Technical Report

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Corrosion resistance of copper canister weld material

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Executive summary

The proposed design for a final repository for spent fuel and other long-lived residues is based on the multi-barrier principle. The waste will be encapsulated in sealed cylindrical canisters, which will be placed in granite bedrock and surrounded by compacted bentonite clay. The canister design is based on a thick cast iron insert fitted inside a copper canister.

SKB has since several years developed manufacturing processes for the canister components using a network of manufacturers. For the encapsulation process SKB has built the Canister Laboratory to demonstrate and develop the encapsulation technique in full scale. The critical part of the encapsulation of spent fuel is the sealing of the canister which is done by welding the copper lid to the cylindrical part of the canister. Two welding techniques have been developed in parallel, Electron Beam Welding (EBW) and Friction Stir Welding (FSW).

During the past two decades, SKB has developed the technology EBW at The Welding Institute (TWI) in Cambridge, UK. The development work at the Canister Laboratory began in 1999. In electron beam welding, a gun is used to generate the electron beam which is aimed at the joint. The beam heats up the material to the melting point allowing a fusion weld to be formed. The gun was developed by TWI and has a unique design for use at reduced pressure. The system has gone through a number of improvements under the last couple of years including implementation of a beam oscillation system. However, during fabrication of the outer copper canisters there will be some unavoidable grain growth in the welded areas. As grains grow they will tend to concentrate impurities at the new grain boundaries that might pose adverse effects on the corrosion resistance of welds.

As a new method for joining, SKB has been developing friction stir welding (FSW) for sealing copper canisters for spent nuclear fuel in cooperation with TWI since 1997. FSW was invented in 1991 at TWI and is a thermo mechanical solid-state process, i.e. not a fusion welding method. The FSW tool consists of two parts: a tapered pin (or probe) and a shoulder. The function of the tool is to heat up the material by means of friction and, by virtue of its shape, force the material to flow around it and create a joint. This means that the problems encountered in fusion welding, for example unfavourable grain structure and size and segregation phenomena, can be avoided. The microstructure in copper resulting from FSW resembles the microstructure resulting from hot forming of the copper components in the canister. However, some impurities from the tool, such as metal particles, have been detected in the weld material.

This study aimed to investigate whether the driving force of galvanic corrosion between weld material and base material could pose a problem and whether metallic particles originating from the FSW tool could induce and sustain corrosion. In this study, a surface untreated FSW tool was used to simulate the worst case scenario. For today's FSW welds, the tools have been surface treated which results in no detectable levels of metal particles in the weld. For the study described in this report, 9 samples from FSW (produced with surface untreated tools) and 1 EBW sample were investigated in this study. As result, the FSW samples show less corrosion compared to EBW and the residues from FSW tool do not influence corrosion adversely. Furthermore, copper oxides do not influence the corrosion properties of FSW welds noticeably. In conclusion, FSW for sealing copper canisters for spend nuclear fuel provides more durable welds from a corrosion point of view.

Contents

1 Introduction

The report R-05-73 summarizes the development of Friction Stir Welding (FSW) at the Canister Laboratory under the period 2003 to middle of 2005 /SKB 2005/. The report describes the results from 49 welds with 5 cm thick copper performed in the laboratory. Several important technical advances have been made during that period. A large test programme (according to RD&D-programme 2004 /SKB 2004/) has been performed in order to test the welding system and performance in respect to reliability, capacity, availability and the properties of the weld material. One open question was the corrosion resistance of the weld materials, especially whether residuals from the FSW tool and formed copper oxides in the weld material might influence the corrosion properties negatively.

1.1 Previous tests

During fabrication of the outer copper canisters there will be some unavoidable grain growth in the welded areas, if Electron Beam Welding (EBW) is used. As grains grow, they will tend to concentrate impurities within the copper at the new grain boundaries. During the Friction Stir Weld (FSW) process, impurities from the FSW tool have been found in weld materials, as well as up to 20 ppm copper oxides in the weld roots and close to the surface. However, the latter will be machined off during the final production steps /SKB 2005/. As a consequence, the tool material is today surface treated, resulting in not detectable tool impurities in the weld material. The work described in /Gubner et al. 2006/ was undertaken to determine whether there is any possibility of enhanced corrosion at grain boundaries within the copper canister, based on the recommendations in /Fennel et al. 2001/. Grain boundary corrosion of copper is not expected to be a problem for the copper canisters in a repository. However, as one step in the experimental verification it was necessary to study grain boundary corrosion of copper in an environment where it may occur. A literature study aimed to find one or several solutions that are aggressive with respect to grain boundary corrosion of copper. Copper specimens cut from welds of real copper canisters where exposed to aerated ammonium hydroxide solution for a period of 14 days at 80°C and 10 bar pressure. The samples were investigated prior to exposure using the scanning Kelvin probe technique to characterize anodic and cathodic areas on the samples. The degree of corrosion was determined by optical microscopy. No grain boundary corrosion could be observed in the autoclave experiments, however, a higher rate of corrosion was observed for the weld material compared to the base material. The work suggests that grain boundary corrosion of copper weld material is most unlikely to adversely affect SKB's copper canisters under the conditions in the repository. The friction stir welded samples demonstrated a much smaller rate of corrosion compared to the electron beam welded samples. The relatively high surface potential differences (90–200 mV) between the weld material and base material could set up a corrosion cell with the weld material being a small anode and the base material a large cathode, leading to a higher corrosion rate of the welds compared to the rest of the canister. Furthermore, if metallic particles from the FSW tool would prove to be anodic compared to the copper weld material, they could be sites for local corrosion initiation (small anode, large cathode).

1.2 Aim of this study

The aim of this study was to:

1) investigate whether a corrosion cell could exist between the base materials and the weld material for FSW and EBW,
2) investigate whether small metal particles from the FSW tool would influence the corrosion properties of the weld material negatively.

2 Experimental programme

A total of 9 samples produced from friction stir welding and one reference sample produced by electron beam welding type was used to perform comparative electrochemical corrosion measurements.

List of samples used (values in brackets describe the location in degrees along the weld):

FSWL22-1 (13–35) FSWL22-2 (155–177) FSWL22-3 (177–199)
FSWL23-1 (145–167) FSWL23-2 (167–189) FSWL23-3 (189–211)
FSWL38-1 (5–27) FSWL38-2 (317–339) FSWL38-3 (339–1)
EBWL060 (18–40)

2.1 Electrochemical measurements

Electrochemical measurements where performed with a Solatron 1286 Electrochemical Interface and a Radiometer Copenhagen PGP201 Potentiostat/Galvanostat. The samples where degreased using ethanol and acetone but otherwise used as received.

The test solutions where prepared from analytical grade chemicals in deionised water (reverse osmosis, conductivity 0.025 µS cm^{-1}).

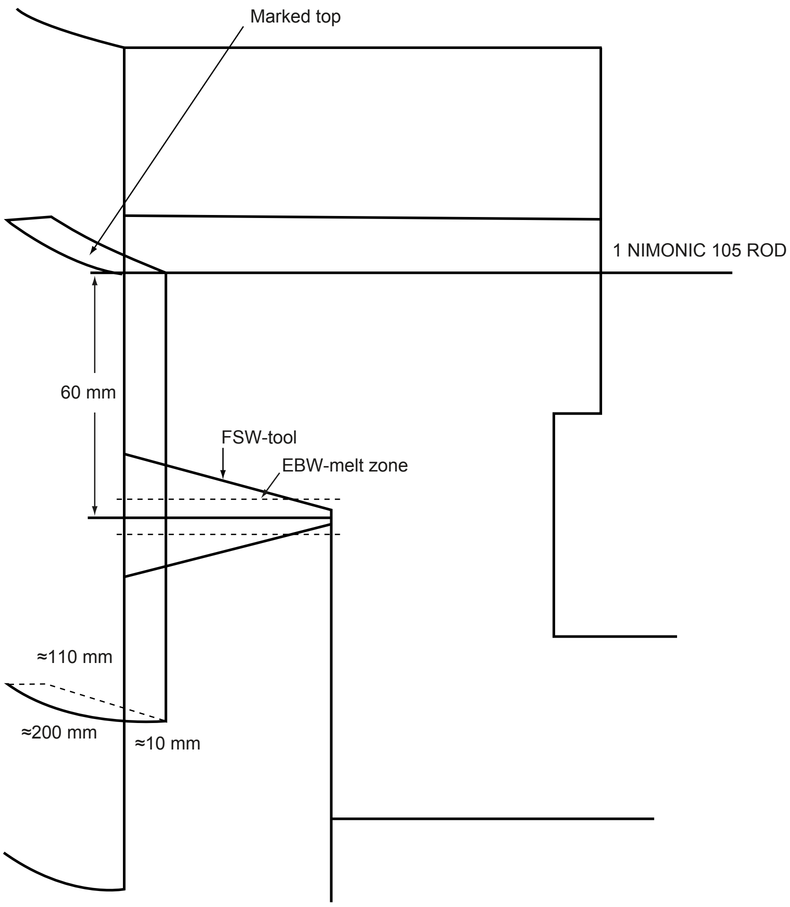

Figure 2-1. *Schematic drawing of samples cut from canister.*

2.1.1 Galvanic corrosion studies between weld and base materials

The samples were used to measure galvanic currents between the weld-, lid- and base materials in aerated 0.5 M NaCl solution, pH 6.5. In order to be able to measure currents between the weld and base materials, the samples where cut into three parts: a) lid material, b) weld material and c) tube material. The cutting surfaces and the back of the samples where coated using an insulating barrier coating, so that only the outer surfaces of the canister material was exposed to the testing solutions.

The measurements were performed by shorting together the weld material with the lid/tube material as two 'working' electrodes. The current flowing between the weld and lid/tube material, as well as the potential between the materials and a reference electrode is monitored (Figure 2-3).

The potentiostat was set up to actively hold the working electrode connection at the 'ground' potential by a small amplifier circuit. If one 'working' electrode is directly connected to ground and the other is connected to the working electrode cable, they are both held at the same potential and are, in effect, 'shorted' together. Any current which flows between the two electrodes is measured by the instruments current measurements circuits thus creating a Zero Resistance Ammeter (ZRA).

The potential is measured between the 'working' electrodes (since they are shorted together, both 'working' electrodes are at the same potential) and a reference electrode.

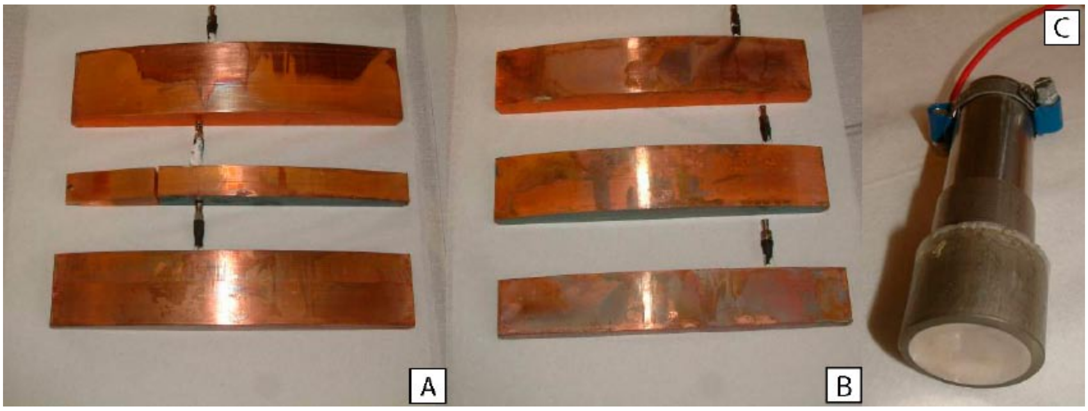

Figure 2-2. *Weld samples cut into three parts (A: EBW, B: FSW) and FSW tool for electrochemical measurements.*

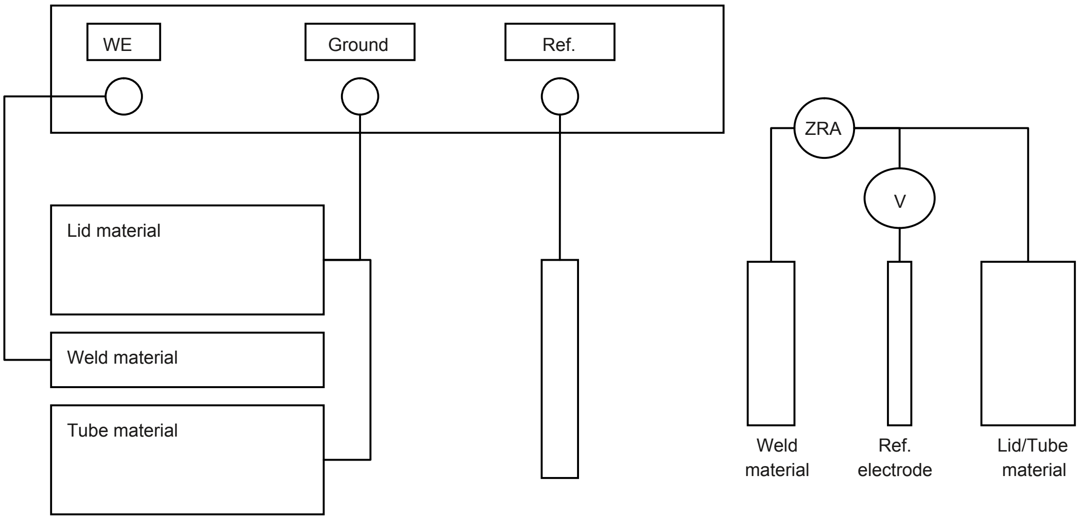

Figure 2-3. *Schematic setup to measure galvanic corrosion currents between weld and base materials.*

2.1.2 Galvanic corrosion study between FSW tool and weld material

Samples of the same material as the friction stir probe was used to measure if a galvanic current can be measured between copper weld material and metal fragments originating from the friction stir welding process (0.5 M NaCl, pH 6.5, aerated).

2.1.3 Measurement of free corrosion potential and polarisation curves under aerated and de-aerated conditions

The following electrochemical experiments were performed in 0.1 M and 0.01 M NaCl solution, pH 8.5 ($NaHCO_3$, Na_2CO_3) (aerated and de-aerated) using as received but degreased specimens at 40°C:

1) Free corrosion potential in medium of weld material.
2) Polarisation curve.

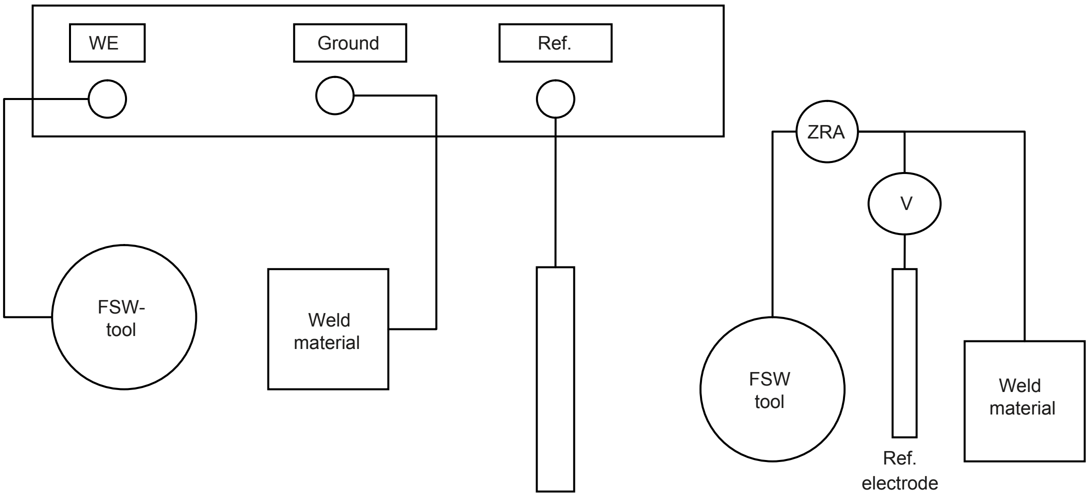

Figure 2-4. *Schematic setup to measure galvanic corrosion currents between weld and FSW tool material.*

3 Results and discussion

The experiments where performed in sodium chloride solutions (0.01 M, 0.1 M to 0.5 M) at room temperature and 40°C; and a pH of 6.2 to 8.5.

3.1 Galvanic corrosion studies between weld and base materials

For this experiment, aerated 0.5 M NaCl solution at room temperature was used in order to stimulate corrosion. Figure 3-1 shows that the free corrosion potential varied between the different samples.

It could be observed, that there was no trend in respect to the direction of the corrosion currents: as often as the weld material showed anodic behaviour did the base materials.

The only sample that showed some initiation of localised corrosion was the single EBW sample (Figure 3-2), where a few incidences of corrosion initiation where observed. However, these incidences where not initiated on the weld material and, furthermore, the corrosion currents flattened out after short period of time and towards the end of the experiment close to zero.

Figure 3-3 shows how similar the corrosion currents between the weld and base materials where across all FSW samples. The differences in the free corrosion potential are probably due to differences in the surface properties, since the samples where used as received (but degreased). This is even more prominent shown in Figure 3-4.

Figure 3-5 shows an example where the corrosion current changed direction during the experiment, indicating there is general trend of preferred weld material corrosion.

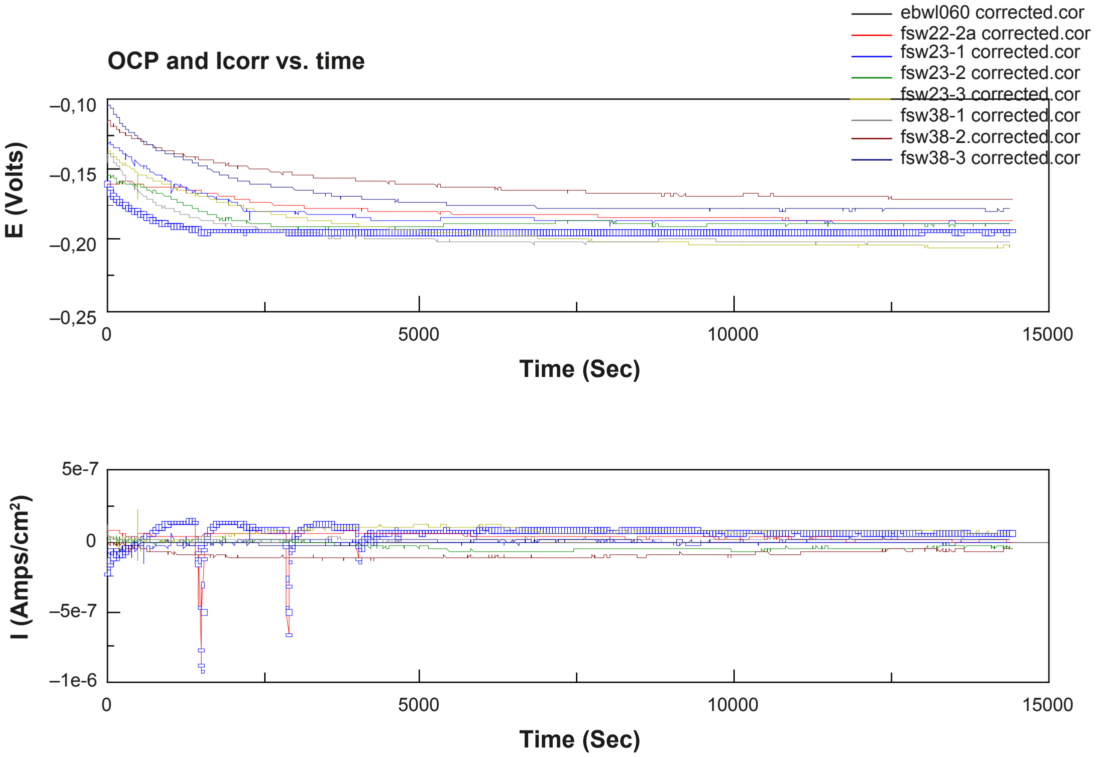

Figure 3-1. Summary graph of all galvanic corrosion studies between weld and base materials.

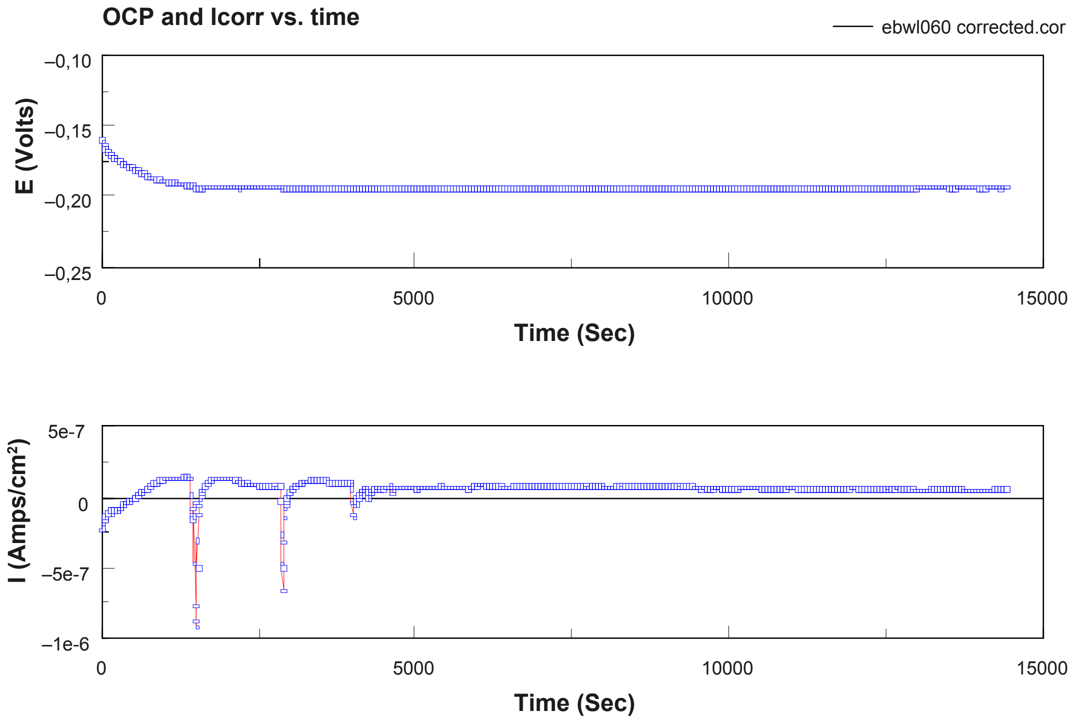

Figure 3-2. *Galvanic corrosion study of EBW sample.*

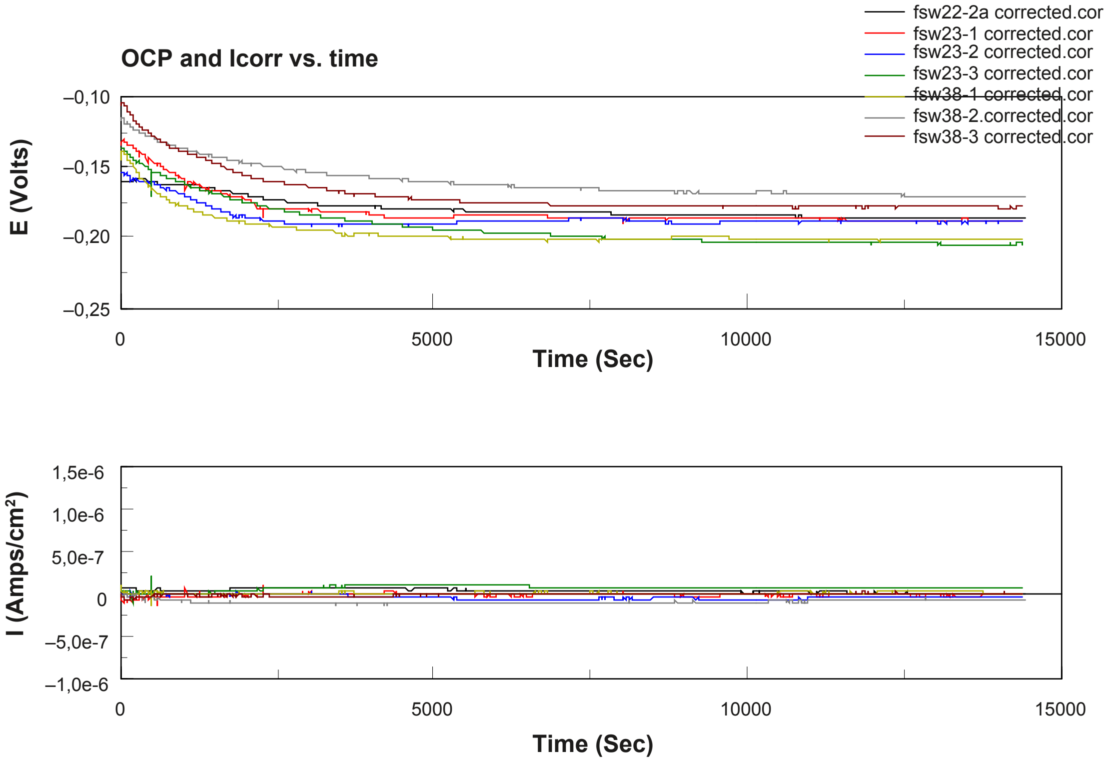

Figure 3-3. *Galvanic corrosion study summary of all FSW samples.*

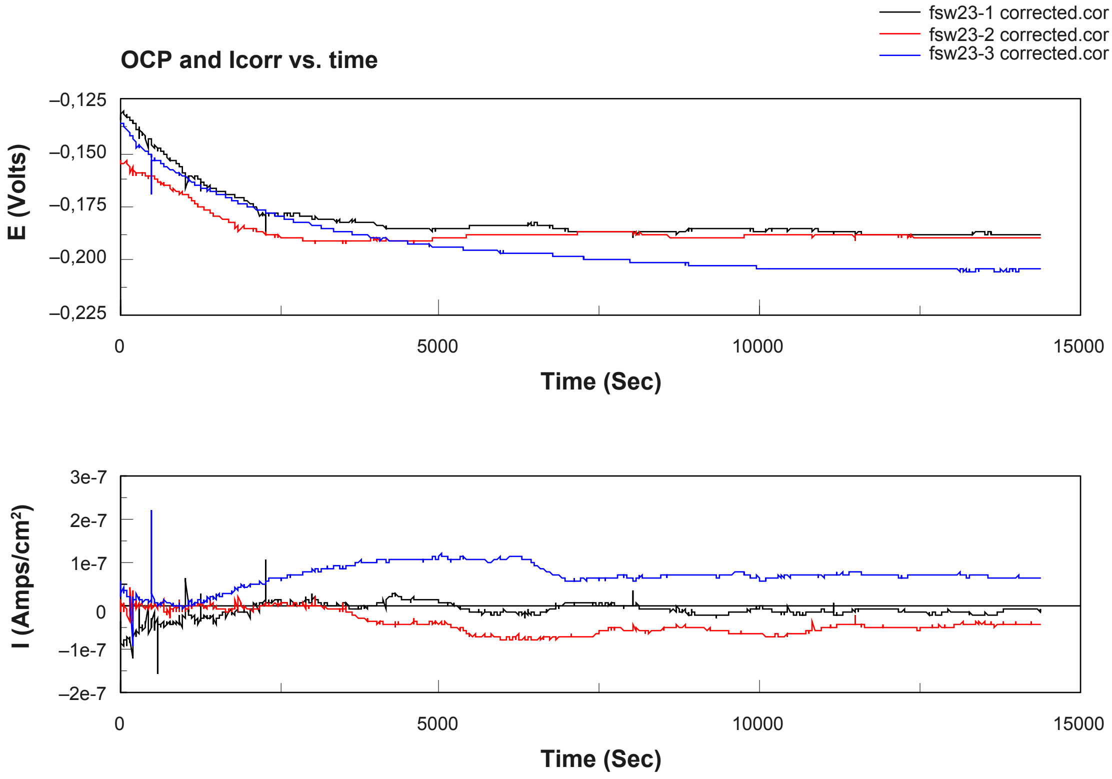

Figure 3-4. *Galvanic corrosion study results from FSW samples 23-1, 23-2 and 23-3.*

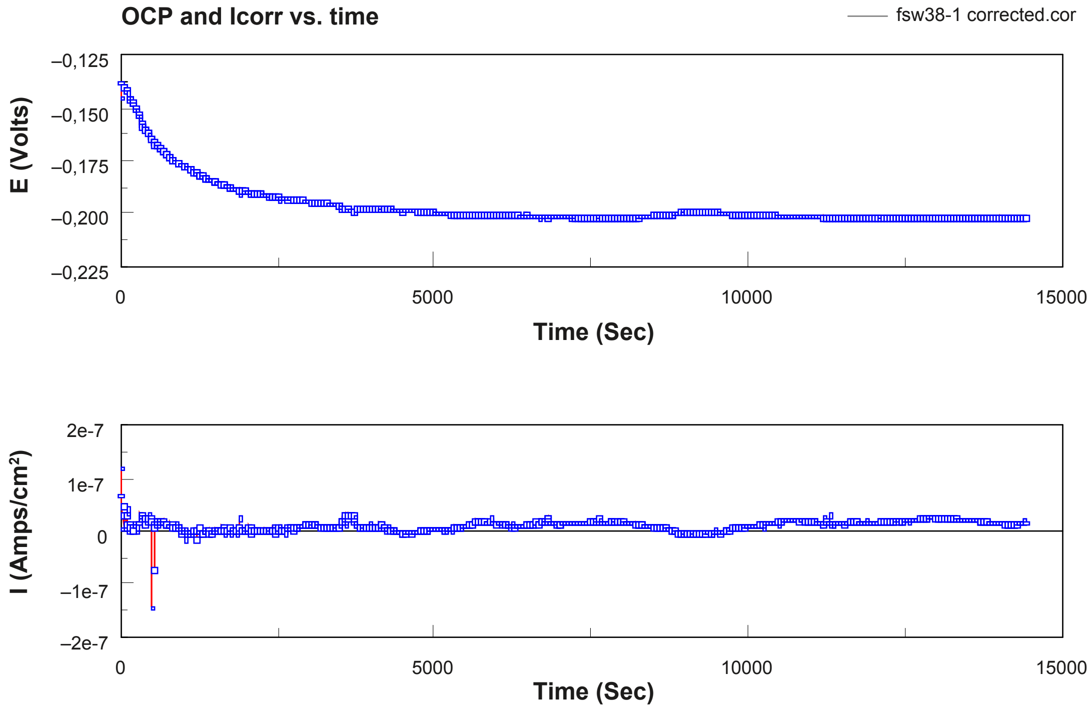

Figure 3-5. *Galvanic corrosion study of FSW sample 38-1.*

Table 3-1. Free corrosion potential measured at the end of the galvanic corrosion experiments (after electrically isolation).

OCP vs. SCE (mV)	FSWL 22-1	FSWL 22-2	FSWL 22-3	FSWL 23-1	FSWL 23-2	FSWL 23-3	FSLW 38-1	FSWL 38-2	FSWL 38-3	FSW mean	EBWL0 60
Lid	–186	–190	–162	–151	–175	–188	–143	–127	–180	–167 ± 22	–168
Tube	–175	–190	–158	–169	–173	–188	–140	–130	–168	–166 ± 20	–152
Weld	–177	–182	–159	–153	–177	–179	–136	–130	–163	–162 ± 19	–147

The observations made from the galvanic corrosion experiments could be confirmed by measuring the open circuit (free) corrosion potential (OCP) of the samples at the end of the experiment. For this purpose, all three sample parts (Lid, Weld and Tube material) where electrically isolated and the OCP measured. Looking at the mean values, the potentials are nearly identical.

The results of the galvanic corrosion studies (weld-base material) are not surprising, but confirm results from a previous study on initiation of grain boundary corrosion, where the FSW sample showed superior corrosion resistance compared to the EBW samples /Gubner et al. 2006/. Surface potential measurements performed in the study using Kelvin Probe measurements, indicated surface potential differences of 90–200 mV between the weld material and base material. In the present study, it could be demonstrated that the set up a corrosion cell with the weld material being a small anode and the base material a large cathode is most unlikely, despite the differences in potentials.

The thin oxide rich layer (up to 20 ppm copper oxide, /SKB 2005/) on the surface of FSW did not cause increased corrosion compared to EBW. Thus, if this layer has any negative influence of the corrosion behavior of FSW it is compensated by other factors, such as microstructure. Furthermore, this layer will be machined off during the final production steps and, therefore, will not be present on the final capsule.

3.2 Galvanic corrosion study between FSW tool and weld material

The report R-05-73 raised the question whether remains/contamination from the FSW tool might have an adverse effect on the corrosion properties of the FSW welds. Up to 20 ppm of nickel has been found in the weld material and it is thought that small shavings from the tool are embedded in the copper matrix. The tool is made from a precipitation-hardenable nickel-cobalt-chromium alloy (Nimonic 105, Table 3-2) with an addition of molybdenum for solid-solution strengthening. The relatively high aluminium content enhances both strength (through greater precipitation hardening) and oxidation resistance. The alloy has high creep-rupture properties at temperatures to about 950°C and is also used in gas turbines for blades, discs, and shafts.

In order to investigate, whether the FSW tool contamination of the copper has an influence, a similar experimental setup as for the galvanic corrosion measurements above was employed, but in this case the FSW tool materials and the material from FSW welds where electrically connected and the resulting corrosion currents measured using zero resistance ammetry.

Figure 3-6 show the results obtained in 0.5 M NaCl aerated solution, pH 6.2 at room temperature with a surface area ratio of tool-material to copper = 1 to 2. This solution was chosen because the high chloride content and pH are aggressive towards copper and stainless steels. As result, the corrosion current flowing between the tool and copper showed that the copper material was anodic compared to the tool material and, furthermore, the already at the beginning very low current flattened out and reached values close to 0 nA cm^{-2} at the end of the experiment. In conclusion, the tool material is not providing an active cathodic surface to stimulate copper corrosion. Since in reality, the surface area of the tool material (small metal fragments embedded in the copper matrix) will be very small in comparison to the copper matrix, a negative effect of such metal fragments upon the corrosion resistance of the FSW material can be excluded from future considerations.

Table 3-2. Composition (wt%) of FSW tool material (Nimonic 105).

Aluminum	Boron	Carbon	Chromium	Cobalt	Copper	Iron
4.5–4.9	0.003–0.01	0.12 max	14–15.7	18–22	0.2 max	1 max
Manganese	Molybdenum	Nickel	Silicon	Sulphur	Titanium	
1 max	4.5–5.5	Balance	1 max	0.01 max	0.9–1.5	

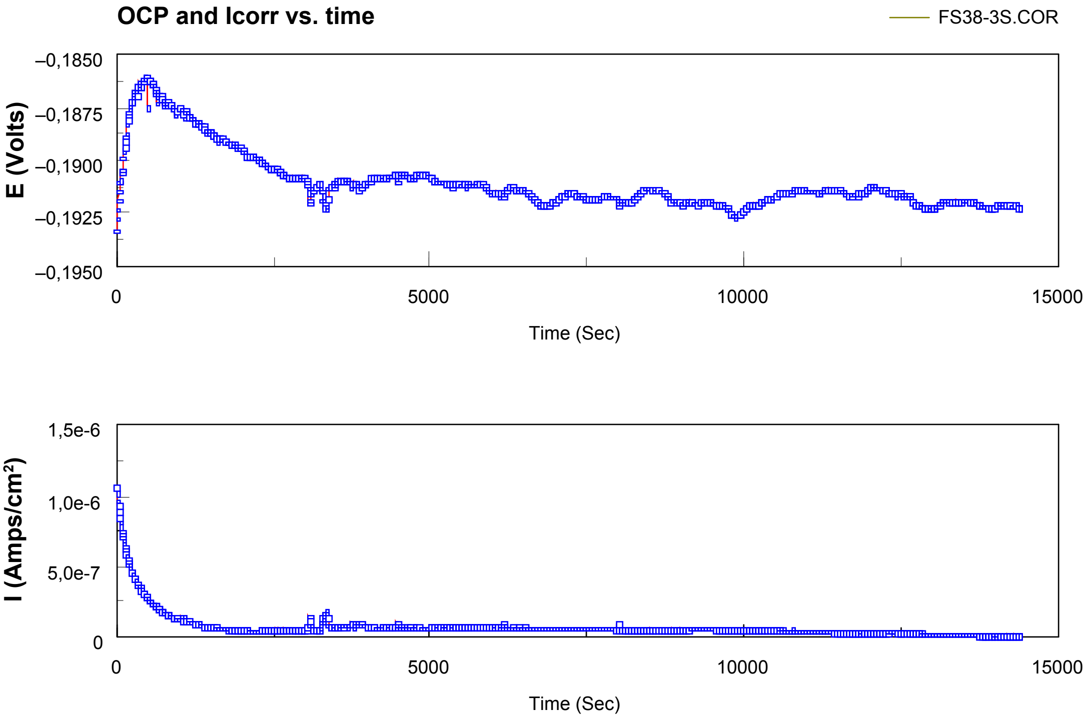

Figure 3-6. *Galvanic corrosion study between FSW tool and FSW weld material (FSWL38-3).*

3.3 Measurement of free corrosion potential and polarisation curves under aerated and de-aerated conditions

The results above can be graphically presented in form of a polarisation curves in Figure 3-7. Since copper is the main component, the free corrosion potential of the copper canister will be basically that of copper. At that potential, the FSW tool material is cathodically protected by the surrounding copper. Furthermore, the excellent corrosion properties of the FSW tool (Nimonic 105) result in very low corrosion currents even at higher potentials. Thus, electrical coupling of the FSW tool material to the copper does not result in the development of a galvanic corrosion cell.

The experiments above have been performed in aerated solutions, since the presence of oxygen is more problematic for copper corrosion than anoxic conditions. In order to verify that under anaerobic conditions the polarity between FSW tool and copper is not reversed, measurements of the free corrosion potential have been performed in a comparative study.

As a result, it could be demonstrated that free corrosion potential of the FSW tool is only changing minutely when the conditions are changed from aerobic to anaerobic. The effect is much more pronounced for the copper material. In conclusion, anaerobic conditions provide even less probability of initiating selective corrosion of impurities in the copper matrix originating from the FSW tool in form of small metal shavings.

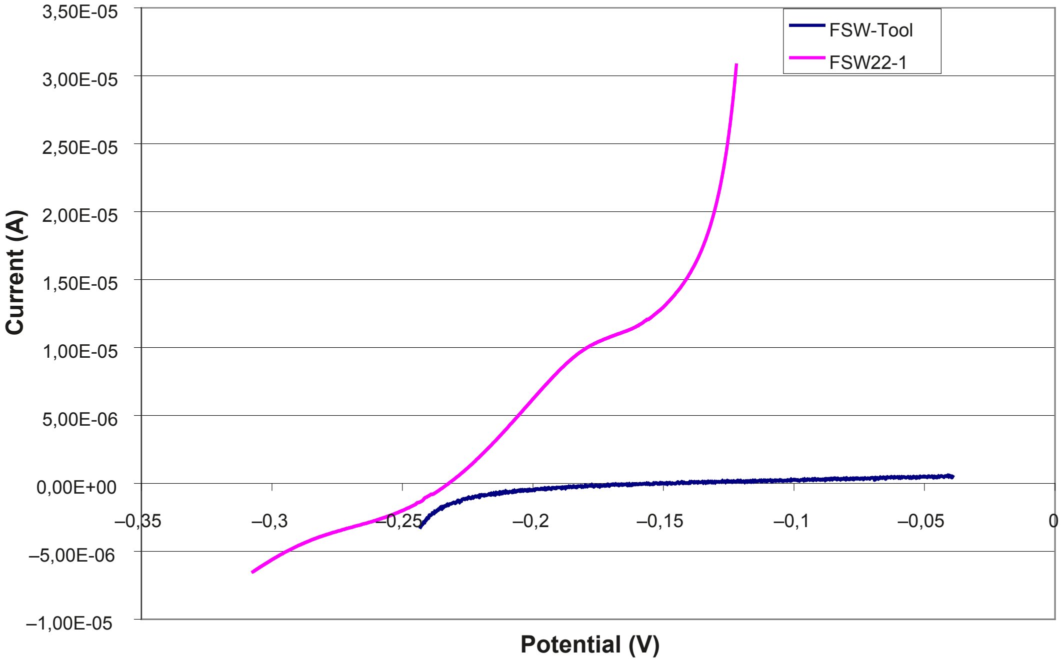

Figure 3-7. *Polarisation curves from FSW tool and weld material FSWL23-1 in aerated 0.5 m NaCl, pH 6.2.*

Table 3-3. Open circuit potential measurements in aerated and de-aerated 0.1 M NaCl solutions at 40°C.

OCP vs. SCE (mV) in c(NaCl) = 0.1 M				
	FSW tool	FSWL22-2	FSWL22-3	FSWL23-1
Aerated	–44	–140	–207	–149
De-aerated	–45	–267	–223	–258

4 Conclusions

- The galvanic currents measured between base and weld materials are generally very low (0.5 M NaCl, pH 6.2, aerated solution).
- The weld material of FSW is not anodic compared to base material.
- Differences measured are most probably due to surface conditions. These will diminish with build up of corrosion products.
- The FSW tool is cathodic compared to the FSW material – small particles in the weld are cathodic protected by surrounding copper, resulting in a very small cathode (FSW tool residues) compared to large copper anode.
- The good corrosion resistance of the FSW tool material will even further reduce the risk of corrosion of the surrounding weld material.
- Therefore, small metallic particles from FSW tool do not pose a risk for accelerated corrosion of the welds.
- A negative effect of copper oxides close to the surface could not be detected in this study.
- FSW is providing better corrosion resistance compared to EBW.

5 Recommendations

No further corrosion studies on the influence of the FSW tool on the corrosion resistance of FSW joining technique are necessary, unless the FSW tool material is changed. Concerns from previous studies (e.g. /Gubner et al. 2006/) could be eliminated and the open questions raised concerning corrosion stability of the FSW in R-05-73 are answered.

6 References

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