the Pd foil and epoxy sealing in the Cu3 test. Separate tests were started to see the stability of the epoxy in the glove box and in air. Approximately 1 g of epoxy was added on two watch glasses and one was allowed to stay in the glove box and the other in air. The weights of the epoxy+watch glasses were followed. The results for the time period of 650 days (see Figures A1-6 to A1-8 and Table A1-4) show that steel epoxy loses weight, apparently humidity, slowly in the glove box conditions, where the humidity is low (a few ppm). The surface area of the steel epoxy sample on the watch glass was bigger than the surface area of the epoxy sealing in the E-flasks. The epoxy sample was spread on the watch glass. This may increase the loss of humidity. In air, a similar loss of weight was not observed (Figure A1-8). The weight of the epoxy+watch glass in air fluctuated and showed an increasing trend. The peaks were observed in August or September (8th Sept. 2011, 17th Aug. 2012, see Figure A1-6 and Table A1-4). A seasonal variation in the humidity of the laboratory conditions has probably had influence.

The appearance of the Cu strips has not changed visibly from the initial one in any of the tests (see Figure A1-9). The surface of Cu strips looked shiny and unaltered after the experimental time of 988 days in Cu1, Cu2 and Cu4 tests, as well as at the end of Cu3 test after the experimental time of 746 days.

The experiment in air atmosphere (Cu5):

The weight of the test vessel Cu5 increased slowly until 272 days' experimental time (Table A1-3 and Figure A1-6). This suggests the intrusion of air through the Pd-foil or epoxy sealing. A change in the appearance of Cu surface was observed. After one month's reaction time, tarnished spots or patches were observed. After four months, the amount of dark-brown patches had increased (see Figure A1-10). This suggests the reaction of oxygen with the Cu surface and the formation of Cu(I) oxide. The black colour of Cu(II) oxide was not visible. Some greenish-greyish spots were seen on top of dark brown patches. The solution was initially equilibrated with air (Table 2-1). The pH was 5.8. The CO₂ from air and possible additional CO₂ from leakage probably explain the greenish colour. One explanation could be a formation of a copper hydroxycarbonate, e.g. malachite (Cu₂CO₃(OH)₂). This must be confirmed by analysis after the termination of the test. There are two peaks in the weights, one in August 2010 and the other in September 2011, and lowest values in May 2011 and March 2012. This suggests similar seasonal variation due to the humidity of the laboratory conditions as in the separate stability test of the epoxy (see above). The weight of the test vessel seems to have a decreasing trend between 272 and 974 days. This suggests the evaporation of water through the Pd foil or epoxy sealing.

4 Preliminary plans for post-test analysis methods

Gas phase

A gas sample is taken for hydrogen analysis with gas chromatography.

Aqueous phase

First, a sample is taken for pH measurement. The measurement is performed with a commercial Orion Ross pH electrode. Subsequently, unfiltered and micro- and ultrafiltered samples are taken for analyses of Cu content in solution. The measurement of Cu content is made with ICP-MS method. Samples are taken also for relevant elemental analyses of water (e.g. silicate, Cu impurities). Milli-Q deionized water works as reference sample. The remaining test solution is transferred to a new sample bottle and acidified. 1 M nitric acid is added to the test vessel to dissolve any sorbed material from the surface. A sample is taken from this acid strip solution for Cu analysis.

Analyses of post-test Cu surface

The residual water on Cu foils is allowed to evaporate under argon atmosphere in the glove box after removing Cu foils from solution. The amount of Cu foils is weighed out. The foils are stored in a closed vessel in the glove box until samples are transferred for different analyses. For the transfer, the samples are closed in a metallic vessel (with gas in- and outlets) in the glove box to protect the Cu surface from air during the transfer. The vessel is opened just before the measurement.

The following methods were preliminarily planned:

- ESEM/EDS (Environmental scanning electron microscopy/Energy Dispersive x-ray spectroscopy). This technique is used to study the sample's surface topography and composition. The multistage differential pumping system of ESEM allows the usage of pressures between 10 and 2,700 Pa. SEM/EDS analyses are available at VTT.
- XPS (X-ray Photoelectron Spectroscopy). The method allows determining the valence state of the surface copper (Cu, Cu(I) or Cu(II)). The method requires vacuum. XPS instrumentation is available at the Aalto University in Otaniemi.
- Raman spectroscopy is used to investigate chemical bonds and symmetry of molecules and their environment. Raman spectroscopy is available University of Helsinki. It does not require vacuum.
- SIMS (Secondary Ion Mass Spectrometry) instrumentation is available at VTT in Otaniemi. The thickness of the corrosion product layer can be determined using this method. The hydrogen content can be determined if its amount is sufficient to distinguish it from the hydrogen background in the vacuum.
- XRD (X-Ray Diffraction) instrumentation is available at Geological Survey of Finland in Otaniemi. This technique is used to analyse the atomic and molecular structure of a crystal. The corrosion layers are probably too thin to allow characterization with XRD.

5 Termination of the Cu3 test

The Cu3 test was terminated after a duration of 746 days (see Table A1-3 and Figure A1-4).

5.1 Gas and solution analyses

Prior to opening the test flask, a gas sample was taken from the empty volume above the solution. The volume of the empty space in the flask was 15 cm³. The gas sampling was carried out with the help of a vacuum-pumped transport cylinder, see Figure 5-1. The volume of the cylinder was 25 cm³. The gas cylinder had an injection needle attached to its reducer. The injection needle was forced through the Pd foil of the test flask. The cylinder was opened immediately allowing the gas sample to flow to the evacuated part of the cylinder.

The gas sample was subsequently transported to an analytical laboratory (Ramboll Oy) and analysed by gas chromatography (Hewlett Packard HP6890) using a thermal conductivity detector, see Table 5-1.

The gas phase in the test was originally N₂. The working gas of the glove box was changed from N₂ to Ar after 357 days from the initiation of the corrosion test. After 400 days, the gas atmosphere had probably entirely changed from N₂ to Ar.

The Cu3 corrosion test was continued for 340 days in the glove box with Ar atmosphere. It seems that the original N₂ gas phase of the test vessel has partly changed from N₂ to Ar in the progress of the test. This suggests that the sealing with steel epoxy has not been completely tight, because only H₂ should permeate through Pd foil. It is also possible that the gas sample was diluted with Ar from the atmosphere of the glove box in the sampling process. The loss of gas in the flask may have compensated by the intrusion of box Ar. Hydrogen was not found in the gas sample. The detection limit for H₂ was 0.003 vol-%.

Subsequently (after two hours), the test flask was opened cutting out the Pd foil with a surgical knife as carefully as possible. The Pd foil was stored in a small sample jar until further analysis of hydrogen content. Any macroscopic changes could not be observed on the surfaces in the test vessel, either on the surface of Cu foils or of the glass. No visible change could be seen in the water phase.

Table 5-1. Results from gas analyses.

Gas	Vol-%
Argon (Ar)	76
Nitrogen (N ₂)	32
Hydrogen (H ₂)	< 0.003



Figure 5-1. Cylinder used for transport of the gas sample. With courtesy of Ramboll Oy.

The pH of the solution was measured with a combined MetroSensor glass electrode (Biotrode, Methrom). AVS titrimetric buffer solutions (pH 4 and 7) were used as calibration solutions. The pH value of the solution phase has increased from the initial value of 7.0-7.1 to 8.8-8.9 (see Figure A1-11). This is caused by the dissolution of Si, Na and B from the E-flask surface. The concentrations of Si, B and Na in the solution were analysed with ICP-MS and are given in Table A1-5.

The concentration of Cu in the solution was 3.8 µg/l ($5.98 \cdot 10^{-8}$ mol/l). This value is for ultrafiltered solution (Whatman UF, 12 K MWCO), representing the soluble Cu. The concentration of Cu is in the range of the solubility of Cu₂O (Palmer 2011). The concentration in unfiltered solution is higher, 21.6 µg/l ($3.40 \cdot 10^{-7}$ mol/l), suggesting the precipitation of Cu. Cu was found in the desorption solution of the test vessel surface, suggesting the presence of adsorbed Cu ions or precipitated (colloidal) Cu oxide. The concentration of Cu in the desorption solution was 90.2 µg/l ($1.4 \cdot 10^{-6}$ mol/l) (Table A1-5).

The total dry weight of ten Cu foils at the end of the Cu3 test was 3.96757 grams. The Cu foils were allowed to evaporate to dryness on a piece of paper in the glove box before weighing. The initial dry weight of the foils was 3.9680 grams. The difference between the initial and final weights was 0.0004 g. This suggests a small weight loss of ~0.4 mg during the test. However, the fourth decimal cannot be considered accurate in the weighing with the older analytical balance (Mettler-Toledo AG 104) in the glove. A new, more accurate analytical balance was available in the later stages of the test (Table A1-3).

5.2 Hydrogen analyses

The H₂ contents were analysed in a sample of the Pd foil, which was removed from the Cu3 test flask. Additionally, two Cu foils were analysed in hydrogen. H₂ Automatic Analyser (Leybold-Heraeus H₂ A 2002) was used. All the samples were placed in separate glass bottles and the bottles were closed tightly in the glove box. These glass bottles were transported in tightly closed bigger bottles to the analyser to keep air contact as low as possible.

The method is based on thermal conductivity. The H₂ analyser operates on the principle of the hot extraction of hydrogen from the samples into the carrier gas flow. The samples are raised to the extraction temperature in a resistance-heated furnace. Hydrogen then diffuses from the heated sample into the nitrogen carrier gas as a result of the hydrogen partial pressure gradient between sample and carrier gas flow. The carrier gas stream then takes it up, CO and H₂O are filtered out and the H₂ brought to a thermal conductivity detector (TCD). The detector continuously measures the hydrogen content of the carrier gas; this content is integrated over the full analysis cycle by the electronics system. This integral concentration is then referenced to the sample weight and displayed in ppm. The measuring resolution is 0.01 ppm, accuracy ± 0.1 ppm and measuring range from 0 to 60 ppm. The calibration was done with a dose of 5 ml H₂ to carrier gas, which gives 9.68 ppm H₂. A LECO sample with 5.8 ± 0.3 ppm hydrogen in steel was used as a reference standard.

The weight of the Pd sample was 0.123 g, corresponding to a foil area of 1.023 cm². The total Pd foil area of Cu3 test flask was estimated to be triple the amount of the sample. Two Pd references were measured in addition to the Cu3 test sample. The reference samples were cut from the same Pd foil sheet as the Pd foil of Cu3. The foil sheet has been stored in the glove box from the start of the test (2 years). The samples were cleaned with ethanol before measurements. Measured H₂ contents are given in Table 5-2.

The H₂ content of the Pd sample in the Cu3 test, 390 ppm, was outside the measuring range of the analyser (from 0 to 60 ppm). It was necessary to change the weight of the sample tenfold (1.23 g) in the middle of analysing process. It is not possible to repeat analysing using the same sample because the method destroys the sample. The method of changing weight in the middle of measurement has been shown to be workable method previously. The result in this case is not an exact value but the order of magnitude is right. The reference samples had a small content of H₂. The reason for the hydrogen content in the reference samples is not known. The supplier of the Pd foil did not report any data for H₂ in the foil.

Two Cu foils from the Cu3 test were analysed for hydrogen using the same method. Each Cu foil was cut to three samples. In total, six samples from the test were analysed (see Table 5-3). A reference Cu foil sample was cut from a polished Cu foil, which had been stored in the glove box throughout the test duration.

Table 5-2. Results from H₂ analyses (Pd foil).

	Weight (g)	H ₂ content (weight-ppm)
Pd reference (1)	0.211	5.46
Pd reference (2)	0.326	4.86
Cu3 sample	0.123	390

Table 5-3. Results from H₂ analyses (Cu foil).

	Weight (g)	H ₂ content (weight-ppm)
Cu reference	0.057	2.65
Cu3 sample (1)	0.074	6.35
“ (2)	0.074	2.70
“ (3)	0.160	2.92
“ (4)	0.126	2.90
“ (5)	0.133	2.90
“ (6)	0.127	2.20

The H₂ contents varied from 2.20 to 2.92 ppm, Cu3 sample (1) as an exception gave a higher result, 6.35 ppm. The H₂ content in the reference was at the same level. The producer of the Cu foil used in these tests was Goodfellow from England. They do not report any H₂ content for the material.

5.3 XPS analyses

X-ray photoelectron spectroscopy (XPS) was used to analyse the chemical composition of the surface of Cu foils at the end of the Cu3 corrosion experiment. In this method, the sample is irradiated with X-rays of known energy, thus causing emission of electrons by the photoelectric effect. The binding energy spectrum of these photoelectrons is recorded, and by analyzing the spectrum, the elements and their chemical states can be determined within a few nanometers from the sample surface.

Two Cu foils were removed from the water phase in the glove box. They were allowed to dry up on a piece of paper. Macroscopic changes could not be observed on the surface of the foils. The foils looked shiny and unaltered. Small samples were cut from each foil (1 cm in length, 0.9 cm in breadth). The samples were placed in 50 ml glass bottles in the glove box and the bottles were closed tightly. Two reference Cu foil samples were sealed in similar glass bottles. These were an unpolished one and the other one, which had been polished together with the test foils prior to the start of the experiments. Both Cu foil samples had been stored in the glove box for the test duration of 2 years. All four glass bottles with samples were sealed in a metallic vessel in the glove box in order to provide oxygen free transport. The samples were transported in the metallic vessel to the XPS of Aalto University.

The sample bottles were opened just before the mounting of the samples into the sample holder. The short exposure at ambient conditions was unavoidable, though the exposure time needed for mounting and securing the samples into the sample holder and into nitrogen filled XPS preparation chamber was recorded to be less than five minutes. The samples were secured sequentially into the sample holder in the following order:

1. Ref 1 (polished Cu reference).
2. Ref 2 (unpolished Cu reference).
3. Cu3 foil sample (1).
4. Cu3 foil sample (2).

The purpose was to keep the air exposure time for the Cu3 test samples as short as possible.

The analysed percentage elemental compositions for all samples are given in Table A1-6, and the spectra for the polished reference and the test samples are given in Figure A1-12. The interpretation of XPS data is complicated by the fact that the samples were exposed to air for a few minutes before the measurements. There is no fully oxidised copper, Cu(II), on the polished reference or on the test samples, while all the copper seen in the unpolished reference seems to be present as Cu(II). Surface oxygen in the test samples is less than in the polished reference. It is possible that the reference sample has got more oxygen before measurements, because it was mounted first and the exposure time to air was somewhat longer. On the other hand, it is also possible that the polishing with SiC paper at the start of the tests did not entirely remove the oxidized layer from the surface and the oxide layer of the test samples has partly dissolved and it explains the difference between the polished reference and the test samples. A carbon contamination layer was seen on all Cu samples. Both High Resolution components (Table A1-6) and the spectral background in the C 1s fit well with normal surface contamination layer, seen on practically all air-exposed metals. Thick carbon contamination layer covered the unpolished reference.

The unpolished reference has a surface composition of carbon and oxygen. The oxygen/carbon ratio is 0.16. This also seems reasonable considering the number of carbon atoms bound to one or two oxygen atoms as deduced from the C 1s spectrum.

The polished reference has a surface composition of mainly copper, oxygen and carbon. The oxygen/carbon ratio is about 0.38. This increase in the ratio would be reasonable since there is a relatively strong copper signal. The increased relative abundance of oxygen could then correspond to Cu₂O. This would have been a reasonable interpretation if the composition of the carbon containing surface compound had been the same as in the unpolished sample. According to the analysis (Table A1-6 and Figure A1-12), it is not. The carbon compound on polished sample is much richer in oxygen and seems to account for 90 % of the oxygen on the sample surface. This means that most of the XPS copper signal should correspond to metallic copper.

The reference sample was exposed to air, if only for 5 minutes, and there should be some copper oxide on it. This is also supported by the fact that the O 1s peak for the polished reference has a shoulder on the low binding energy side (at about 530.8 eV) that corresponds well to the Cu₂O oxygen binding energy. The Cu 2p spectrum excludes the presence of any Cu(II), which in addition to the main peaks also has very strong shake-up peaks (see Biesinger et al. 2010). It is not possible, however, to distinguish between metallic copper and Cu₂O. The binding energy difference is only about 0.4 eV. The estimate for the FWHM for the copper 2p_{3/2} is 0.8 eV and the peak is symmetric. This would appear to exclude the possibility of being composed of both Cu(0) and Cu(I).

The main O 1s peak is at 532.7 eV, which supports the interpretation that it comes from oxygen in an organic oxygen-containing compound; alternatively, it could come from a hydroxide or silica. Silica appears unlikely since there is no reported detection of silicon. Hydroxide will have to be Cu(I) hydroxide and there are no spectra recorded from CuOH. For adsorbed OH on copper, the peak should coincide with the Cu₂O O 1s peak (Andersson et al. 2005, 2008). The ratio O-C/O-Cu could be as large as 10. It is difficult to assess the area of a peak riding on the “shoulder” of a larger peak. The Cu₂O peak was visible but the amount was not large. This is consistent with the estimate from the C 1s spectrum. It is not compatible with the determined surface concentration of Cu of 20 at%. 50 % of the detected oxygen would have been needed to match this concentration of copper. The inelastic mean free path (IMFP) for the O 1s photoelectrons (ionized by Al K α) is in the range 6 to 9 nm. The 2p Cu photoelectrons have lower kinetic energy and the IMFP would be 4 to 6 nm. The discrepancy can, thus, not be explained by assuming that the copper signal comes from sampling a deeper surface layer than what was the case for oxygen.

The test samples also show oxygen from at least two different compounds; one is most likely Cu₂O. The ratio of the two clearly discernible oxygen peaks differs between the two samples. In Sample 3, the oxide peaks are lower and the ratio O-C/O-Cu is about 2 based on peak area while for Sample 4 the ratio is about 5 (the O-C oxygen peak is broader than the O-Cu peak). The surface concentration of oxygen is about half that on the reference sample, while the copper concentration was the same. The fraction of carbon bound to oxygen is also lower on test samples, but enough to account for all the detected oxygen atoms, i.e., also those that are identified as Cu₂O oxygen.

5.4 SIMS analyses

The remaining Cu foils were stored in the test solution for additional two months after the opening of the Cu3 test vessel. The analyses were postponed because of problems with SIMS analysis equipment. A Cu foil was removed from the water phase in the glove box. It was allowed to dry up on a piece of paper. Any macroscopic changes could not be observed on the surface of the foil. Small samples (1×1 cm) were cut from the Cu3 test foil and the polished reference foil. The reference foil was the same foil, which was used in XPS analyses. Subsequently, the sample holder of SIMS was brought into the glove box. The samples were mounted under Ar atmosphere on the sample holder. The sample holder with the samples was placed in a glass vessel and the vessel was closed tightly. The sample vessel was carried to the SIMS laboratory (located in the same house). The vessel was opened and the sample holder was transferred to the vacuum chamber of the SIMS. The air exposure time was very short and equal for the reference and the test sample.

The analyses were performed with VG IX70S double focusing magnet sector SIMS with 20 nA Cs⁺ (12 keV) primary-ion bombardment. The bombarded area was 270×280 μm². The analysed area was 10 % of the bombarded area. Two points were tested in each sample. The sputtering rate was approximately 0.16 nm/s (Cu). It is based on the earlier determination when analysing a Cu sample with higher primary beam current. The sputtering rate was scaled down by using the ratio of beam currents. SIMS depth profiles are qualitative, and it is not possible on the basis of signals to determine the composition, or the composition of oxide layers or valence states (compounds). The measured depth profiles are given for the reference and Cu3 test samples in Figure A1-13 and A1-14, and in Figure A1-15 and A1-16, respectively. Depth profiles were measured with secondary ion mass spectrometer for the following components: hydrogen (¹H), carbon (¹²C), oxygen (¹⁶O), hydroxide (OH), silicon (²⁸Si), copper (⁶³Cu), copper oxide (CuO) and copper dioxide. The parallel depth profiles for two points in each sample are in good agreement with each other.

An oxide layer was seen on the surface of the reference sample (Figure A1-13 and A1-14). The thickness of the oxide layer is not known, since SIMS-measurement could not penetrate it. Apparently, the manual polishing with SIC paper at the start of the experiments was not sufficient to remove all oxide layer from the surface of the foil. Cu(II)O was found only on the surface of the unpolished reference on the basis of the XPS analysis. Apparently, Cu(II)O was removed but there was some Cu(I)₂O left. It is not possible to determine the oxidation state of Cu on the basis of SIMS analyses. One can deduce only that the surface was partly oxidised. The signal of 28 is more or less constant down to a depth of ~ 200 nm in the reference sample. One possibility for constant (and high) 28 signal could be that there was SiC particles left on the surface of the reference sample despite the purification of the surface with wet paper and alcohol after polishing with SiC paper. If the SIMS primary beam hits a SiC particle, then there is a constant Si (and C) signal, which will never decrease because the SiC particles can be some microns in thickness. Hence, the constant 28 signal for the reference sample could be an artefact. The signal of carbon is large on the surface of the reference sample and the carbon content remains approximately constant as a function of depth. In the outermost layers, the amount of carbon is larger in the Cu3 test sample. It decreases quickly with the depth in the test sample. This suggests there is a carbon-containing surface layer in the test sample.

It is possible that the signal 28 could also be the signal of CO, but according to the SIMS data (Vickerman et al. 1989) the negative 28 signal is most likely Si⁻. On the other hand, Wilson et al. (1989) state that the negative 28 signal can also be CO⁻. Thus, further analyses would be required to identify signal 28.

The amount of hydrogen seems to be slightly less in the Cu3 test sample than in the reference sample. This cannot be concluded with certainty on the basis of these measurements, because the measurement of the reference sample was not made through the oxide layer to the substrate. The oxide layer can change the H/Cu signal ratio due to matrix disturbance.

The amount of oxygen in the very surface of the oxide layer in the Cu3 test sample is larger than in the reference sample (see Figure A1-15 and A1-16). The amount of oxygen decreases quickly with the depth. The thickness of the oxide layer is approximately 6 ± 1 nm. There is an OH surface peak in the test sample and it is larger than in the reference sample. OH may originate from water.

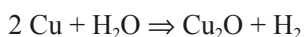
It is not possible to determine the valence state of copper on the basis of CuO (mass 79) and CuO₂ (mass 95) signals, because these molecular ions are partly generated after the primary sputtering process. However, the depth profiles for CuO and CuO₂ are very different in the test sample compared to the reference sample. In the reference sample, the CuO signal has no surface peak, the CuO₂ signal has some kind of surface peak, while the depth profiles of the test sample have clear surface peaks of CuO and CuO₂. This suggests that there is a thin surface layer containing a copper oxide and a carbon-containing compound in the test sample (as discussed above). The oxide was confirmed to be Cu₂O by XPS. This is in agreement with XPS analyses. The influence of a short air exposure in SIMS results is probably very little, because the signals of Cu oxides are completely different on the surface of the test sample compared to the reference. If the air exposure had had influence on the surface of the samples, this would mean that the reference sample would probably have larger surface peaks for Cu oxides.

O/Cu ratio was estimated by comparing the SIMS result of Cu3 test sample with the corresponding XPS result. The O/Cu was calculated from the SIMS depth profiles within the depth range of 0 to 2.3 nm, which corresponds to the analysis depth in the XPS analyses. SIMS result for the O/Cu ratio is 2.35 (Cu reference sample) and 17.3 (Cu sample no. 3). According to the XPS analyses the O/Cu ratio is 0.519 for Cu3 test sample. If the corresponding SIMS result is normalised to the XPS result then the O/Cu ratios are 0.071 (reference sample) and 0.519 (Cu sample 3), respectively.

6 Discussion

The total amount of copper found from the Cu3 test vessel was 5.6 μg ($8.8 \cdot 10^{-8}$ mol). This includes the Cu measured in the unfiltered solution and the Cu desorbed from the surface of the E-flask (Table A1-5). The Cu concentration in the ultrafiltered solution ($5.98 \cdot 10^{-8}$ mol/l) was in the range of the solubility of Cu_2O (Palmer 2011).

The Cu3 test vessel showed a clear weight loss throughout the test period of 746 days. The weight losses were 0.0055 g and 0.0224 g during the N_2 and Ar periods, respectively. Originally, the palladium sealed test vessel was supposed to be closed for everything except hydrogen. Hydrogen can escape through the Pd foil or get trapped in the foil. If all the hydrogen gets trapped in the Pd foil, there should be no weight change. It does not affect the weight if the oxygen is bound to hydrogen as in H_2O or to Cu as in Cu_2O . Moving oxygen from H_2O to Cu_2O does not change weight if the hydrogen is left in the system. The total weight loss in Cu3 was 0.0279 g. If one considers the weight loss as caused by escaped hydrogen, it corresponds to 0.0138 moles H_2 . If Cu_2O is formed, it is formed as follows:



If 0.0138 moles H_2 had escaped, 0.0276 moles copper would have corroded. That is 1.75 g of copper. The weight of Cu foils in the Cu3 test was originally 3.9680 g. This would mean that the corrosion product thickness would be in the order of many micrometers and it would be observed by the eye. This is not the case, in contrast the surface of the Cu foils looked shiny and unaltered at the end of the experimental time. The measurements of the weight change with time for the steel epoxy showed a decrease in weight for the separate sample exposed in the glove box. It is possible that the weight loss of the Cu3 test vessel was caused partially by the evaporation of the epoxy sealing. It is probable that the weight loss of the Cu3 test vessel is caused by something else than hydrogen escape. The evaporation of water through the epoxy sealing may have happened if the sealing was not completely tight. The weights for the ten Cu strips before and after the test period of 746 days suggest a small weight loss of ~ 0.0004 g. This corresponds to $6.8 \cdot 10^{-6}$ mol copper.

The measurement of the H_2 content of the Pd foil from the Cu3 test vessel showed that hydrogen was present in the test system. The test vessel was stored during the experiment in a closed stainless steel vessel to protect it from the trace oxygen of the gas atmosphere of the glove box and light (see Figure A1-1). The Pd foil of the test vessel was open to the atmosphere of the closed stainless steel vessel. If water evaporated from the test vessel through the epoxy sealing to the closed steel vessel, the anaerobic corrosion of steel surface in humid oxygen-free atmosphere could be a source for hydrogen. The H_2 content of the Pd foil was measured to be $7.20 \cdot 10^{-5}$ mol (390 weight-ppm). The measured H_2 content was outside the measurement range of the analyser. Hence it is not an exact content. However, the order of magnitude is right. According to Yun and Oyama (2011) the solubility of hydrogen in Pd at room temperature is approximately 10^{-4} $\text{cm}^3/100$ g of metal ($T=293$ K, $P=1$ atm= $1.01 \cdot 10^5$ Pa). In moles it is 0.43 moles H/100 g of metal, or 4,300 weight-ppm. The measured concentration of H_2 in the Pd foil of the Cu3 test was 390 weight-ppm. It is approximately 5 times less than the solubility of H_2 in Pd. Hence, the concentration of H_2 in Pd was far from saturation. A H_2 content of $7.20 \cdot 10^{-5}$ mol would correspond to $1.44 \cdot 10^{-4}$ mol corroded Cu, or a 200 nm thick corrosion product layer if Cu_2O is formed (see Appendix 2). The layer is too thin to be observed by the eye. A layer above 360 nm would be visible to the eye.

The XPS analyses showed that there was no fully oxidised copper, Cu(II), on the surface of the Cu3 test samples after the reaction period of 746 days. A thin surface layer of a carbon containing compound and of a copper oxide was observed to be present. The oxide was confirmed to be Cu_2O by XPS. The thickness of the oxide layer was approximately 6 ± 1 nm according to the SIMS analysis. The analyses showed an oxide layer to be present also on the surface of the reference sample. It is possible that manual polishing with SiC paper did not entirely remove oxide layer due to air exposure before the start of the tests. The interpretation of XPS data was complicated by the fact that a short air exposure before the analyses was unavoidable.

7 Conclusions

There were no visible changes in the copper surfaces in any of the E-flasks in the glove box (Cu1 to Cu4).

The analysis of copper in Cu3 resulted in:

- 5.6 μg copper ($8.8 \cdot 10^{-8}$ mol) was found in the solution and on the glass walls.
- A layer of Cu_2O was confirmed by XPS, with a thickness of 6 ± 1 nm according to the SIMS measurement (corresponding to about $4.3 \cdot 10^{-6}$ mol copper).
- No Cu(II) was detected with XPS.
- The weight of the copper foils decreased with ~ 0.4 mg. If we assume the weight loss to be accurate, 0.4 mg corresponds to $6.8 \cdot 10^{-6}$ mol copper, which is in the order of magnitude of the copper in the oxide layer.

The analysis of the Pd-membrane in Cu3 resulted in:

- The amount of hydrogen in the Pd was about $7.2 \cdot 10^{-5}$ mol.
- If this was the result of formation of Cu_2O this would correspond to a 200 nm thick corrosion layer, which is not consistent with the measured layer thickness (though consistent with the absence of any visible product).
- This amount is an order of magnitude larger than the amount of copper freed from the bulk (corrosion layer plus solution and on glass vessel).

For the E-flask standing in air (Cu5)

- Visible development of corrosion products (first blackening, then also green spots).
- There were seasonal variations of the weight due to the humidity of the laboratory conditions. Anyhow, some trends could be seen. Initially, there was weight gain suggesting the intrusion of air through the Pd-foil or epoxy sealing. Afterwards, there was a decreasing trend between 272 and 974 days. This suggests the evaporation of water through the Pd foil or epoxy sealing.

8 Acknowledgements

Dr. Leena-Sisko Johansson from Aalto University and Dr. Jari Likonen from VTT are greatly acknowledged for performing XPS and SIMS analyses. The contribution of Dr. Lars Werme in the interpretation of the analysis data is gratefully acknowledged.

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Table A1-1. Composition of the gases used in the experiments.

Gas quality	H ₂ O (ppm)	O ₂ (ppm)	H ₂ (ppm)	CO ₂ (ppm)	N ₂ (ppm)
N ₂ 5.0	≤ 3	≤ 3	≤ 2	–	–
N ₂ 6.0	≤ 1	≤ 0.1	≤ 0.1	–	–
Ar 5.0	≤ 3	≤ 2	–	–	≤ 5
Ar 6.0	≤ 0.6	≤ 0.1	≤ 0.1	≤ 0.1	≤ 0.1

Table A1-2. Average monthly values for measured temperatures in the glove box during the first 11 months of the corrosion tests.

	Average T (°C)	Average deviation*
December (from 19 th), 2009	25.6	0.9
January, 2010	24.9	0.8
February, 2010	25.3	0.5
March, 2010	24.7	1.0
April, 2010	24.9	0.3
May, 2010	25.2	0.2
June, 2010	25.2	0.3
July, 2010	24.8	0.9
August, 2010	24.5	0.7
September, 2010	24.9	0.4
October, 2010	25.1	0.4
November, 2010	24.9	0.4
December, 2010	25.1	0.4
January, 2011	24.8	0.4
February, 2011 (till 19 th)	24.8	0.3

* Average deviation gives the average of the absolute deviations of data points from their mean.



Figure A1-1. The test E-flasks are stored in a closed metallic vessel in the glove box.

Table A1-3. Weight data for the test vessels in Cu corrosion tests.

	Cu1 (N₂) (g)	Cu2 (N₂) (g)	Cu3 (N₂) (g)	Cu4 (N₂) (g)	Cu5 (air) (g)	Air pressure** (hPa)
Ten Cu strips, dry weight	4.0400 ± 0.0001	3.9201 ± 0.0003	3.9680 ± 0.0002	3.9667 ± 0.0002	3.9739 ± 0.0001	
E-flask with Cu foils, water and closing, 19 th December 2009 (start date)	95.3074 ± 0.0002	93.7202 ± 0.0003	90.5720 ± 0.0001	89.0219 ± 0.0004	88.2118 ± 0.0001	1,019.3
30 th March 2010 (101 days)	95.3074 ± 0.0001	93.7205 ± 0.0002	90.5696 ± 0.0001	89.0217 ± 0.0002	88.2166 ± 0.0001	1,007.5
10 th June 2010 (173 days)	95.3070 ± 0.0005	93.7197 ± 0.0002	90.5687 ± 0.0003	89.0204 ± 0.0003	88.2206 ± 0.0001	1,016.1
17 th September 2010 (272 days)	95.3075 ± 0.0001	93.7205 ± 0.0002	90.5687 ± 0.0003	89.0209 ± 0.0003	88.2297 ± 0.0001	999.0
11 th November 2010 (327 days)	95.3077 ± 0.0001	93.7179 ± 0.0002	90.5679 ± 0.0006	89.0208 ± 0.0004	88.2218 ± 0.0001	993.9
17 th November 2010 (335 days)	95.3046 ± 0.0004	93.7144 ± 0.0002	90.5640 ± 0.0004	89.0175 ± 0.0006	88.2182 ± 0.0001	1,034.4
25 th November 2010 (343 days)	95.3074 ± 0.0002	93.7170 ± 0.0004	90.5665 ± 0.0003	89.0198 ± 0.0004	88.2197 ± 0.0001	1,002.0
9 th December 2010 (357 days)*	Cu1 (Ar)	Cu2 (Ar)	Cu3 (Ar)	Cu4 (Ar)		
15 th December 2010 (363 days)	95.2718 ± 0.0002	93.6816 ± 0.0003	90.5311 ± 0.0001	88.9846 ± 0.0001	88.2177 ± 0.0001	1,022.4
27 th January 2011 (406 days)	95.2694 ± 0.0001	93.6798 ± 0.0003	90.5275 ± 0.0005	88.9825 ± 0.0003	88.2160 ± 0.0002	1,038.1
21 st March 2011 (459 days)	95.2692 ± 0.0003	93.6802 ± 0.0004	90.5262 ± 0.0007	88.9829 ± 0.0002	88.2149 ± 0.0001	930
2 nd May 2011 (501 days)	95.2682 ± 0.0002	93.6786 ± 0.0002	90.5235 ± 0.0009	88.9829 ± 0.0003	88.2142 ± 0.0001	932
28 th June 2011 (558 days)	95.2687 ± 0.0003	93.6778 ± 0.0001	90.5181 ± 0.0002	88.9802 ± 0.0003	88.2163 ± 0.0001	1,020
8 th September 2011 (630 days)	95.2707 ± 0.0001	93.6800 ± 0.0001	90.5170 ± 0.0001	88.9829 ± 0.0001	88.2193 ± 0.0001	995
4 th November 2011(687 days)	95.2670 ± 0.0001	93.6762 ± 0.0001	90.5102 ± 0.0002	88.9793 ± 0.0001	88.2128 ± 0.0001	1,023
11 th November 2011 (694 days)	95.26491 ± 0.00004	93.67408± 0.00007	90.50780±0.00007	88.97706±0.00002	–	1,037
22 nd November 2011 (705 days)					88.2100±0.0001	1,027
2 nd January 2012 (746 days)			90.50866±0.00004			1,003
5 th January 2012 (749 days)	95.27302±0.00008	93.68187±0.00004		88.98476±0.00004	88.2075±0.0001	976
15 th March 2012 (819 days)	95.27429±0.00005	93.68316±0.00002		88.99267±0.00006	88.2038±0.0001	1,022
22 nd May 2012 (887 days)	95.27205±0.00003	93.68105±0.00005		88.98901±0.00008		1,021
4 th June 2012 (900 days)					88.2052±0.0001	1,006
17 th August 2012 (974 days)	95.26793±0.00004	93.67622±0.00004		88.97983±0.00002	88.2071±0.0001	1,017

* The inert gas of the glove box was changed from nitrogen to argon.

**The values for air pressure were measured at 2 p. m.

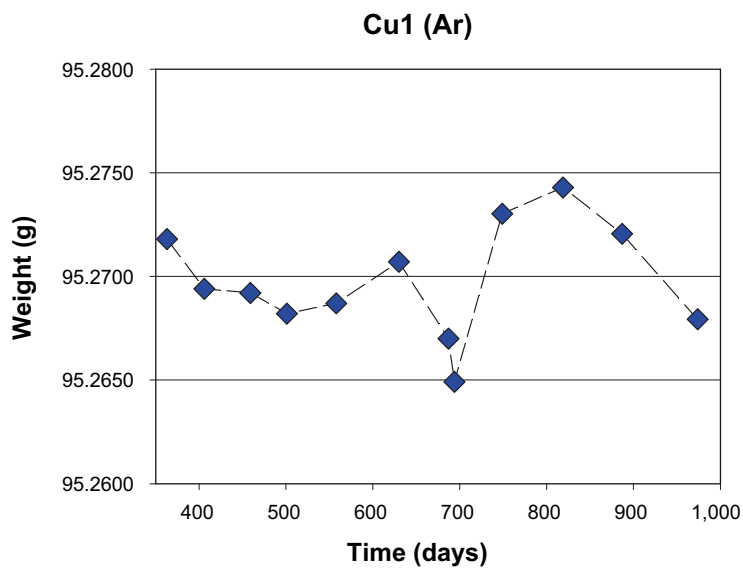
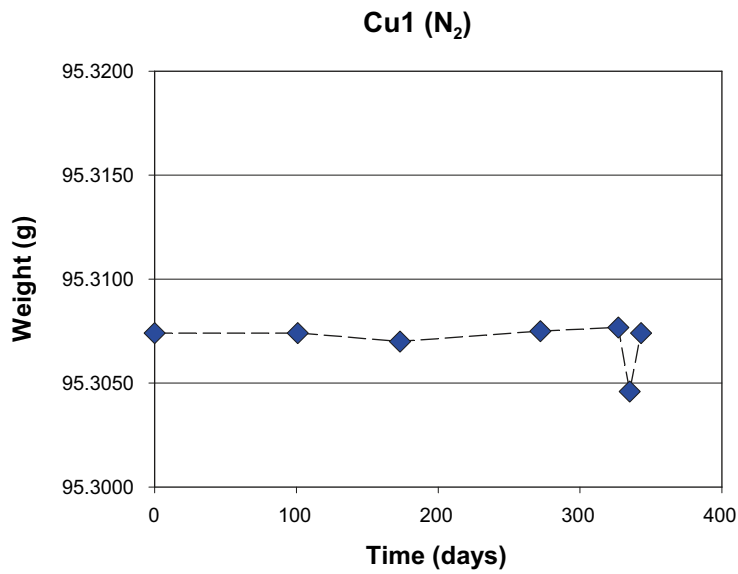


Figure A1-2. The evolution of weight for the test vessel Cu1 vs. time (numerical values are given in Table A1-3). This vessel was closed with a glass stopper and sealed with steel epoxy. The upper figure gives the weights in N₂ atmosphere. The lower figure gives the weights after the working gas bottle of the box was changed from N₂ to Ar (at 357 days). At 406 days, the gas atmosphere has entirely changed from N₂ to Ar.

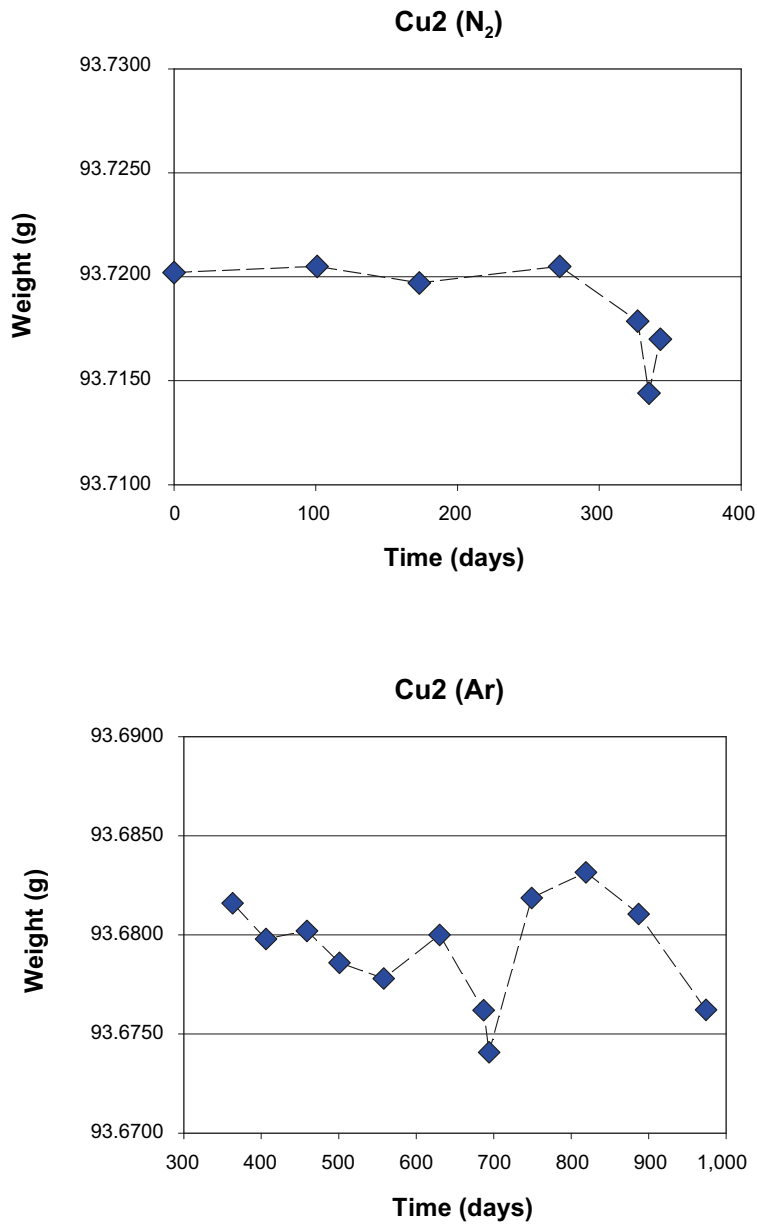


Figure A1-3. The evolution of weight for the test vessel Cu2 vs. time (numerical values are given in Table A1-3). This vessel was closed with a glass stopper and sealed with steel epoxy. The upper figure gives the weights in N₂ atmosphere. The lower figure gives the weights after the working gas bottle of the glove box was changed from N₂ to Ar (at 357 days). At 406 days, the gas atmosphere has entirely changed from N₂ to Ar.

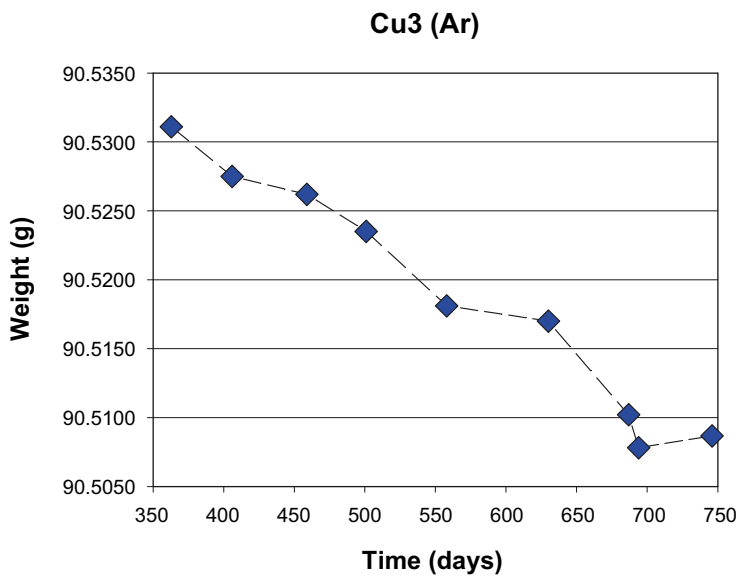
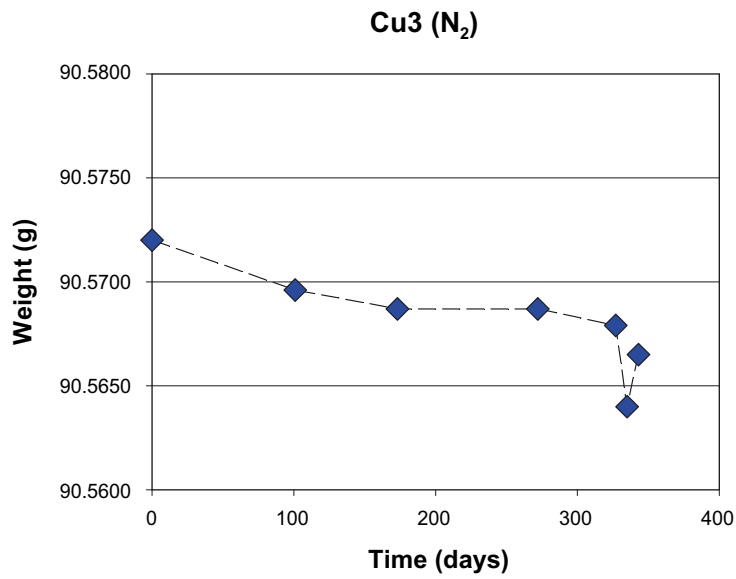


Figure A1-4. The evolution of weight for the test vessel Cu3 vs. time (numerical values are given in Table A1-3). The vessel was closed with Pd foil, which was attached and sealed with steel epoxy. The upper figure gives the weights in N₂ atmosphere. The lower figure gives the weights after the working gas bottle of the glove box was changed from N₂ to Ar (at 357 days). At 406 days, the gas atmosphere has entirely changed from N₂ to Ar. The Cu3 test was finished after 746 days.

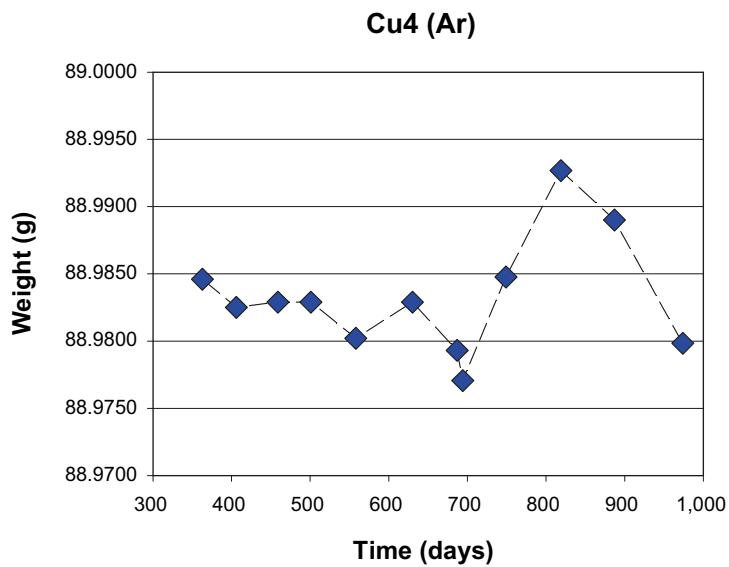
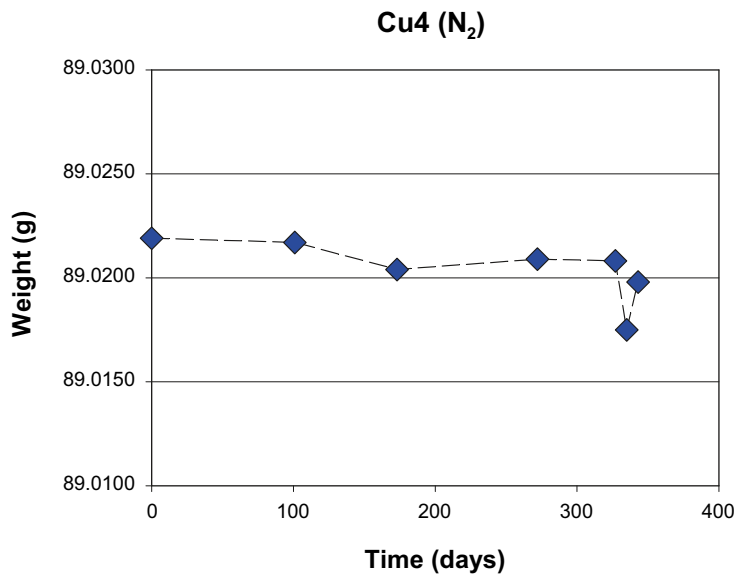


Figure A1-5. The evolution of weight for the test vessel Cu4 vs. time (numerical values are given in Table A1-3). The vessel was closed with Pd foil, which was attached and sealed with steel epoxy. The upper figure gives the weights in N₂ atmosphere. The lower figure gives the weights after the working gas bottle of the glove box was changed from N₂ to Ar (at 357 days). At 406 days, the gas atmosphere has entirely changed from N₂ to Ar.

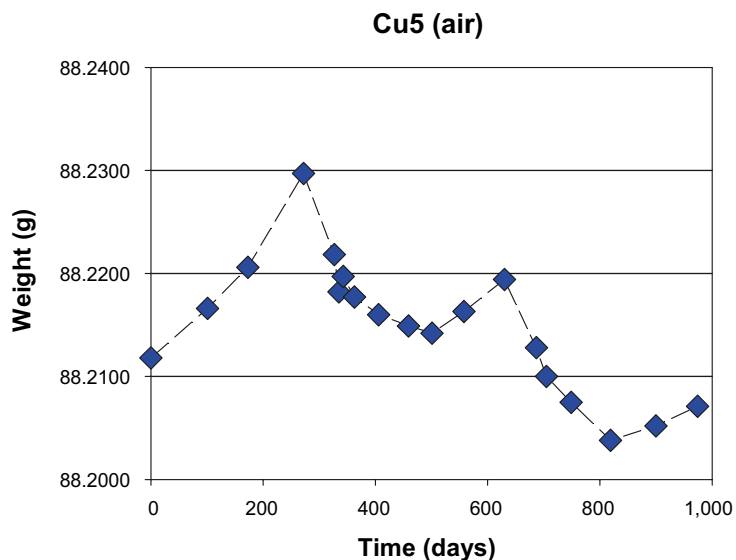


Figure A1-6. The evolution of weight for the test vessel Cu5 vs. time (numerical values are given in Table A1-3). The vessel was closed with Pd foil, which was attached and sealed with steel epoxy.

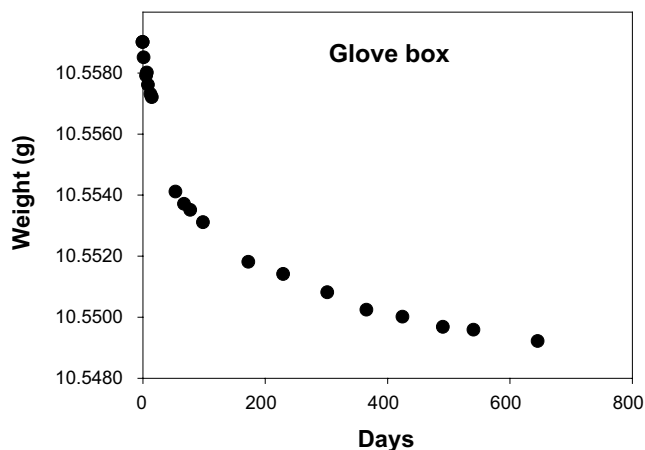


Figure A1-7. Steel epoxy (~ 1 g) was added on a watch glass in the glove box. Measured weights of the steel epoxy+watch glass are given vs. time in the figure. The data until 20 days were measured in N_2 atmosphere and the rest of the data in Ar atmosphere. (The volume of the watch glass was small, and hence the effect of the different buoyancies on the weights in N_2 and Ar atmospheres is small.)

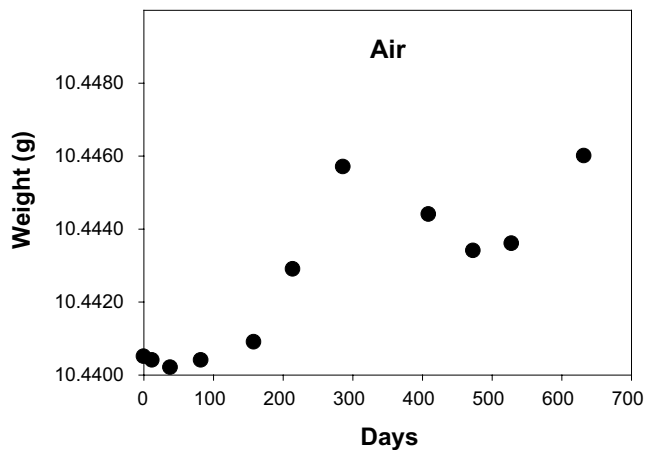


Figure A1-8. Steel epoxy (~ 1 g) was added on a watch glass in air. Measured weights of the steel epoxy+watch glass are given vs. time in the figure.

Table A1-4. The weights for the watch-glass with steel epoxy sample in the glove box (N₂, Ar) and air atmospheres.

Atmosphere	(d)	(g)
N₂		
10th Nov. 2010	0.08	10.5590
	0.17	10.5590
12th Nov. 2010	2	10.5585
16th Nov. 2010	6	10.5579
17th Nov. 2010	7	10.5580
19th Nov. 2010	9	10.5576
23rd Nov. 2010	13	10.5573
25th Nov. 2010	15	10.5572
Ar		
3rd Jan. 2011	54	10.5541
17th Jan. 2011	68	10.5537
27th Jan. 2011	78	10.5535
17th Feb. 2011	99	10.5531
2nd May 2011	173	10.5518
28th June 2011	230	10.5514
8th Sept. 2011	302	10.5508
11th Nov. 2011	366	10.55023
9th Jan. 2012	425	10.55000
15th March 2012	491	10.54967
4th May 2012	541	10.54957
17th Aug. 2012	646	10.54920
Air		
26th Nov. 2010	0	10.4405
8th Dec. 2010	12	10.4404
3rd Jan. 2011	38	10.4402
16th Feb. 2011	82	10.4404
3rd May 2011	158	10.4409
28th June 2011	214	10.4429
8th Sept. 2011	286	10.4457
9th Jan. 2012	409	10.4444
13th March 2012	473	10.4434
7th May 2012	528	10.4436
17th Aug. 2012	632	10.4460



Figure A1-9. Cu2 (with glass stopper) and Cu3 (with Pd foil) test vessels after 292 days' reaction time N_2 atmosphere.



Figure A1-10. Cu5 test vessel after 116 days' reaction time (left), and after 344 days' reaction time (right) in air atmosphere.

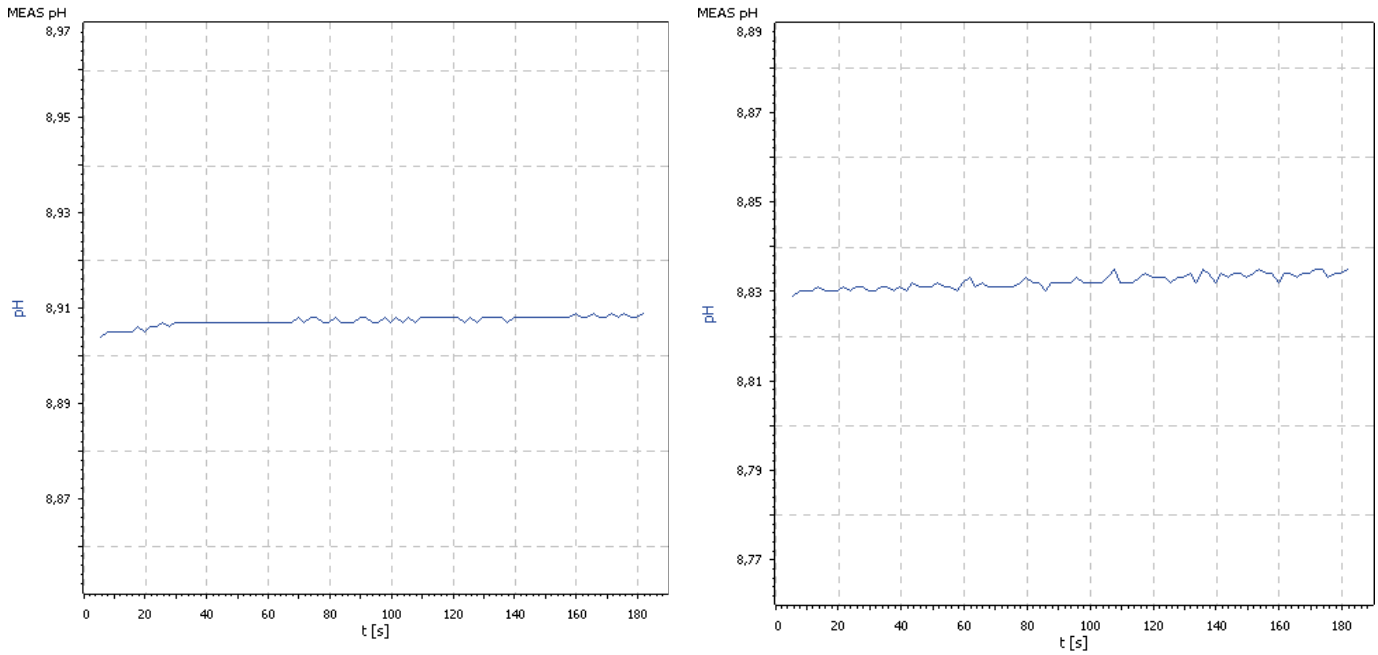


Figure A1-11. The measured pH values for the solution phase at the end of the Cu3 corrosion test. The left figure gives the pH measured with the electrode immersed in the test vessel (with Cu foils in solution) without stirring. The right figure gives the result of the measurement for a solution sample taken to a separate beaker (with magnetic stirring).

Table A1-5. Composition of the solution phase at the end of Cu3 corrosion test. The analyses were performed with HR-ICP-MS.

	Background sample* (unfiltered) (µg/l)	Unfiltered solution (µg/l)	Filtered solution (Whatman UF, 12 K MWCO) (µg/l)	Desorption solution of the test vessel*** (1 M HNO ₃ , up) (µg/l)	Test solution µg/50 ml
Cu**	0.3	21.6	3.8	90.2	5.6
Si**	9.0	3,103	3,189	335	176
B	1.2	947	–	–	–
Na	< 10	328	–	–	–

* Original deionised water before the immersion of Cu foils. The water sample has been stored in a bottle (polyethylene) in the glove box for the test duration of 2 years.

** Cu and Si concentrations are average values of duplicate samples.

*** 50 ml of 1 M HNO₃ (ultrapure quality) was added to the the empty Cu3 test vessel to desorb potential adsorbed Cu material from the surface. The acid was allowed to stay in the vessel at room temperature. In one week's time, samples were taken for analyses with ICP-MS.

Table A1-6. Samples were unpacked just before the experiment, air exposure time less than 5 minutes Dset file 12-01-05.

set 12-01-05, refs	#	Cu 2p	Atomic Concentrations, wides (AC's)								notes
			O 1s	C 1s	N 1s	S 2p	Cl 2p	P 2p	Ca 2p	Zn 2p	
Ref 1 polished reference	1	20.2 %	19.6 %	54.7 %	0.4 %	2.8 %	0.9 %	1.3 %	trace	trace	Thick carbon contamination layer covers the sample
	2	21.3 %	21.1 %	53.1 %		3.3 %	0.7 %	0.6 %	trace	trace	
	3	18.4 %	21.6 %	55.1 %	1.0 %	2.3 %	0.4 %	1.2 %	trace	trace	
Ref 2 unpolished reference	1	2.0 %	13.5 %	82.4 %	0.4 %	trace	trace	trace	1.2 %	0.6 %	
	2	1.5 %	13.3 %	83.0 %	1.2 %	trace	trace	trace	0.9 %	0.1 %	
	3	1.5 %	13.0 %	82.2 %	1.7 %	trace	trace	trace	1.2 %	0.4 %	
set 12-01-05, samples	#	Cu 2p	O 1s	C 1s	N 1s	S 2p					
Sample no 3 Cu foil 1	1	21.9 %	10.5 %	64.6 %	2.1 %	0.9 %					
	2	22.1 %	12.3 %	64.0 %	1.4 %	0.2 %					
	3	21.9 %	11.5 %	63.2 %	2.1 %	1.3 %					
Sample no 4 Cu foil 2	1	19.8 %	13.4 %	62.2 %	1.6 %	3.0 %					
	2	24.1 %	10.5 %	63.6 %	0.0 %	1.8 %					
	3	26.6 %	12.1 %	56.3 %	2.6 %	2.4 %					
XPS ref, Aalto			O 1s	C 1s							
S&S			41.7 %	58.3 %							UHV vacuum ok
			41.0 %	59.0 %							

Table A1-6. Samples were unpacked just before the experiment, air exposure time less than 5 minutes Dset file 12-01-05 (cont.)

set 12-01-05, refs	C 1s HiRes components						Correlation graph		
	C-C	C-O	C=O	COO	<CC>		set 12-01-05, refs	O/C	Cu series
Ref 1 polished reference	67.5 %	23.2 %	2.9 %	6.5 %		105.43	Ref 1 polished reference	0.36	67.5 %
	65.4 %	23.8 %	3.8 %	7.0 %	66.5 %	104.52		0.40	65.4 %
	66.7 %	23.1 %	3.6 %	6.6 %		104.94		0.39	66.7 %
Ref 2 unpolished reference	91.8 %	2.7 %	2.0 %	3.5 %		102.11	Ref 2 unpolished reference	0.16	91.8 %
	92.9 %	2.2 %	1.4 %	3.5 %	92.6 %	102.18		0.16	92.9 %
	93.0 %	2.3 %	1.2 %	3.5 %		103.25		0.16	93.0 %
set 12-01-05, samples							set 12-01-05, samples		
Sample no 3 Cu foil 1	82.6 %	10.0 %	2.8 %	4.7 %		102.99	Sample no 3	0.16	82.6 %
	83.2 %	9.7 %	2.7 %	4.5 %	83.5 %	101.58		0.19	83.2 %
	84.6 %	9.3 %	2.7 %	3.4 %		103.36		0.18	84.6 %
Sample no 4 Cu foil 2	82.4 %	10.0 %	3.0 %	4.6 %		104.61	Sample 4	0.22	82.4 %
	82.6 %	10.2 %	2.9 %	4.3 %	81.3 %	101.81		0.17	82.6 %
	78.9 %	12.1 %	3.0 %	6.0 %		105.01		0.21	78.9 %
XPS ref, Aalto							XPS ref, Aalto		Cellulose ref
S&S	6.5 %	74.2 %	18.4 %	0.9 %		99.99	S&S	0.71	6.5 %
	7.4 %	74.0 %	17.5 %	1.1 %	6.9 %	100.00		0.69	7.4 %

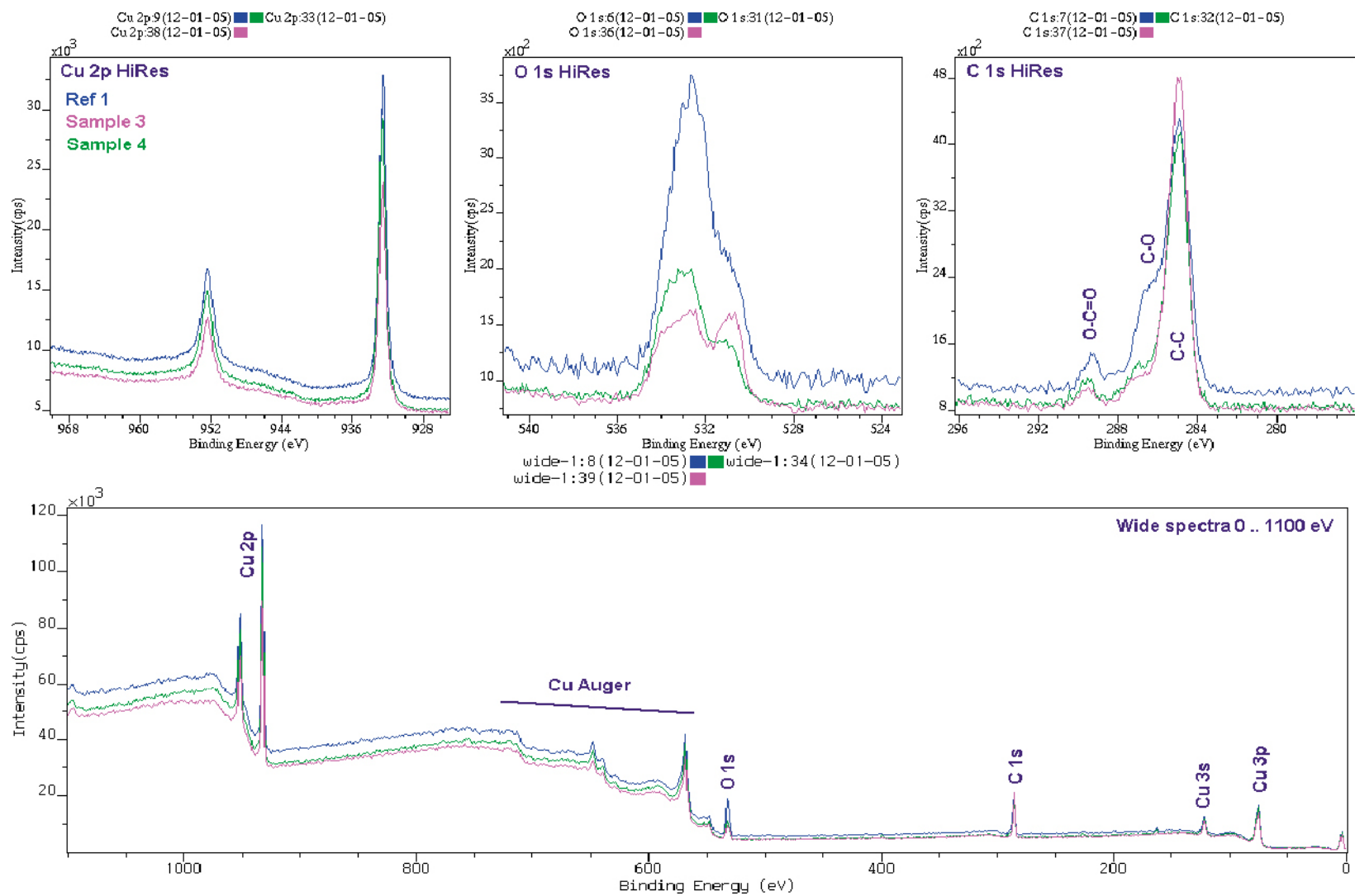


Figure A1-12. XPS spectra for two Cu foil samples from Cu3 corrosion experiment (Sample 3 and 4) and reference sample (Ref 1).

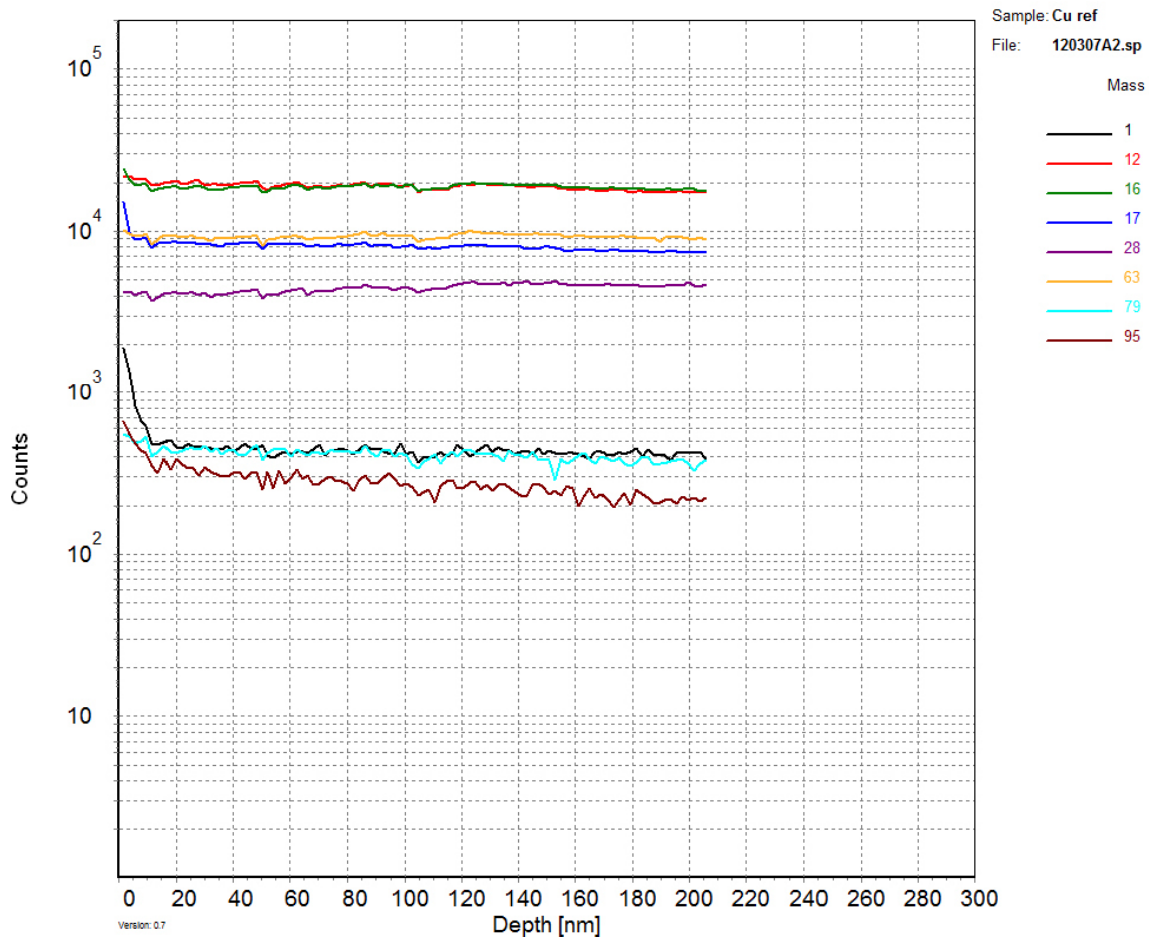


Figure A1-13. SIMS analyses for Cu reference sample (1. point). The depth profiles for the following components are included: hydrogen (^1H), carbon (^{12}C), oxygen (^{16}O), hydroxide (^{17}OH), silicon (^{28}Si), copper (^{63}Cu), copper oxide (^{79}CuO) and copper dioxide ($^{95}\text{CuO}_2$).

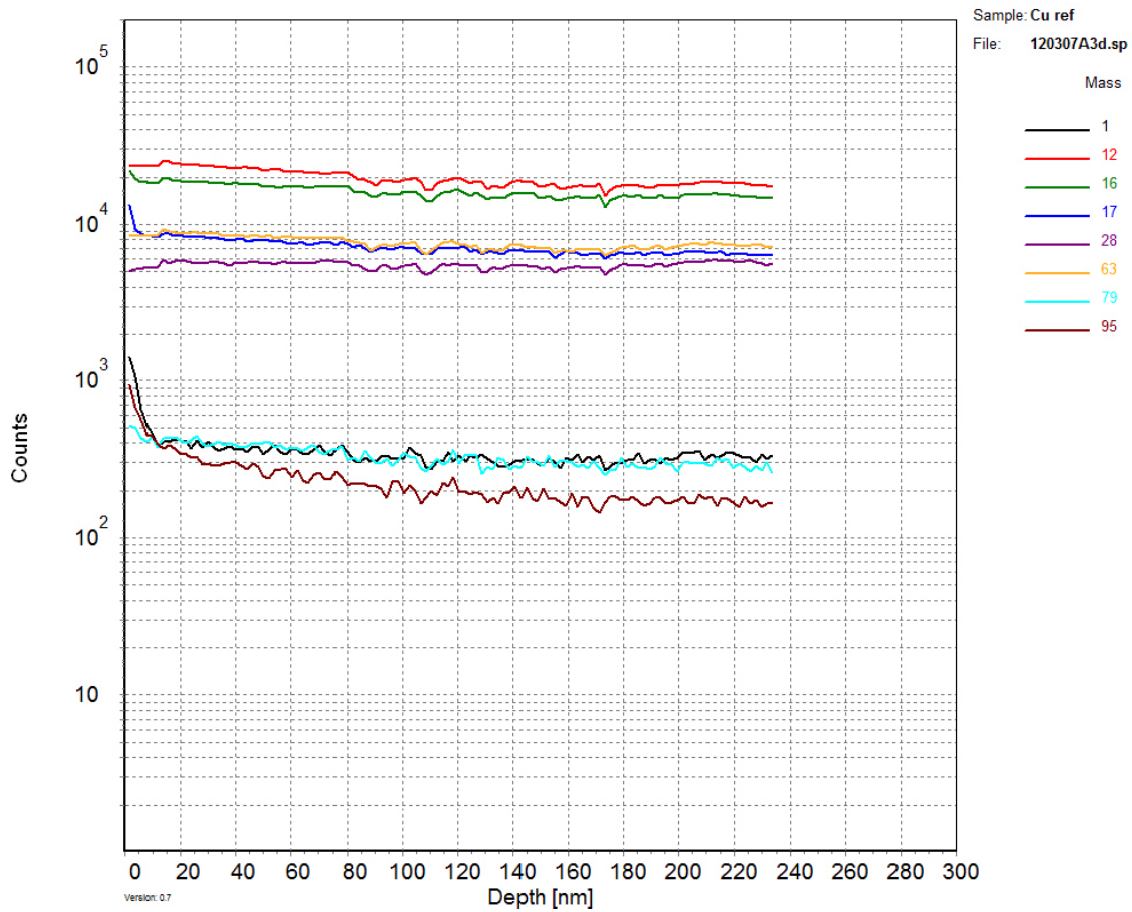


Figure A1-14. SIMS analyses for Cu reference sample (2. point). The depth profiles for the following components are included: hydrogen (^1H), carbon (^{12}C), oxygen (^{16}O), hydroxide (^{17}OH), silicon (^{28}Si), copper (^{63}Cu), copper oxide (^{79}CuO) and copper dioxide ($^{95}\text{CuO}_2$).

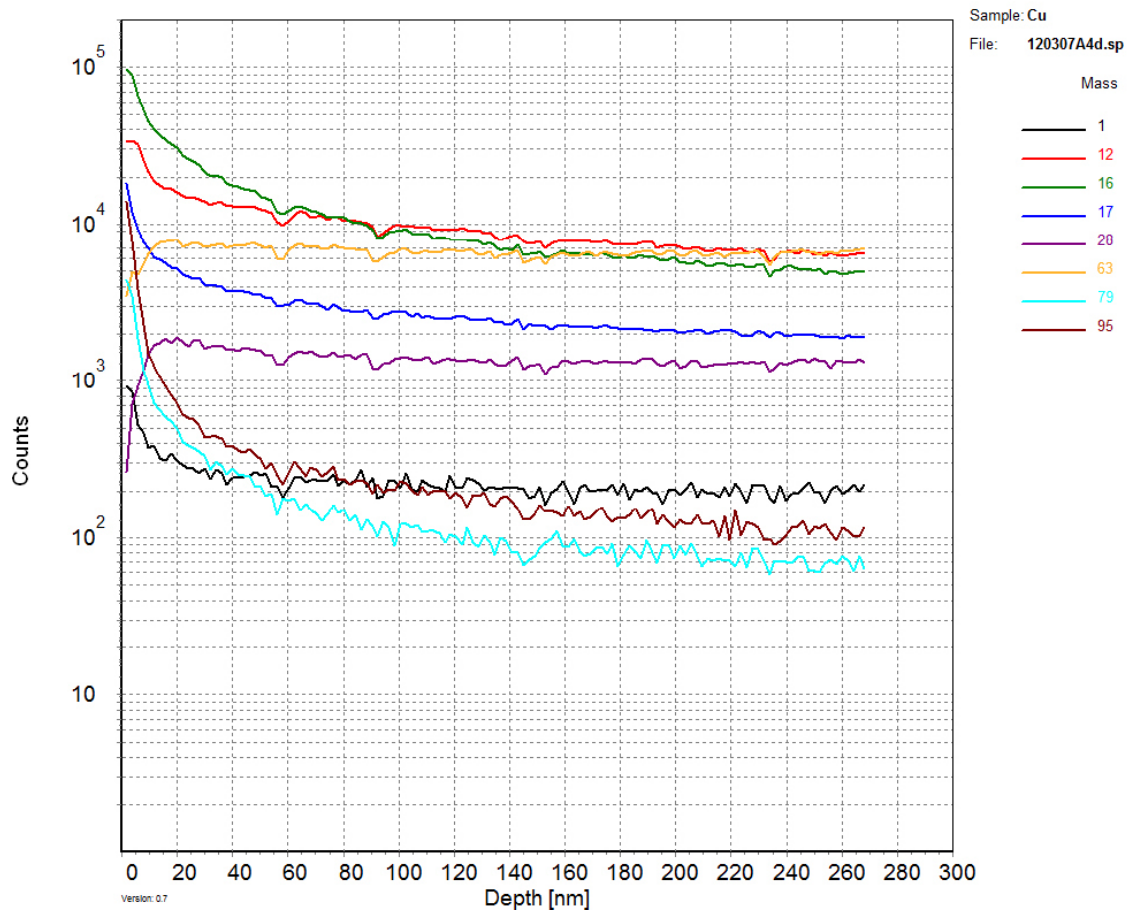


Figure A1-15. SIMS analyses for Cu3 foil sample (1. point). The depth profiles for the following components are included: hydrogen (^1H), carbon (^{12}C), oxygen (^{16}O), hydroxide (^{17}OH), silicon (^{28}Si), copper (^{63}Cu), copper oxide (^{79}CuO) and copper dioxide ($^{95}\text{CuO}_2$).

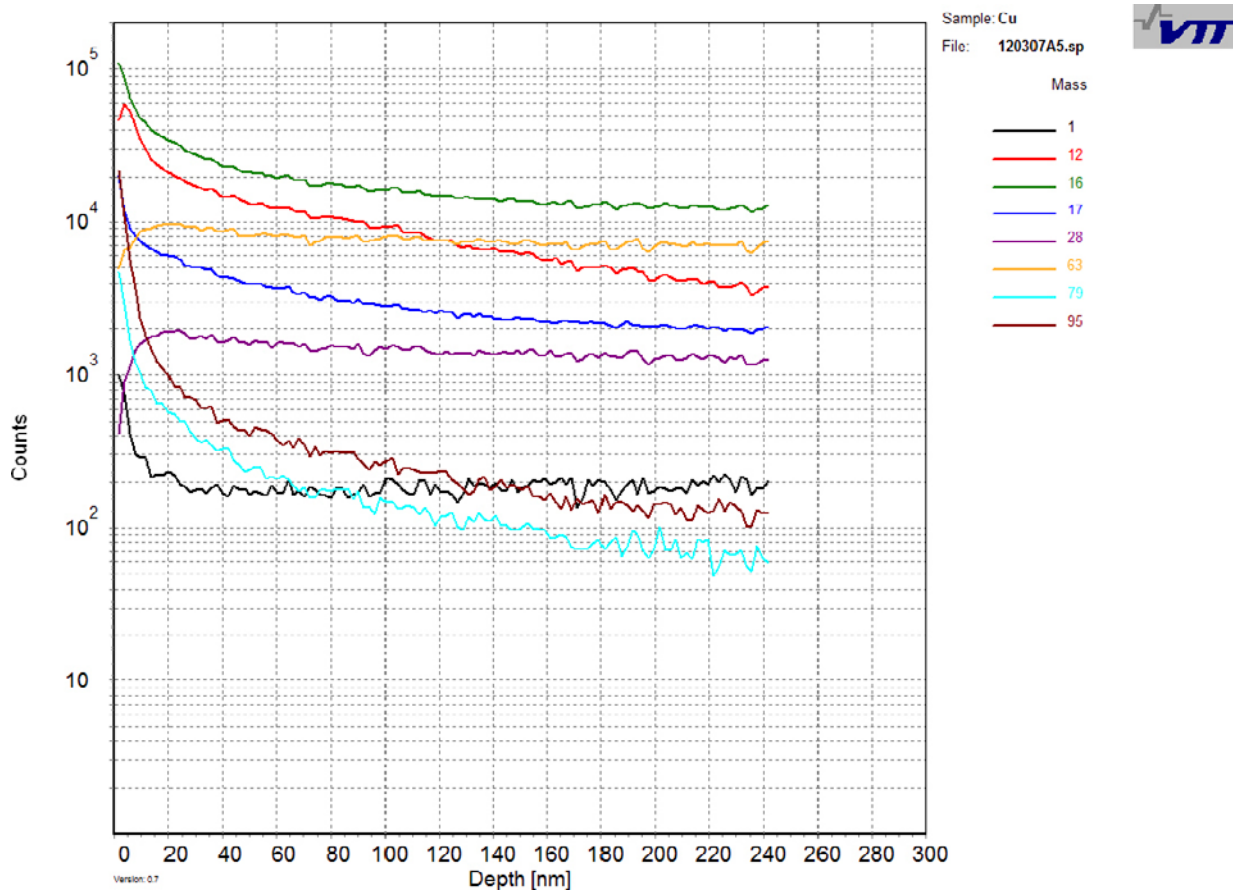


Figure A1-16. SIMS analyses for Cu3 foil sample (2. point). The depth profiles for the following components are included: hydrogen (^1H), carbon (^{12}C), oxygen (^{16}O), hydroxide (^{17}OH), silicon (^{28}Si), copper (^{63}Cu), copper oxide (^{79}CuO) and copper dioxide ($^{95}\text{CuO}_2$).

Pd foil in Cu3

Analysed sample:

Weight:	0.123 g
Thickness:	0.010 cm
Density:	12.020 g/cm ³
Area:	1.023 cm ²
H ₂ concentration in Pd:	390 weight-ppm

⇒

Weight H ₂ :	4.80 · 10 ⁻⁵ g
Moles H ₂ :	2.40 · 10 ⁻⁵ mol
Estimated total Pd foil area:	3 × sample area
Total moles H ₂ :	7.20 · 10 ⁻⁵ mol
Cu ₂ O is assumed to form as follows: 2 Cu + H ₂ O ⇒ Cu ₂ O + H ₂	

⇒

Cu corroded:	1.44 · 10 ⁻⁴ mol (9.15 · 10 ⁻³ g)
Cu ₂ O formed:	7.20 · 10 ⁻⁵ mol (1.03 · 10 ⁻² g)
Density Cu ₂ O:	6.00 g/cm ³
Cu foil area:	85 cm ²
Cu₂O thickness:	2.02 · 10⁻⁵ cm = 200 nm