SKI Report 2004:56

Research

Whiskers and Localized Corrosion on Copper in Repository Environment

Hans-Peter Hermansson
Peter Gillén

March 2004

ISSN 1104–1374
ISRN SKI-R-04/56-SE

SKI perspective

Background

In the planned repository for spent nuclear fuel in Sweden according to the KBS-3 concept, a canister consisting of an outer copper shell and an cast iron insert plays a critical role in isolating the waste. The function of the copper shell is to provide the necessary corrosion resistance.

SKI has in earlier studies evaluated different forms of general and localised corrosion on copper, as a basis (among others) for its reviews of SKB's RD&D programmes and performance assessments. In these studies, it has been demonstrated that whiskers consisting of copper oxides and sulphides can grow on the surface of copper in sulphide containing water.

Purpose of the project

Corrosion of copper in the form of whisker growth would be more severe to the canister integrity if the corrosion is localized to the root of the whisker rather than affecting a larger area. The purpose of this project was to improve the understanding of the root behaviour of the whisker and thereby determine if the corrosion attack is of general or localized nature.

Results

A combination of optical methods was used to study the very fragile whiskers: video documentation during the whisker growth, and Laser Raman Spectroscopy and Raman video microscope examinations of the surface and whiskers. The results show that two different kinds of whiskers can be identified. One smaller diameter type, with a clear and distinct corrosion attack under the root, and one larger diameter type with a more spread attack (beneath the root as well as outside).

Effects on SKI work

The whisker growth on copper in sulphidic environment has been further investigated, and the nature of the whisker growth has been identified as, at least partly, localized attacks. The implications of this corrosion type on canister integrity are strongly dependant on the possibilities for the obviously very fragile whiskers to grow in the environment of a swelling bentonite.

SKI will use the results both in developing its own knowledge of corrosion processes and as a basis in its forthcoming reviews of SKB's programme.

Project information

Responsible for the project at SKI has been Christina Lilja.
SKI reference: 14.9-011033/02138

SKI Report 2004:56

Research

Whiskers and Localized Corrosion on Copper in Repository Environment

Hans-Peter Hermansson
Peter Gillén

Studsvik Nuclear AB
SE-611 82 Nyköping
Sweden

March 2004

Contents

Summary

Previous studies have demonstrated that whiskers (thread/hair shaped structures) can form on copper in a sulphide containing environment. A remaining important question is whether the attack on the copper metal surface beneath a whisker is of a localized or of a general nature. This issue has not been clarified as whiskers are very fragile and have always detached and fallen off from the surface at some stage of handling. It has therefore been very difficult to link the growth root of the whisker to underlying structures in the metal surface.

A study was therefore initiated to settle the important issue of the relation between whisker position and the type of underlying metal attack. The usage of a porous medium was originally planned to support the whiskers in order to keep them in place and by post examinations characterize the nature of the whisker roots and thus the type of attack on the metal. However, the early stages of the present experimental work clearly indicated that other ways of study were necessary. A photographic method for the registration and positioning of whisker growth was therefore developed. It proved to be a successful means to coordinate whisker position and to link it with the attack on the underlying metal.

Shortage of sulphide in previous experiments caused a retarded growth rate of whiskers. Therefore, in present experiments the sulphide concentration was kept at a more constant level throughout an experiment and a hindered whisker growth did not limit the attack on underlying metal.

Whiskers and substrates were observed with a video camera throughout an experiment and the phase composition was examined with Laser Raman Spectroscopy, LRS and the Raman video microscope. Post examinations were also performed using light optical microscopy.

By combining the results from the optical methods it has been possible to distinguish two kinds of whisker roots (small/large diameter) with the underlying metal surface. It has also been demonstrated that there is a localized attack on the metal surface beneath the whisker root. In the small diameter whisker case this attribution is quite clear, but it is less clear for the large diameter case.

The results could have an implication on the integrity of the copper lining of the waste canister and possible release of radionucleii to the repository environment. The seriousness of this assumption should be evaluated by a study of the ability of whiskers to grow on copper in a bentonite environment.

Sammanfattning

Tidigare studier har visat att whiskertillväxt (tråd/hår formiga strukturer) på koppar kan ske i sulfidhaltig miljö. En viktig fråga är om den underliggande attacken på kopparmetallen är av lokal eller allmän karaktär och kan hänföras direkt till whiskern eller ej. Denna fråga har inte kunnat klarläggas i tidigare undersökningar eftersom bildade whiskers är ytterst sköra och har alltid lossnat och fallit av från den korroderade ytan. Därför har det varit mycket svårt att länka whiskerns tillväxtrot med strukturer i den underliggande metallen.

En studie initierades därför för att avgöra den viktiga frågan om relationen mellan whiskerns växtplats och typen av attack på underliggande kopparmetall. Avsikten var att låta whiskers växa ut i ett poröst medium med efterföljande fixering. Därefter skulle olika metoder användas för att karakterisera sambandet mellan växtplats för whisker och typ av attack på metallen. Redan tidigt blev det klart att en sådan fixering inte lät sig göras med enkla medel på grund av whiskers skörhet och att någon annan metod måste användas. Därför utvecklades en i huvudsak fotografisk metod för att monitera whiskertillväxten och att koordinera växtplats med underliggande attack på metallen. Metoden skulle visa sig vara framgångsrik för sitt ändamål.

I tidigare experiment har sulfidtillgången varit begränsad, vilket lett till en avstannande sulfideringsreaktion och att whiskertillväxten så småningom upphört. I föreliggande verksamhet har därför experimenten utförts med någorlunda konstant sulfidhalt, så att hämningar i whiskertillväxten inte skulle begränsa angreppen på underliggande metall.

Whiskers och substrat observerades med en videokamera genom hela exponeringsförloppet och fassammansättningen analyserades med Laser Raman Spektroskopi, LRS. Ramanutrustningens videomikroskop användes också för morfologiska undersökningar. Efterundersökningar gjordes dessutom med ljusoptisk mikroskopi.

Genom att kombinera resultaten från de optiska metoderna har det varit möjligt att urskilja två typer (liten/stor diameter) av whiskerrötter och att länka dessa till lokal attack på underliggande metall. Kopplingen whisker/lokal attack är tydlig för whiskers med liten diameter men inte lika tydlig för whiskers med stor diameter.

Resultaten kan vara av betydelse för synen på kopparkapselns integritet och den därmed sammanhängande risken för avgivande av radionuklider till slutförvarsmiljö. Allvaret i denna förmodan bör utvärderas genom en studie av whiskertillväxt på koppar i bentonit.

Introduction

Previous studies concerning this work have been reported in [1-7]. In some of those works it has been demonstrated that whiskers (needle or thread shaped growth forms) can grow on copper in a sulphide environment. An important question could be raised if the observed attack on the copper surface is of a localized or a general nature, since a localized attack on the copper lining of the waste canister in the repository environment could jeopardize the integrity of the canister and cause a release of radionucleii to the environment. It has not been possible to clarify this issue before as formed whiskers normally are very fragile and have always detached and fallen off from the surface of the corroding copper sample at some stage of handling.

A study was therefore initiated to settle the important issue of the relation between whisker growth and type of underlying attack on the metal.

A porous medium was originally planned to be used to support the whiskers in order to keep them in place and by post examinations characterize the nature of the whisker roots and thus the type of attack on the metal. However, the early stages of the present experimental work clearly indicated that other ways of study were necessary because of the fragility of the whiskers.

A combination of several photographic methods (video, light and Raman) for the registration of whisker growth was therefore developed and proved to be a successful means to coordinate whisker root position and the type of attack on the underlying metal.

Experimental

Cylindrical copper samples of the kind used in previous work (OFC quality) were used also in this case. The pre-treatment and surface treatment of specimens was also the same [4, 5, 7]. As many as 12 samples were exposed at the same time in a specially design reaction vessel that allowed control of experimental parameters and video photography of samples with a web-camera. Several experiments were performed to develop the experimental technique. The results accounted here are mainly from the second experiment completed with some results from the first experiment.

An experimental development process was necessary in order to meet specific requirements emanating from previous results. In previous experiments the concentration of sulphide always declined as a function of time due to consumption [5, 7]. This process finally halted the reaction in those experiments. One objective in the present work was to maintain the concentration reasonably constant throughout an experiment in order not to halt the reaction. Copper samples were therefore exposed in a large volume vessel in addition to which the concentrations were kept reasonably constant by a feed and bleed system.

Another drawback in previous experiments was that corrosion attacks in the metal under the whiskers roots couldn’t be analyzed because information about the whisker location was lost. Therefore, if new experiments were to be successful, new techniques and equipment had to be used to keep track of whisker growth and location throughout an experiment. This turned out to be a very large problem due to the fragility of the whiskers and had to be solved partly by using unconventional methods.

Physical and chemical environment

As already mentioned, the concentrations in the reacting solution were kept reasonably constant by exposing the copper samples in a large volume vessel in which a feed and bleed system also was active. The volume was 25 dm^3. The feed and bleed flow to the vessel was ≈ 2 ml/min and the system was kept at ambient pressure and temperature.

The solution composition accounted for in Table 1 was used based on experience from previous whisker growth experiments [5, 7].

Table 1
Solution concentration

Compound	**[Compound] ppm**	**Cation**	**[Cation] ppm**	**Anion**	**[Anion] ppm**
NaCl	100	Na^+	40	Cl^-	60
$CaCl_2$	30	Ca^{2+}	10.8	Cl^-	19.2
Na_2SO_4	2.5	Na^+	0.8	SO_4^{2-}	1.7
$MgCl_2 * 6H_2O$	7	Mg^{2+}	0.8	Cl^-	2.4
$Na_2S^{(*1)}$	100	Na^+	59	S^{2-}	41

$^{(*1)}$ Na_2S as Na_2S*8H_2O

Experimental equipment

Several pre-tests were performed in order to develop a method to determine the firm location of whiskers and their roots. The work also involved methods to conserve whiskers to their place of growth. All of this proved to be a very difficult task due to the fragility of whiskers. The work resulted in an experimental set-up in which corrosion rate and solution potential could be recorded simultaneously with a real-time video-camera observation of the samples. The video-camera recordings were later combined with post experimental investigations with optical microscopy and LRS (Raman spectroscopy and Raman video-microscopy) to locate the whisker roots and to study the under-lying metal. The equipment used in an experiment is accounted in the following list. All material that is in contact with the sulphide solution is made of resistant plastic, rubber and copper. The experiments were performed in a plastic feed and bleed flow vessel kept in a fume hood as shown in Figure 1. Due to the light sensitivity of some copper sulphides, the fume hood was kept dark during an experiment except at periods of photography.

Equipment list:

- A big transparent plastic feed and bleed flow reactor/vessel charged with 12 Cu samples, 1 reference electrode and 1 corrosion monitor entrance for on-line monitoring of the corrosion rate.
- A high-resolution web-camera with ability to take pictures and record videos.
- Turned and grinded Cu-cylinders of OFC quality.
- An Agilent 34970A data logger for measurement of 13 potential channels, 1 current channel (corrosion monitor data) and 3 voltage channels (corrosion monitor data).
- Corrosion monitor: constant current supply device, measure device for 1 current and 3 voltages (Agilent 34970A).
- Corrosion monitor equipment in the reactor: One Cu wire consisting of 2 U:s, (3 U:s in experiment 2). One U is isolated from the solution (used for temperature correction at resistance calculation) and the other is in contact with the aggressive solution. The voltage drop is measured over each U.
- A prominent pump for dosage of the feed solution
- A PC for measurement administration using the software “labview” for measurement of potentials, corrosion monitor data, camera control and filing of comments.
- A digital relay for triggering of pictures, turn on and off of the corrosion monitor current and for photo flash control from the software program.
- A big storage vessel for the reacting solution.

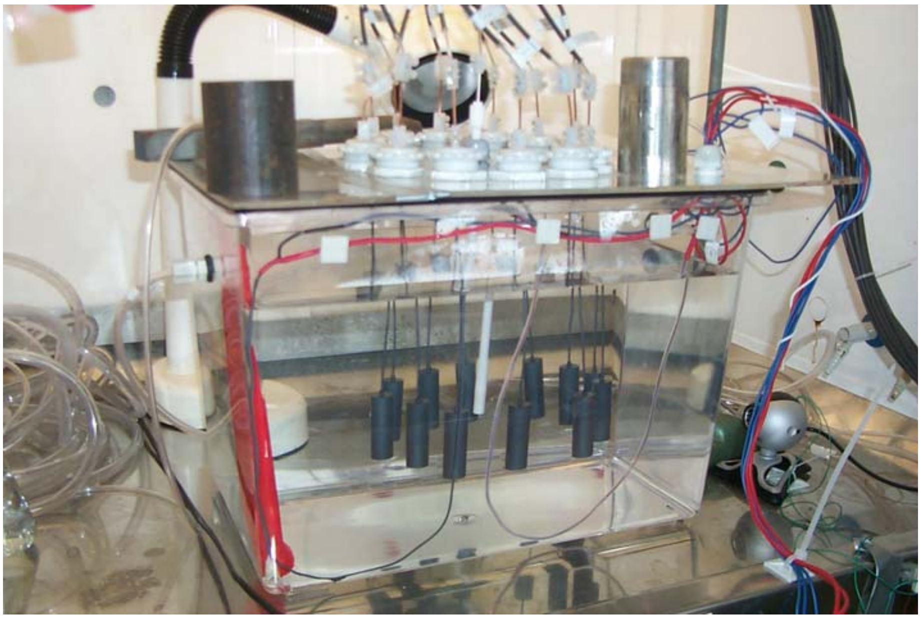

Figure 1
Picture showing the plastic reactor vessel with 12 Cu samples, the web-camera, electrodes and the corrosion monitor (U-bent wires).

The control and recording environment is shown in Figure 2. The PC with software environment, the control and measurement system, solution storage vessel, dosage pump, etc. can be seen in the figure.

Figure 2
Control and recording environment.

Potential measurement

The individual potential of each corroding copper sample was recorded in relation to a Ag/AgCl reference electrode. The recorded potentials were then recalculated to SHE-values, which are those accounted in this report.

Corrosion rate measurement

In order to be able to monitor the average corrosion rate, a DC corrosion monitor was built. A DC corrosion monitor consists of a long wire in which half the wire (U-bent) is shielded from the environment but is exposed to the solution temperature. The other part (also U-bent) is in contact with the solution. A constant current is driven through the wire and the voltage is measured over the two wire parts and this gives information on the average thickness of the cu-wires.

The following equations are used calculating the average corrosion rate:

$$R = \frac{\rho \bullet L}{A}$$

$$\rho(material_{\text{coefficient}}, temperature)$$
$$\text{R} = \text{resistance}$$
$$\text{L} = \text{the length of the wire material}$$
$$\text{A} = \text{cross section area of the wire}$$

$$\text{T}_{\text{isolated wire}} = \text{T}_{\text{unisolated wire}}$$
$$\text{Material}_{\text{isolated wire}} = \text{Material}_{\text{unisolated wire}}$$
$$\Downarrow$$
$$\rho_{isolated} = \rho_{unisolated}$$

$$\text{U} = \text{R} \bullet \text{I}$$
$$I = \text{constant}$$
$$\frac{\text{U}_{\text{unisoltaed}}}{\text{U}_{\text{isolated wire}}} \Rightarrow \text{Average crosssection area loss speed} \Rightarrow \text{Average corrosion speed}$$

Optical registrations

An automatic on-line video picture recording system, using a high resolution web-camera, was developed and used throughout the experimental work. Both single pictures and video-movies were recorded during the experiments. Recordings were made from the outside of the reactor tank, normally at a rate of about 1 picture/h. The recorded pictures are all date and time tagged (yy mm dd hh mm ss) which makes it possible to monitor the samples in detail as a function of time.

The picture collections have turned out to be very useful to follow the surface change of the corroding samples in correlation with potential and corrosion rate changes and also to se and locate where different types of whiskers (two types observed) are growing.

Ordinary light microscopy was also performed as one of the post examinations. The light microscopy pictures and the videos recorded with the web-camera system made it possible to tell where the whiskers have been located and thus to find the whisker roots.

Raman spectroscopy

As in previous work, Raman spectroscopy, LRS, was used to combine video optical observation in the Raman video microscope and in-situ chemical phase analysis of corroded samples. This technique has been described earlier [7].

Experimental performance

The samples were cleaned in ethanol and high purity water before insertion into the reactor vessel. The reactor was filled with the solution and the Cu-cylinder surface started to react instantly. See Figure 3 for the changes of sample appearance at different exposure times in the second experiment.

As already mentioned a large effort was made to conserve whiskers and to locate whisker roots in order to investigate the corrosion attack on the under-laying metal. This means that samples were taken out of the rector at different times and fresh samples were introduced again. The idea was to achieve information about the whisker growth. However, it was very hard to conserve whiskers on the samples with these methods. The reason is that whiskers are very, very fragile. A lot of different sampling techniques were tried, as:

1. Carefully removing the sample through openings in the top lid of the reactor vessel. See Figure 1.
2. Embedment of samples in plastic at a process of under-water casting.
3. Careful drainage of the rector vessel and drying of samples in the emptied reactor vessel.

The third method was used to take out samples that were post examined in detail.

The removed samples as a function of exposure time give a lot of information about the morphology and phases on the sample surface, which seems to be depending on time and potential. These results coincide very much with results from previous investigations [5, 7].

Two full scale experiments were run for more that 400 hours each. At all times the samples and the system were also monitored using the video optical system, the potential measurement and the corrosion monitor. The first experiment was run mostly to develop experimental technique. Most samples that were post examined in detail were taken from the second experiment.

Results

Observations during an experiment

Data from experiment 2 were selected for the following account. The results from the first experiment became complicated as it involved many changes in order to develop the experimental technique.

An example of a series of pictures taken with the web-camera on sample 1 in experiment 2 is shown in Figure 3. The series show the development of the surface morphology clearly demonstrating that a set of different stages occur. The reaction starts on a metallic copper surface that rapidly turns grey. Already after a couple of days dark grey areas are developing and forms axial stripes on the surface. After about 10 days this morphology has taken over the surface almost completely and the solution has at the same time turned light green.

At about 260 hours whiskers start to grow, especially on the bottom surface of the cylinder. Whiskers stay in place until the solution is drained at which time they disconnect and fall to the bottom of the reactor vessel. The whiskers exist on the sample during approximately 170 hours.

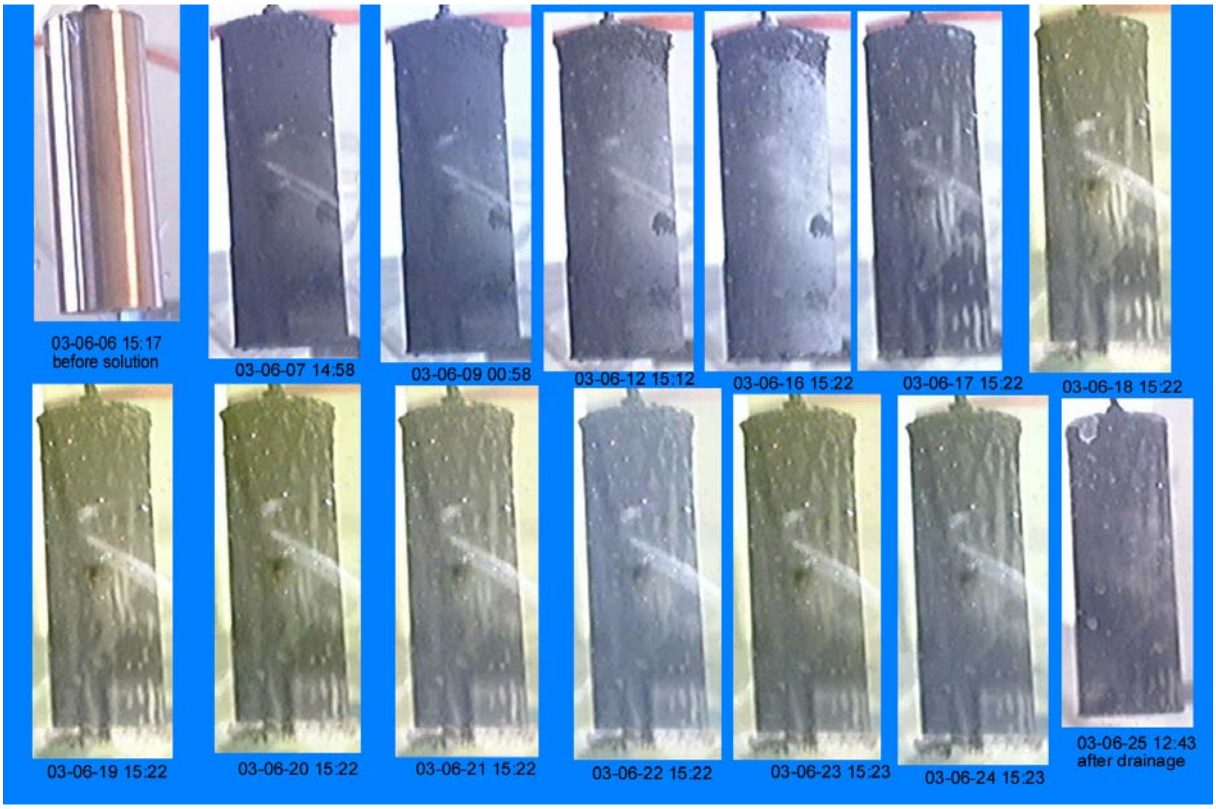

Figure 3
Automatically taken pictures (web camera) on copper sample 1 during experiment 2.

Pictures like those found in Figure 3 can be used to identify whiskers and whisker positions on the bottom of the sample.

In the beginning of the experiment the potential (SHE) was very low, about -700 mV for all samples. After about 9 days, around June 16 and 17, the copper surface started to change from a light grey smooth surface colour to a dark grey, striped “tiger pattern”. Slightly later, after about 10 days, the potential increased rapidly and at the same time whiskers started to grow. See Figure 4 for potential data and Figure 5 for corrosion monitor data. The dates given in the figures are of course the same and constitute the same time axis in all figures. On June 17 (12:30, after the increase in potential) two fresh, unexposed Cu-cylinders were inserted into the reactor. From June 18 and onwards the solution started to become more and more of a greenish colour.

During the introductory part of the experiment, the potential is low and there are no whiskers to be seen. At the same time, the corrosion monitor data show a constant rate of average cross section area decrease of the corroding copper wire of the corrosion monitor.

The average corrosion rate as indicated by the corrosion monitor decreased a couple of days after the start of whisker growth. It was also observed that the main surface didn’t change very much after June 19.

By studying the images from June 19 and forwards, showing the bottom location of the copper cylinder, a couple of phenomena can be seen. First there seems to be two kinds of whiskers. One type is relatively long and thick in an irregular way. The other type is formed like thin strains of hair. Furthermore the number of large whiskers is constant but they become thicker with time. The quantity of the small whiskers increases with time.

The observations thus indicate that an even overall corrosion seems to occur in the first part of the experiment. This is supported by the image data, which shows that there is a homogeneous growth during the first part of the experiment. During change of morphology the general attack seems to decrease as the registered corrosion rate decreases considerably. However, after June 19 it seems as if a supposed local corrosion attack instead increases as the whisker growth is optically observed to increase. This is happening despite the general decrease of simultaneously registered corrosion rate.

The reactor vessel was drained on June 24 (16:16). A surfactant was added at the drainage in order to decrease the surface tension of the solution and thereby try to keep the whiskers in place. It had previously been observed in experiment 1 that the whiskers fell off as the surface tension force pulled them down at drainage.

Despite all steps of care, whiskers were detached at drainage also in experiment 2.

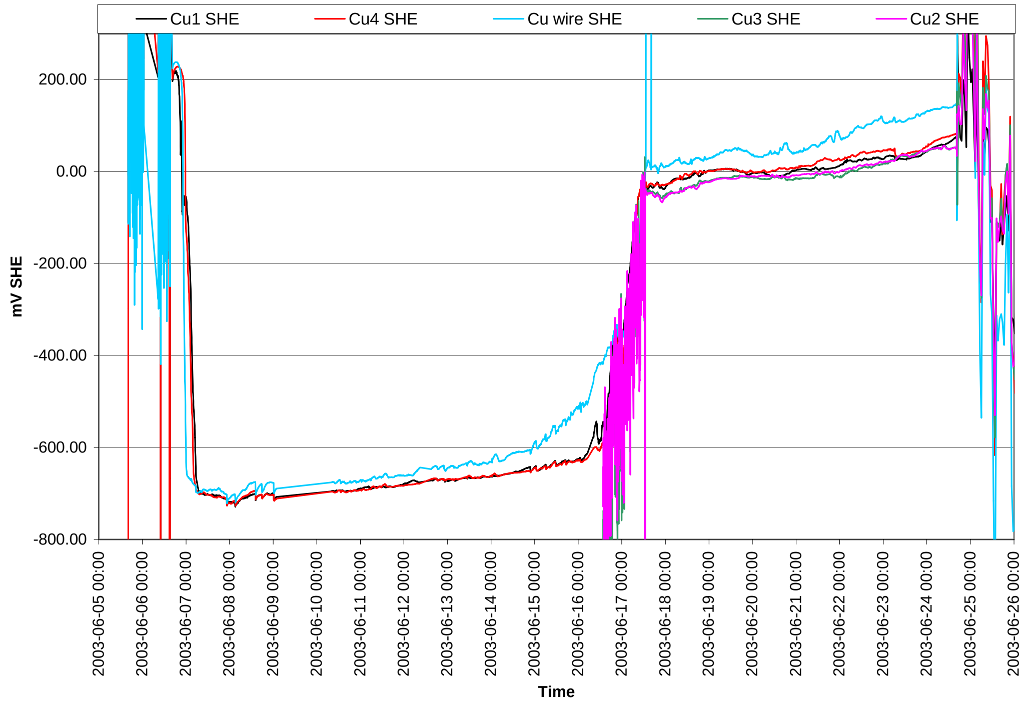

Figure 4
The potential (SHE) as a function of time during experiment 2.

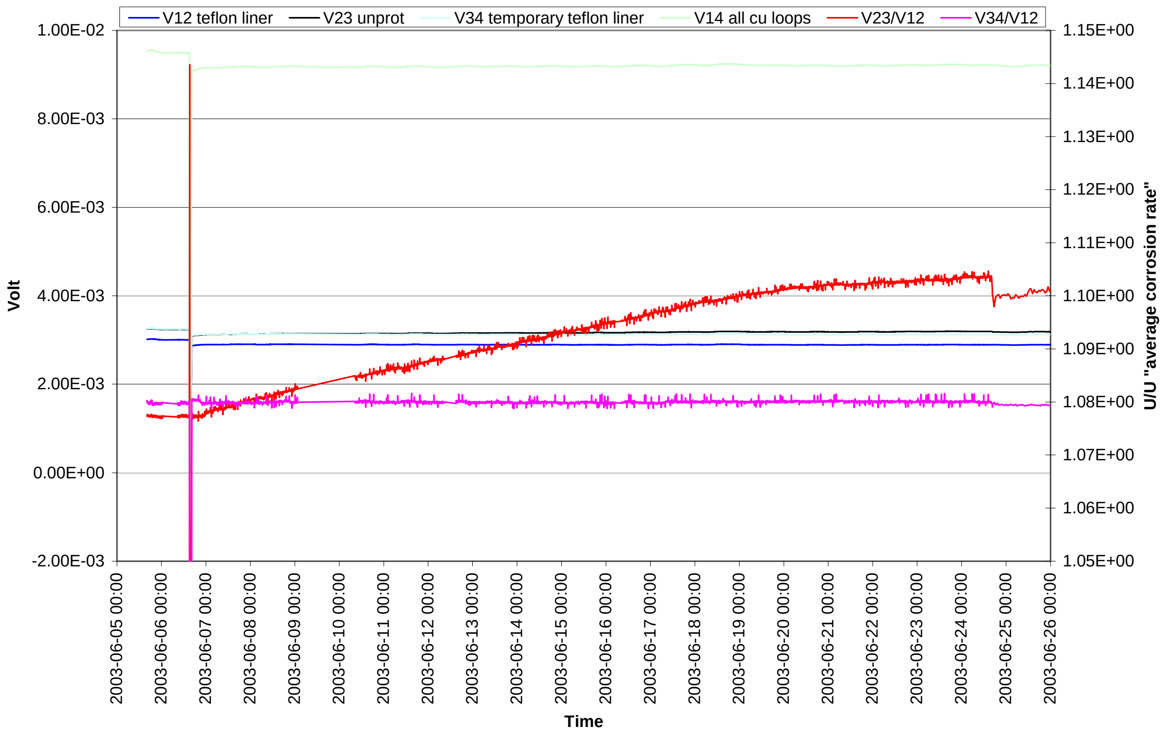

Figure 5
Corrosion rates as indicated by the corrosion monitor during experiment 2.

Post examinations with light optical microscopy

Post examinations were performed using light microscopy and laser Raman spectroscopy in combination with Raman video microscopy. The latter combine spectroscopy and the possibility of video optical observations in the same instrument.

Despite a couple of whiskers were actually fixed on the cylinder surface, it turned out to be a nearly impossible task to securely conserve whiskers on their spots of growth. It was therefore necessary to develop other techniques to correlate growth positions of whiskers with their remaining roots and the underlying metal. The objectives of all post investigations were therefore to combine video information (web camera recordings) from the experiment with post examination results from light microscopy and LRS. This combination yields the positioning of whisker roots and thereby a possibility to determine the type of corrosion attack on the underlying metal. Mostly, the bottom areas of samples were used for this study.

Optical stereo-microscopy

Mainly samples 1 and 4 from the second experiment were used for this study. The following steps were used to localize and examine whisker roots and the underlying metal corrosion on such samples.

1 Localizing and carefully positioning the existing whiskers growing at the bottom of sample 4. Web camera and other optical information and measurements were used.
2 Photographing the position marked bottom of sample 4 using an optical stereo microscope.
3 Photograph the position marked bottom of the other full time exposed sample (sample 1) using an optical stereo microscope. The morphological development of sample 1 is shown in Figure 3.
4 Develop a careful corrosion film removal technique.
5 Pre-test and training of the removal and documentation technique of the corrosion film from the bottom of a sample. In this process a couple of other samples were used.
6 Compare the photographs of corrosion films with observed local corrosion attacks.
7 Perform the same removing procedure on the in-situ photographed samples (1 and 4) and compare the local attack positioning with the in-situ images and thereby correlating the corrosion film morphology (whisker roots, etc) with the type of attacks on the underlying metal.

Optical microscopy of sample 4

Figure 6 shows a picture of sample 4 taken in the optical stereo microscope. A grid system is superimposed on the picture in order to give coordinates for observed details. This is the untouched bottom surface of the sample after drainage and drying.

Whisker roots and remains of whiskers can be observed in Figure 6. First of all a couple of hair-like whiskers (with a small diameter) are still remaining in the upper area of the picture. The diameter of those whiskers is of the same order of magnitude (~ 100 µm) as diameters observed for “small diameter” whisker roots (e.g. in Figure 15). They have their roots positioned in a direction of about 350º at about 70-80 % out on the radius all seen from the very centre of the circular surface. This positioning is also verified by web-camera observations. The whiskers can be correlated with distinct roots and actually ends in an area in which many small diameter whiskers have grown.

The large diameter type of whiskers has grown around the outermost rim of the surface. They are correlated with the same type of axially oriented dark-grey ribs of the “tiger pattern” observed in Figure 3 concerning sample 1. All of those larger whiskers were detached at the drainage process. Nevertheless, their locations have been determined by comparing web-camera recordings with the type of pictures shown in Figure 6.

The roots of larger whiskers are undoubtedly the light grey small half circular/oval patches appearing at the outer rim of the circular bottom surface, especially clearly seen in Figures 7 and 8.

Several different gentle techniques of removing corrosion products without destroying the underlying metal surface were used on sample 4. In the first step of removing corrosion products a soft air flushing was used. The result of this treatment can be seen in Figure 7.

At comparison of differently coloured (light/dark grey) areas in Figures 6 and 7 confirm that the light grey areas seen around the rim of Figure 7 are root areas of the larger type of whiskers as already determined by the other optical method (video observations). The deeply dark-grey areas of Figure 7 (especially the area between 320º and 360º at about 70-80% of radius and the one at 200º-220º at about 90 % of radius) are root areas of small diameter whiskers. This has as also already been observed and confirmed via the video optical method.

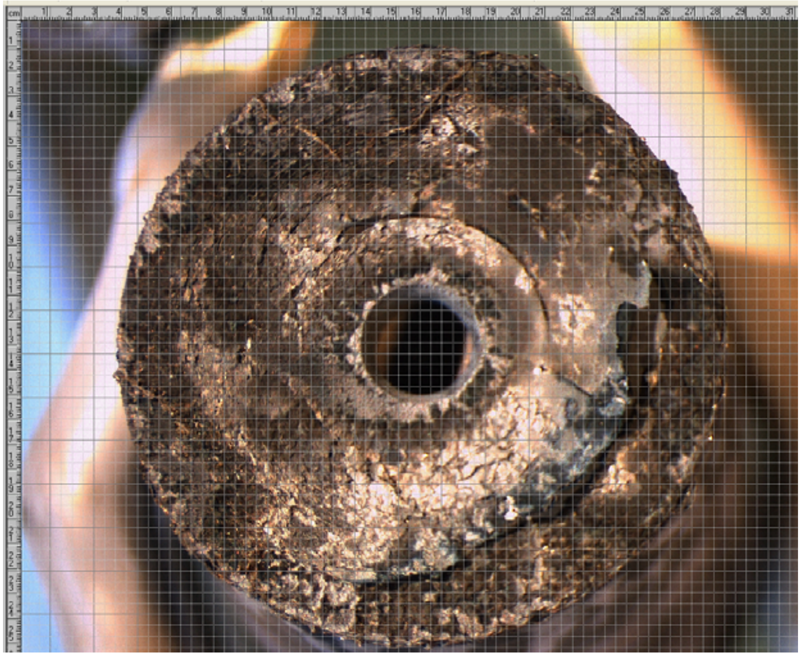

Figure 6
The bottom circular surface of sample 4. A grid system is superimposed for easy positioning of details. The diameter is 20 mm.

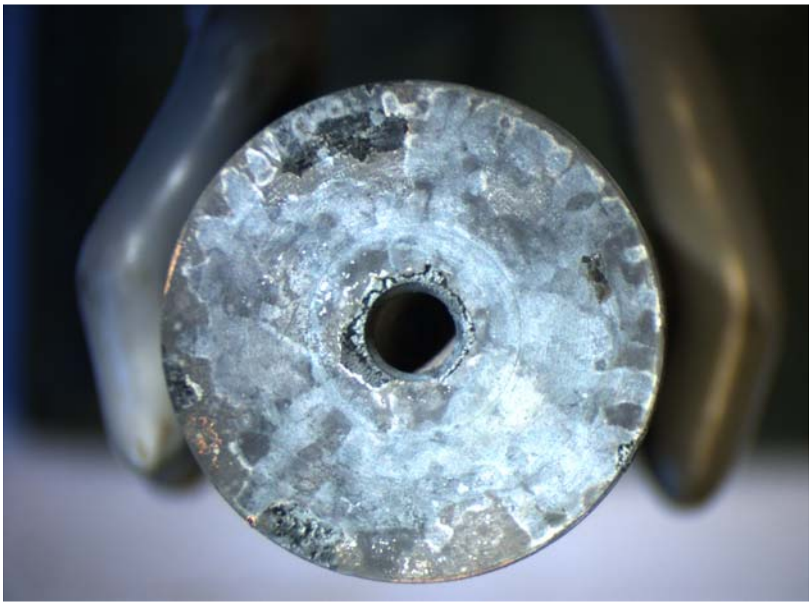

Figure 7
Result of soft air flushing on the bottom surface of sample 4. The diameter is 20 mm.

A lot of material was remaining after soft air flushing. Therefore, after registration of roots, the bottom of the sample was again blown with high-pressure air and then flushed with high-pressure water. See Figure 8. The same general pattern as in Figure 7 still remains but more material has been taken away and metallic (red) copper is seen in some places.

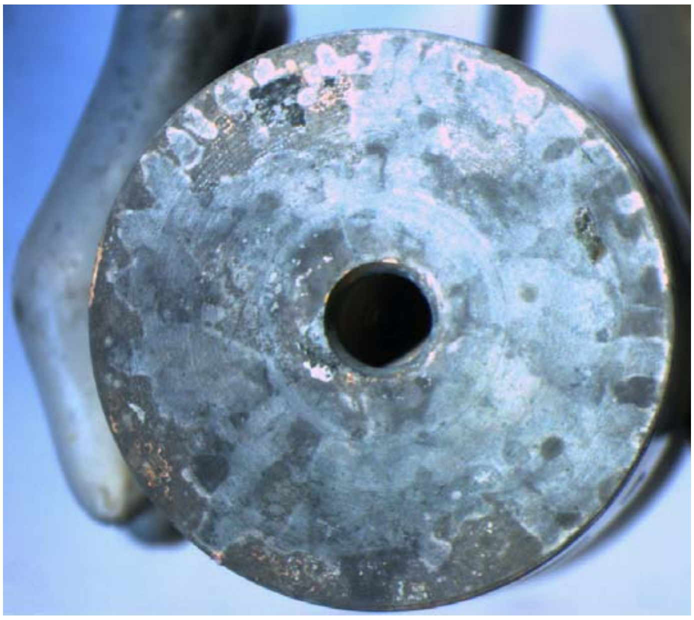

Figure 8
The bottom surface of sample 4, soft air flushed, high-pressure air flushed and high-pressure water flushed. The diameter is 20 mm.

As there was still some corrosion film left on the surface after this treatment, another step was employed by softly brushing the surface with a soft toothbrush under a water stream. See Figure 9.

Figure 9
The bottom surface of sample 4, soft air flushed, high pressure air flushed, high pressure water flushed, and softly brushed. The diameter is 20 mm.

All heavier corrosion films were thereby removed from the surface. The root areas of the two different kinds of whiskers are now clearly identified and signs of localized attacks are observed in areas previously observed to be covered with small diameter whiskers. The sample was used in this condition for the following LRS investigations.

Optical microscopy of sample 1

The original bottom area of sample 1 is shown in Figure 10. In Figure 11 the condition after soft brushing and air flushing is shown.

Figure 10
Untreated bottom surface after drainage and drying of sample 1.

Figure 11
Soft brushed and air flushed bottom surface of sample 1.

The same technique as for sample 4 was used to remove the corrosion products from sample 1. After still some treatment with a soft brush under streaming water, sample 1 was ready for LRS-investigations as accounted below. Also in this case different areas of roots were predetermined with similar results and verifications as for sample 4.

Whiskers and corrosion attack

Positioning

As previously described the correlation of whisker roots with attacks on the underlying metal involved a chain of careful observations and optical measurements using the web-camera for in-situ observations in combination with light optical microscopy as well as the recording of raman spectra and raman video pictures. The track-keeping started by positioning of whiskers in-situ in the reaction vessel by using the web-camera. Thereafter pictures were taken at every step of preparation as well as at post examinations in the Raman instrument. A superimposed grid-system of the type shown in Figure 6 was also used to keep track of whisker positions and the final position on the naked underlying metal. The technique turned out to work well for its purpose of correlating whisker root positions with underlying metal areas.

As already pointed out the bottom areas of samples 1 and 4 from the second experiment were used for the investigation of the relation between whisker position and corrosion attack.

The bottom surface of sample 1

The sample was used after described pre-treatment and had the look as shown in Figure 11. Raman spectra recorded from many points on this surface all show the simultaneous presence of Cu_2O and CuO closest to the metal surface. In many cases there seem to be a higher relative concentration of Cu_2O compared with CuO, which is quite natural at depths close to the metal surface. It should be noted that all lose material as whiskers and flakes, containing sulphide had already been removed by flushing and brushing from the investigated surface.

Whiskers found on the bottom surface of the sample normally remained there until the shut down and drainage of the experiment. Whiskers were also observed growing on the cylindrical surface of the sample. However, because of their fragility, all whiskers on cylindrical surfaces broke and fell to the bottom of the reaction vessel under their own weight at some time during the experiment and did not last till shut down and drainage. This is the main reason why only bottom areas were investigated as whiskers growing there could be tracked throughout the full experiment time.

The approximate positions of LRS sampling on the bottom of this sample are shown in Figure 12. The drawing is to be compared with details in the photograph of Figure 11 to be fully understood.

Different areas of interest have been marked in the figure and reference is given to these areas in the following description of results.

Numerous observations were made of which some examples are accounted in the following. Some examples are given on the surface morphology as recorded in the Raman microscope of some of the different areas indicated in Figure 12. A couple of examples are also given of Raman spectra recorded in the different areas. The Raman spectra all looked very similar and only selected examples are accounted here.

In Figure 13 a Raman microscope picture is shown from the middle of the grey area 1 as shown in Figure 12.

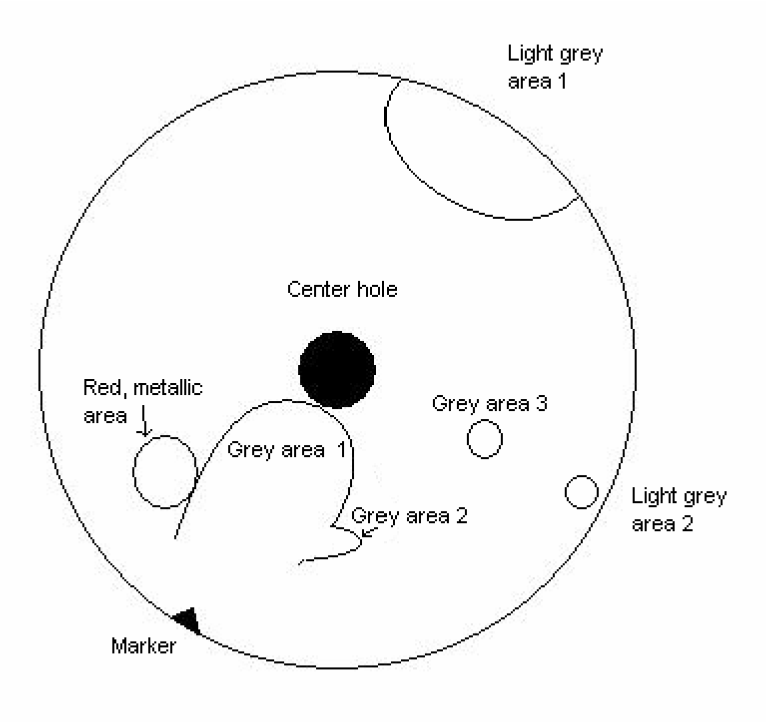

Figure 12
Approximate positions of LRS sampling. See also the photograph in Figure 11.

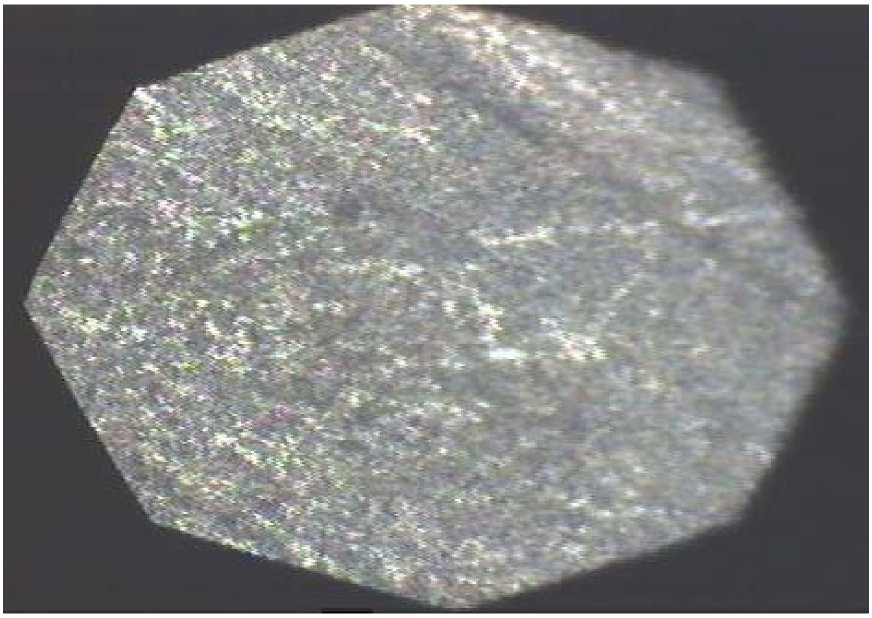

Figure 13
Raman picture taken in the middle of the grey area 1 as shown in Figure 12. The picture height is 300 µm.

The corresponding Raman spectrum is shown in Figure 14. The Raman spectrum shows that the phase present is almost exclusively CuO.

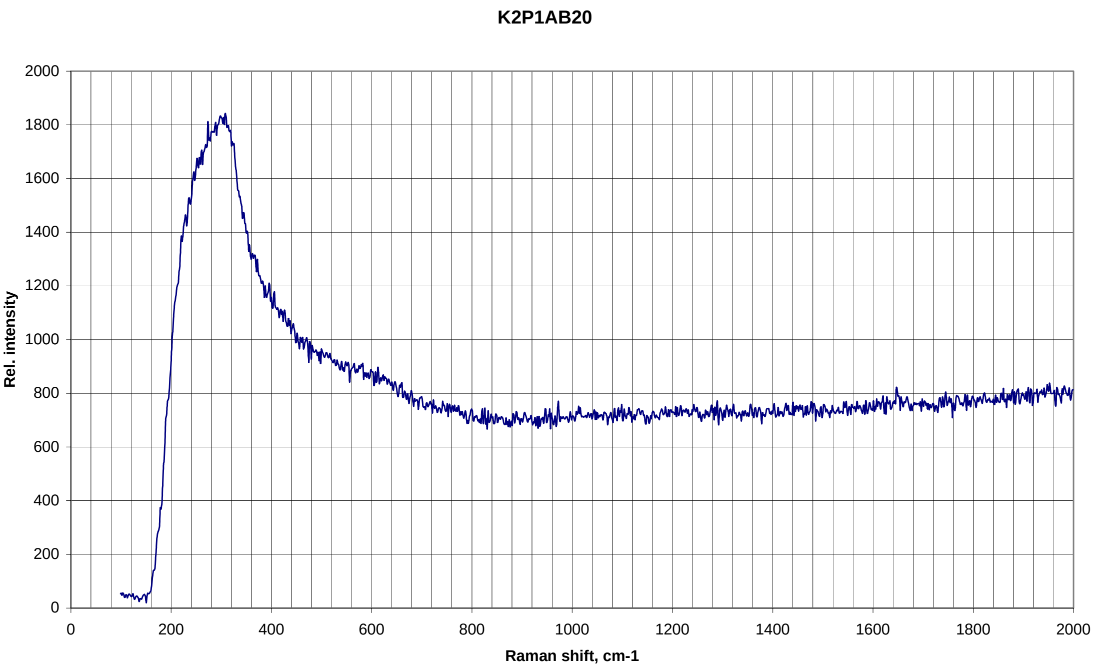

Figure 14
Raman spectrum taken in the middle of grey area 1 as shown in Figure 13.

Figure 15 shows the metal-red area marked in Figure 12. Small diameter, thread formed whiskers were observed in this area and the round formations seen in Figure 15 are the whisker roots as determined by the described optical registration technique.

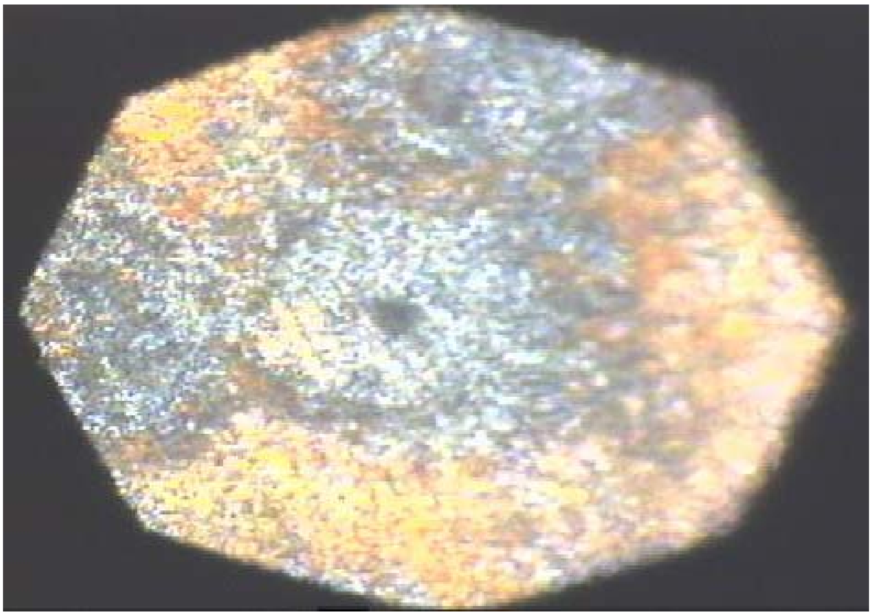

Figure 15
Raman picture taken in the middle of metal red area as shown in Figure 12. The picture height is 300 µm.

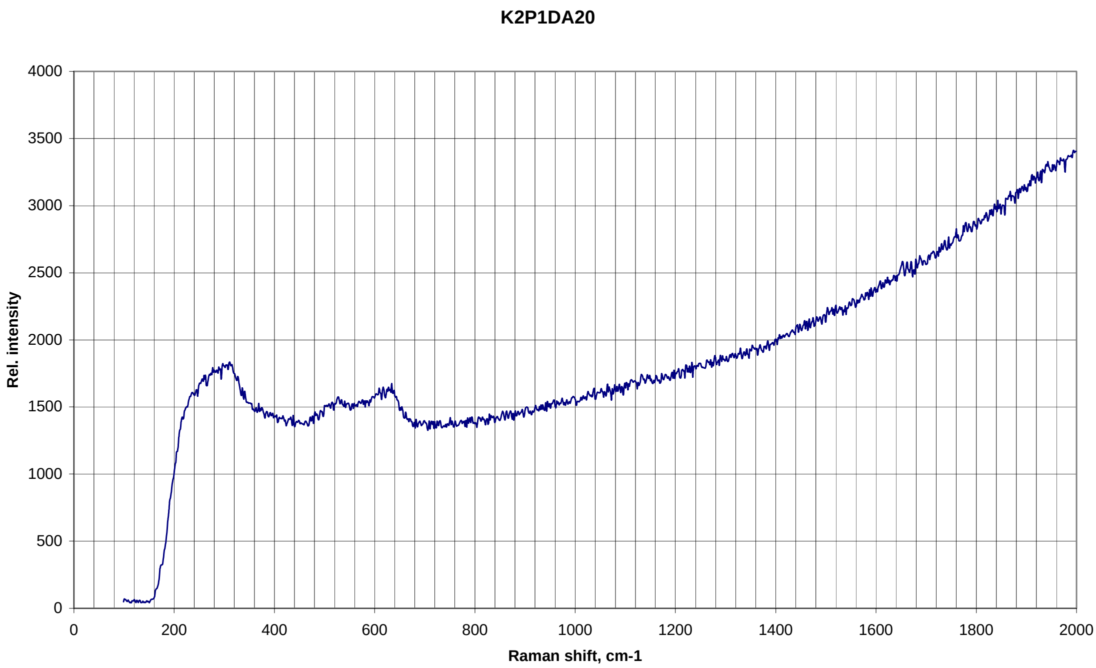

Figure 16
Raman spectrum taken in the middle of root shown in Figure 15.

The red area is a centre for small diameter whiskers and the circular formations shown in Figure 15 are roots of such whiskers. Raman spectra taken in different positions of the root in the centre of Figure 15 show that both CuO and Cu_2O are present in the root formation. An example of a spectrum is shown in Figure 16.

In Figure 17 a Raman picture is shown from the light grey area 1 as seen in Figure 12. In this area the larger diameter type of whiskers were growing. Those whiskers left roots of another kind than the small diameter whiskers. The root area of the large diameter whisker consists of a homogeneous surface film that is light gray with surrounding dark grey areas. Compare patterns and colors in Figures 11 and 12. There are no circular structures to be seen as in the previous case for small diameter whiskers and the root surfaces are much larger.

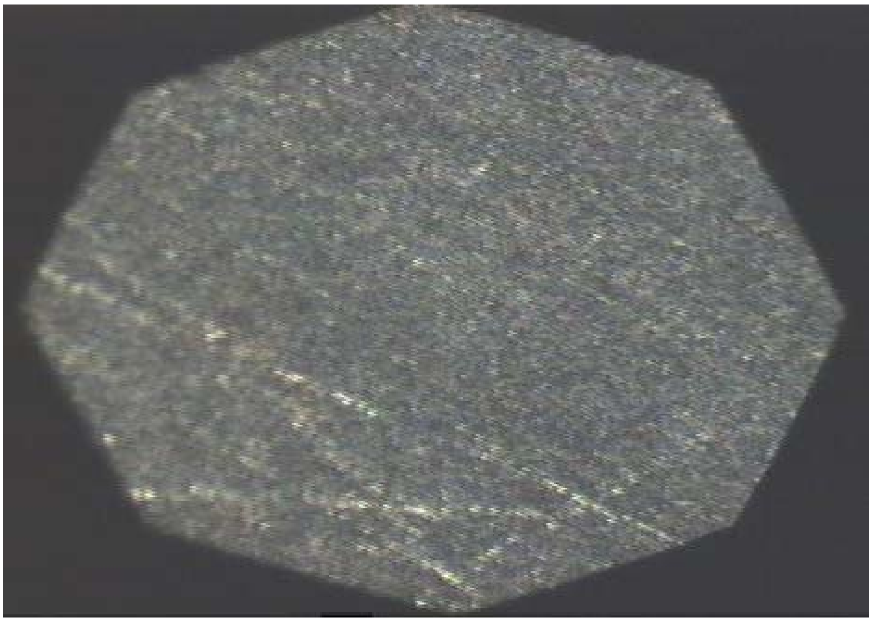

Figure 17
Raman picture taken in the middle of light grey area 1 as shown in Figure 12. The picture height is 300 µm.

The Raman spectrum from this area shows that the light grey surface film mostly consists of CuO. However, there is also a simultaneous presence of Cu_2O.

Pictures and spectra were also recorded in the areas marked as grey area 2 and 3 in Figure 12. The morphology and phase composition of these areas are similar as for the light grey area 1 and are not further accounted here.

It should be noted that the darker areas that appeared in between the light grey areas had a similar morphology and phase composition as the light grey areas. At this stage there are thus no significant difference to be seen between the root areas of the large diameter whiskers and their immediate surroundings.

The bottom surface of sample 4

The bottom of this sample was used after a similar pre-treatment as used on sample 1. The results of the last pre-treatment steps are shown in Figures 8 and 9. Raman spectra recorded from many points on this surface show the simultaneous presence of Cu_2O and CuO closest to the metal surface. From the same reason as for sample 1, there seem to be a higher relative concentration of Cu_2O compared with CuO in many positions. It should be noted that all lose material as whiskers and flakes, containing sulphide had already been removed by flushing and brushing also in this case.

As for sample 1, whiskers were predominately found growing from the bottom surface. A schematic drawing of the bottom of sample 4 is shown in Figure 18, indicating approximate positions of LRS sampling. The drawing is to be compared with details in the photograph of Figures 8 and 9.

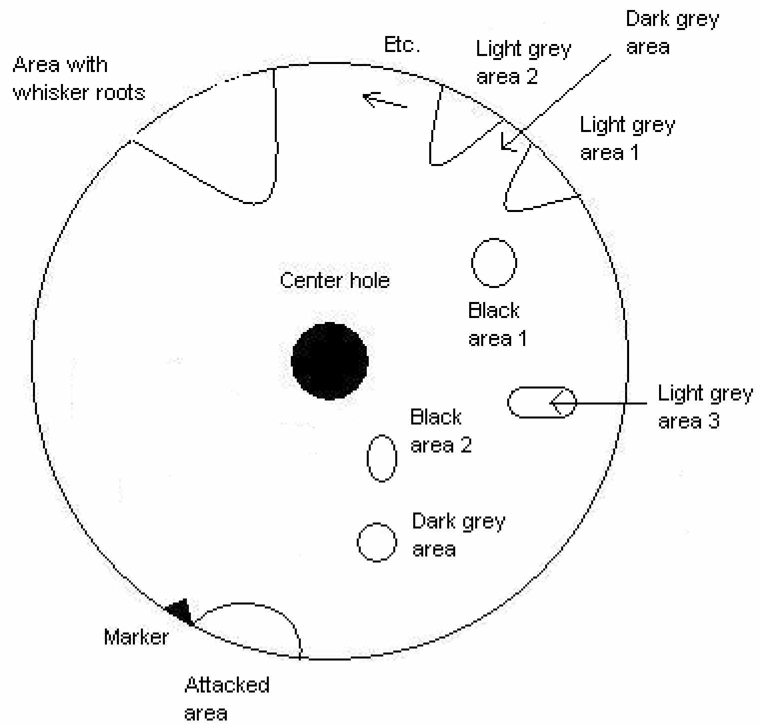

Figure 18
Approximate positions of LRS sampling. The drawing is to be compared with details in the photograph of Figures 8 and 9.

Whiskers of both types (Large/ broad and thin/hair-like, respectively) were observed also in this sample. Whisker roots of the two kinds were also related to the whiskers. Whisker roots of the thinner kind (circular “dots”) were found in several areas and roots of the large diameter whiskers mainly around the rim of the surface, in a similar way as for sample 1. A stereo microscope picture taken in the “Area with whisker roots” found in Figure 18 is shown in Figure 19. The corresponding Raman spectrum of the root in the centre of Figure 19 show simultaneous presence of Cu_2O and CuO.

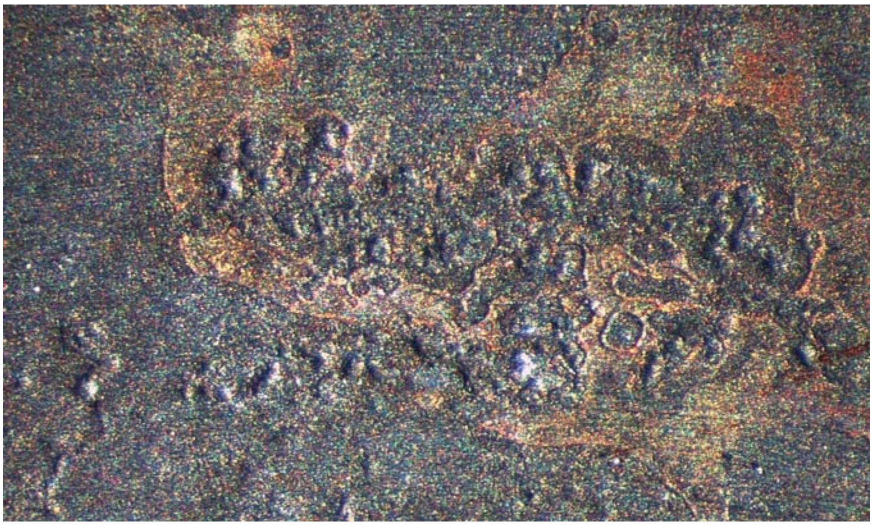

Figure 19
Stereomicroscope photograph taken in “Area with whisker roots” as found in Figure 18. The horizontal length of the picture covers 2.5 mm.

The rounded structures found in Figure 19 are small diameter whisker roots. It can be seen in Figure 19 that the small whisker roots could be associated with localized attacks in the underlying metal. Their diameter is of the order of 100 µm. A Raman picture is shown in Figure 20 as an example of a couple of small diameter whisker roots. The picture is taken in the “attacked area” as shown in Figure 18. There are, as in the case of sample 1, a multitude of examples and a selection of typical cases are accounted only.

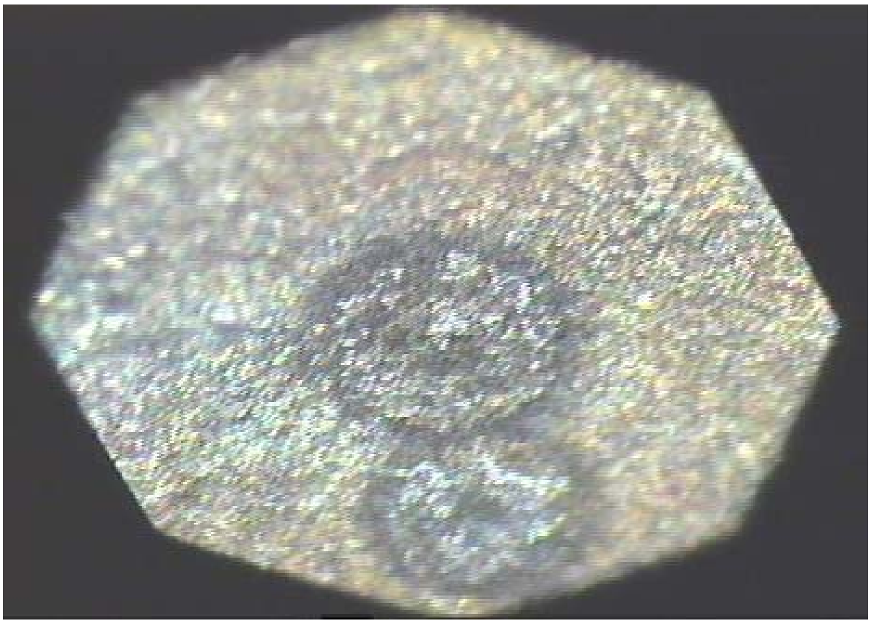

Figure 20
Raman picture taken in the middle of the “attacked area” as shown in Figure 18. The picture height is 300 µm.

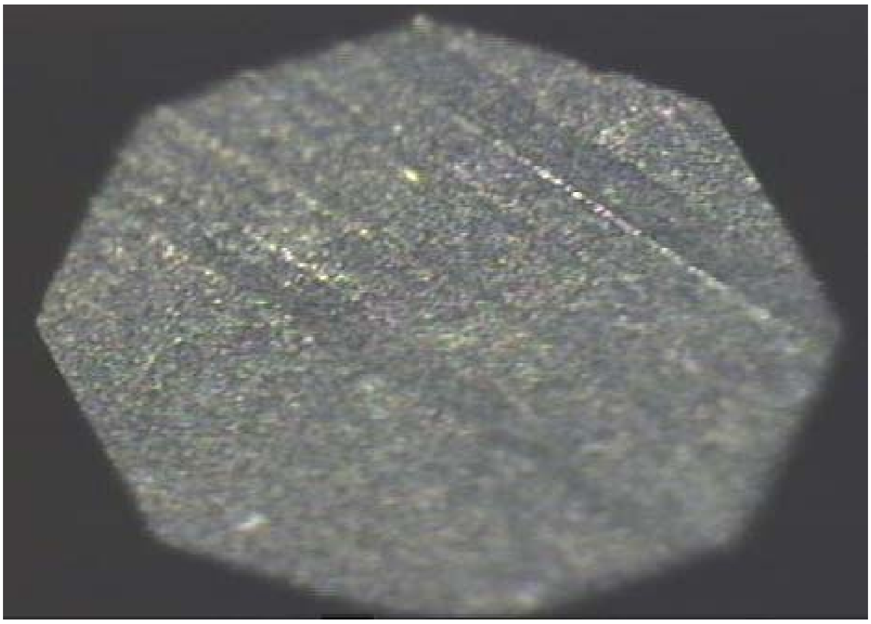

Figure 21
Raman picture taken in the middle of a dark grey area as shown in Figure 18. The picture height is 300 µm.

Figure 21 shows the look of a general dark-grey area without any whisker roots. Cu_2O and CuO with a possible excess of CuO is found. The very black areas indicated in Figure 18 show a purely metallic surface covered with a thin layer of mainly Cu_2O. Figure 22 shows morphology of the light grey area 1 of large diameter whiskers.

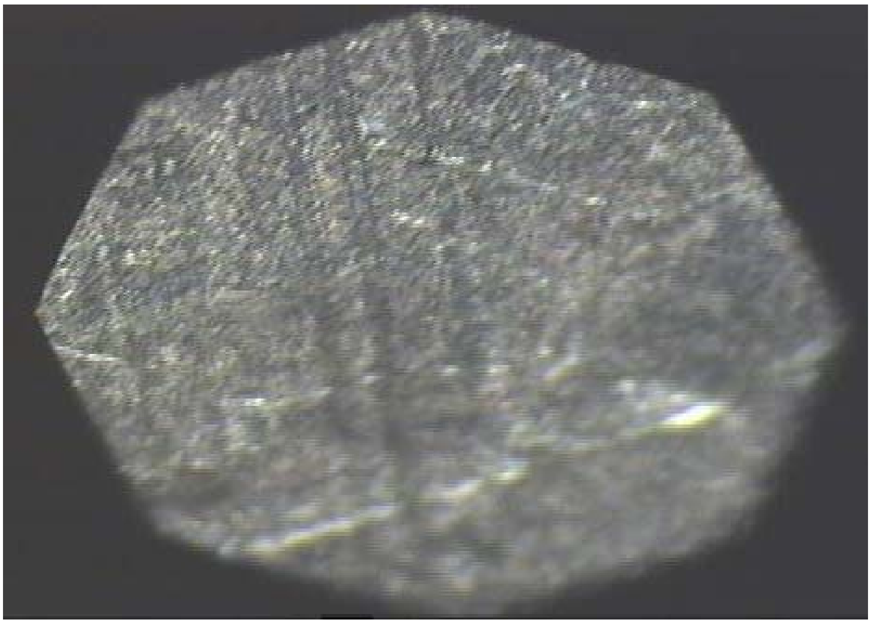

Figure 22
Raman picture taken in the middle of light grey area 1 as shown in Figure 18. The picture height is 300 µm.

Raman spectra show the presence of CuO, which is in accordance with corresponding areas of sample 1. The root areas of large diameter whiskers thus mostly contain CuO.

The morphology of the dark grey area dividing light grey areas 1 and 2 in Figure 18 (whisker roots for large whiskers) is very similar to the morphology shown in Figure 21. Raman spectra show that this area contains both Cu_2O and CuO.

There are many roots from the thin type of whiskers found in the “Area with whisker roots” indicated in Figure 18. One out of numerous examples of roots is shown in Figure 23.

Figure 23
Another root from the “Area with whisker roots” as shown in Figure 18. The picture height is 300 µm.

Raman spectra show that CuO prevails in the middle of the root in Figure 23 and Cu_2O and CuO in the reddish-yellow rim parts.

Removal of the last corrosion product layer from sample 4

In previous chapters the habitus of roots and the predominant phase compositions have been accounted for the two samples used. In this chapter the last step is accounted, which means that the root itself is taken away and the metal surface is bared. The removal was done using a scalpel. After the root removal, the underlying attack on the metal could be observed. This kind of investigation was done both in the Raman microscope and in the stereo microscope. As the fourth sample had the best observations of extended areas of whisker roots of both kinds, this sample was selected for this investigation. A couple of examples of results of this procedure are accounted here.

The first example is from the “area with whisker roots” seen in Figure 18. This area contains small diameter whisker roots. One of the selected roots is shown in Figure 24 before its removal.

The same area as seen in Figure 24 is also shown in Figure 25 after the removal of the whisker root and most of its surrounding layer of corrosion products.

A comparison of Figures 24 and 25 shows that there are both open and filled (with corrosion products) pits under the whisker root seen in Figure 24. The light structure in the upper part and the small root structures in the left part of Figure 24 also essentially correspond to pit structures in Figure 25.

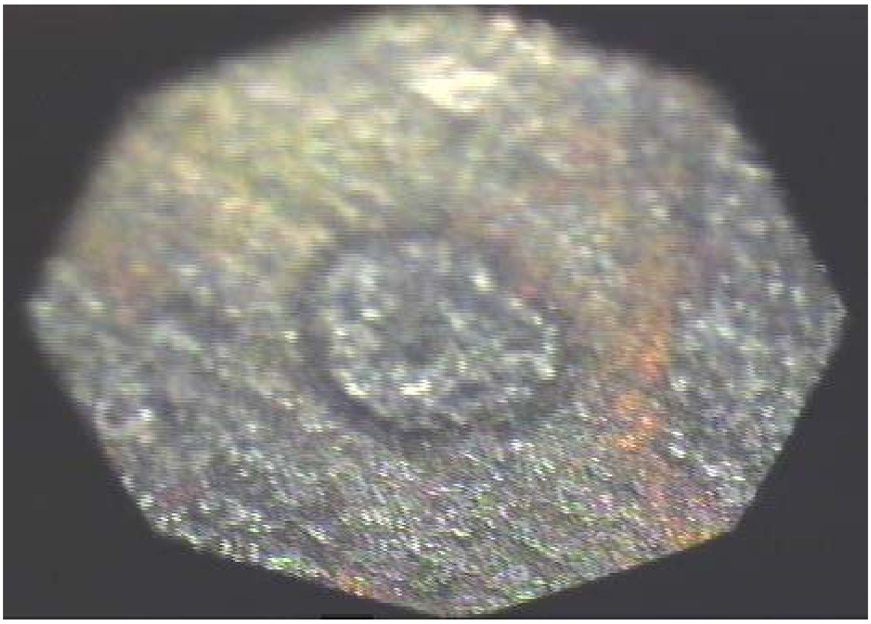

Figure 24
Raman picture taken in the “area with whisker roots” seen in Figure 18. The picture height is 300 µm.

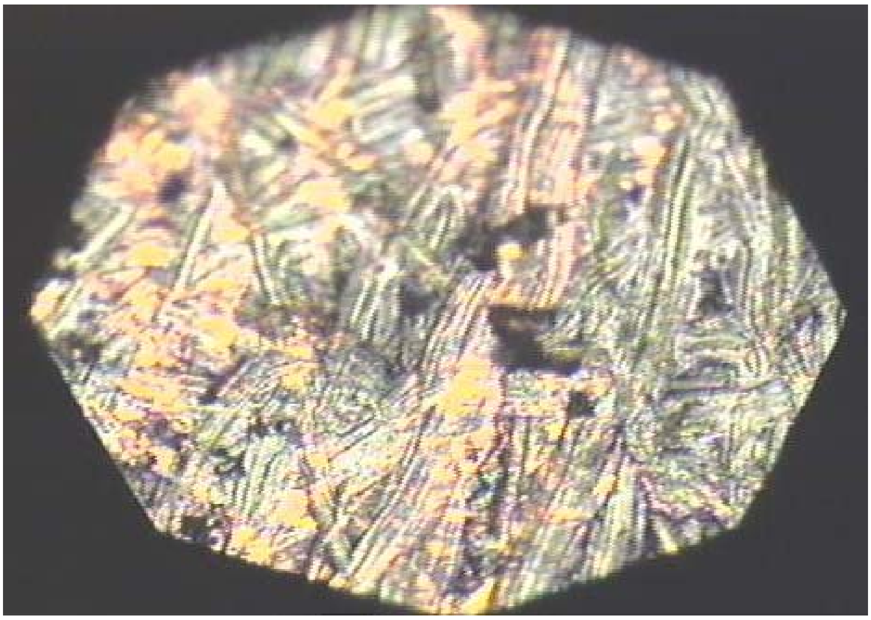

Figure 25
Raman picture taken in the same area as in Figure 24. The picture height is 300 µm.

Another example of the same kind is shown in the picture set 26 and 27. This investigation was made on a cluster of small diameter whisker roots found in the "attacked area" as shown in Figure 18.

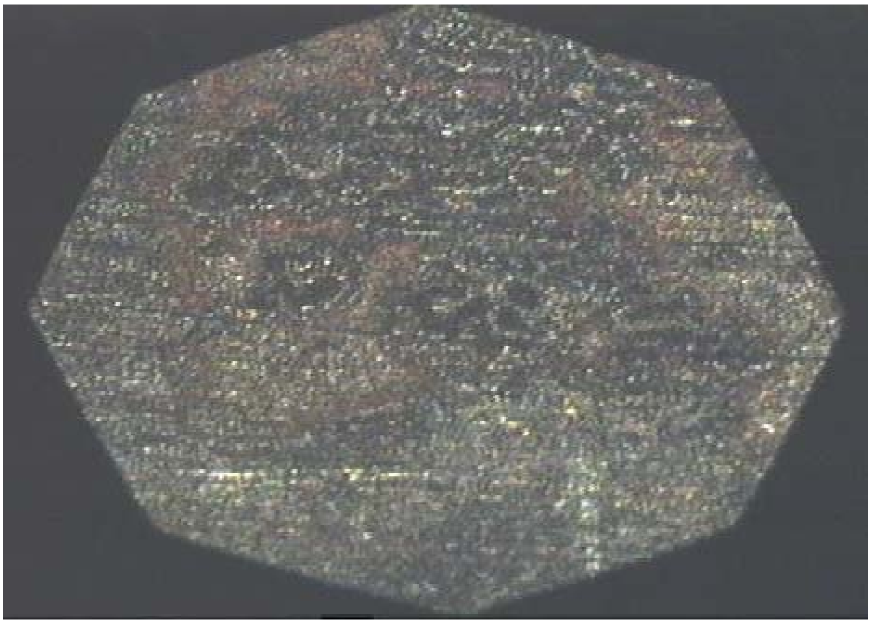

Figure 26
Raman picture of "attacked area" as found in Figure 18. The picture height is 1200 µm.

The same area as seen in Figure 26 is also shown in Figure 27 after the removal of the whisker roots and most of its surrounding layer of corrosion products.

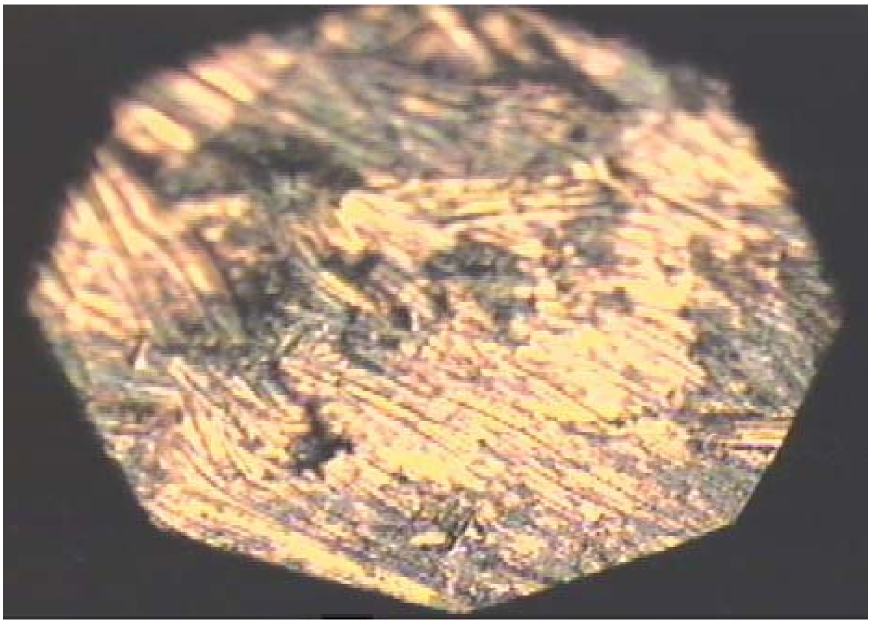

Figure 27
Raman picture taken in the same area as in Figure 26. The picture height is 300 µm.

Unfortunately Figures 26 and 27 have different magnifications. The area of Figure 27 is essentially the lower right part of Figure 26. It can be seen, however, that areas of whisker roots and areas of pits coincide also in this case.

In both accounted cases it should also be noted that there are small or no attacks to be observed in the metal surface outside of a root area.

The general relation between small diameter roots and localized attacks can also be observed in Figure 19. However, in this picture the roots themselves have not been removed.

Both copper oxides are identified in the black material found in the pits.

In the picture set 28 and 29 an example is shown on metal surface attacks under the large diameter whiskers of area “light grey area 1” as seen in Figure 18. Figure 28 shows the light grey area before corrosion product removal and Figure 29 the same area after the removal.

It can be seen from picture set 28/29 that there are localized types of attack in the areas of large diameter whiskers as well. It has to be pointed out, however, that the corrosion layer in this case was difficult to remove and the under-lying metal could have been more or less influenced by the removal process. The conclusion is therefore that there are localized attacks in the metal under the large whiskers, but frequency, amplitude and distribution could be discussed.

Raman spectra show that the black material found in different positions of Figure 29 contain the same chemical phases ($CuO+Cu_2O$) as the surface (large diameter root) found in Figure 28.

It should be pointed out that in the dark grey area separating the two light grey areas 1 and 2 (the latter are root areas of large diameter whiskers) as found in Figure 18, there are similar attacks to be found as in the large whisker root areas.

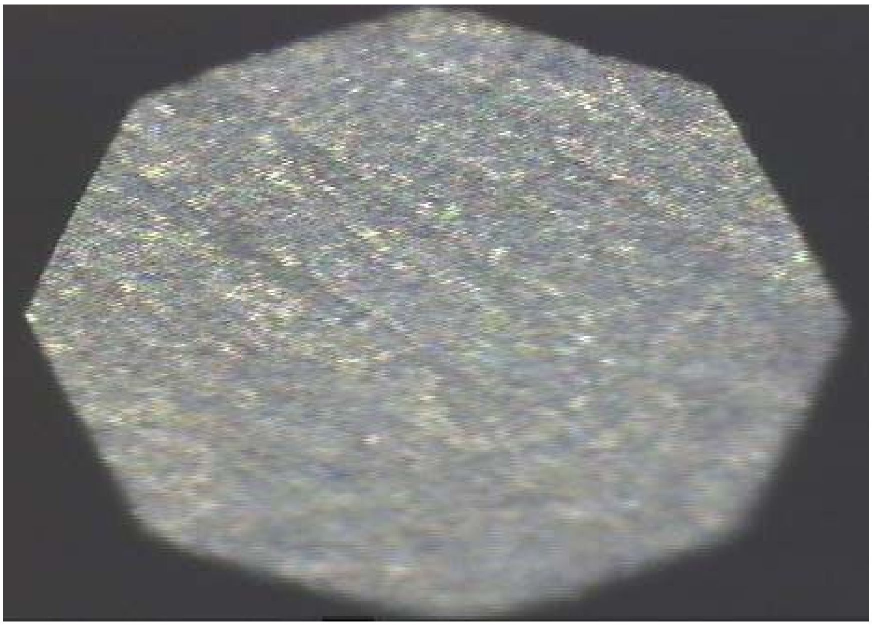

Figure 28
Raman picture taken in the middle of “light grey area 1” as shown in Figure 18. The picture height is 300 µm.

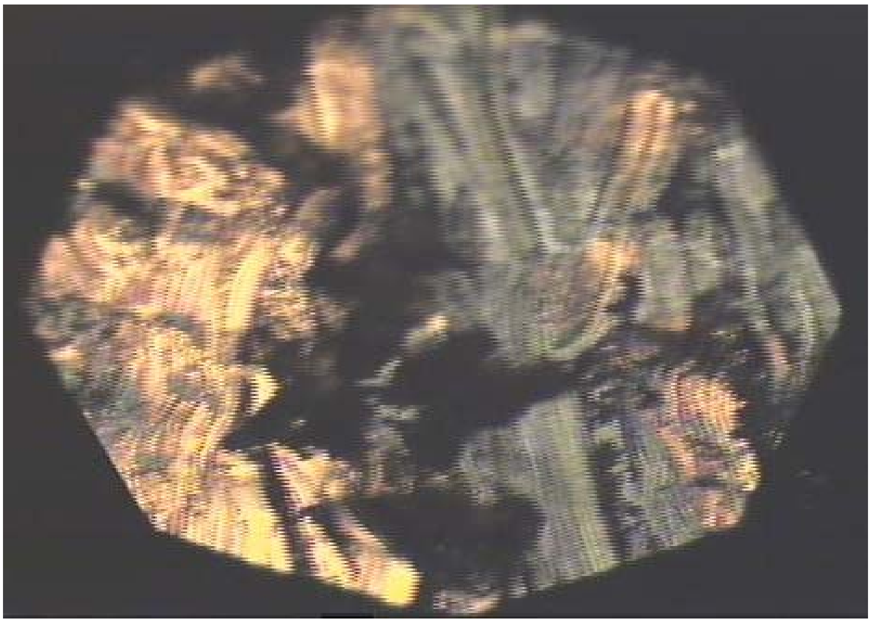

Figure 29
Raman picture taken in the same area as in Figure 28. The picture height is 300 µm.

De-scaled material from experiment 2

As previously indicated it was virtually impossible to capture single whiskers also this time due to de-scaling during the drainage process. The de-scaled material was sampled and turned out to look very much as in Figure 30. A spectrum is found in Figure 31.

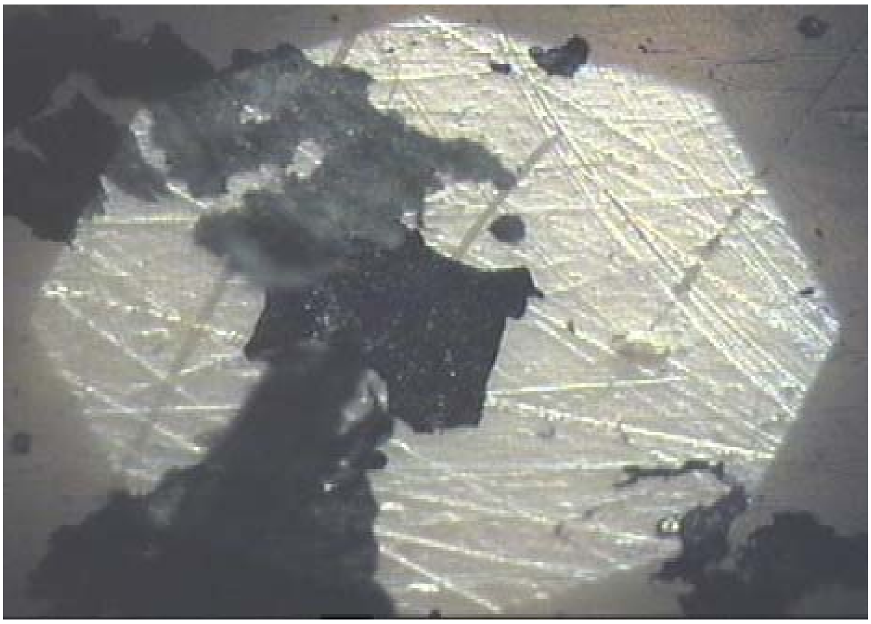

Figure 30
Raman picture of de-scaled material. The picture height is 1200 µm.

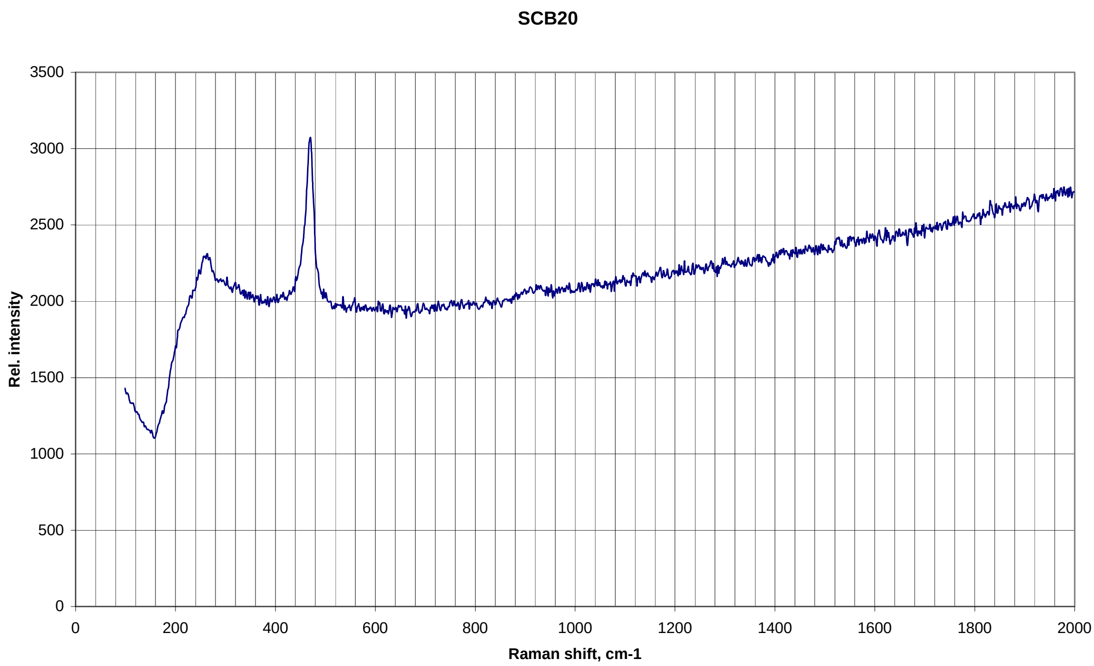

Figure 31
Example of Raman spectra taken in the black, de-scaled material seen in Figure 30.

The material was supposed to contain mostly the scale growing on the copper cylinders as well as the larger type of whiskers. The thinner type of whiskers was never found with certainty in de-scaled material.

The example of Raman spectra shown in Figure 31 was taken on material in Figure 30 and shows the presence of CuS. However, also spectra from the copper oxides were recorded from de-scaled material. This mixture of phases has also been observed in previous investigations [5, 7] and is confirmed here.

Discussion

After careful optical examination of the copper samples exposed in experiment 2 it is quite obvious that there are 2 types of whiskers present. One type has a small radius (~ 100 µm) and a rather regular, thread/hair-like shape. The colour of these whiskers is brown-reddish and the chemical phase building them is probably mostly copper oxides with an intermixture of copper sulphides. The other type has a larger radius (~ 1 mm) and is much more irregular than the first type. The latter type of whiskers is black and the chemical phases mainly copper sulphides with a presence of copper oxides. The two types of whiskers are different in many essential ways and also produce different types of whisker roots, standing directly on the metal surface.

The roots of the thread like, small diameter whiskers are rounded/circular and spot like. They have a remaining morphology that indicates that there has been a centre part of the thread surrounded by an outer “skin”. Such “skins” or layers appearing in whisker structures have also been observed in previous work. The relation between chemical phases present seems to differ slightly between the centre part and the outer parts. In the central part CuO is abundant and in the outer parts the phases Cu_2O together with CuO seem to dominate.

The roots of the broad, large diameter whiskers are very different from the small diameter roots. The root area becomes very smooth and looks homogeneous after soft brushing and there is no sign of distribution of chemical phases as in the small diameter case. The phases present are, however, essentially the same in both cases possibly with a degree of difference.

It should also be underlined that the large diameter whiskers were mainly situated along the perimeter of the circular bottom surface of the copper cylinder and the small diameter whiskers were appearing in several well isolated groups or “islands” inside the perimeter on the circular bottom surface. Probably the large diameter whiskers have a direct relation with the striped side structure of the corroding copper cylinder and the small diameter whiskers have not.

The last step of investigations was to remove the root material and observe the conditions of the under lying metal surface. The objective was to find out if there were any localized types of attacks that could be related to the position of the whisker root. It turned out that removal of material from the area with small diameter whiskers was rather easy and that it was much harder to remove material from large diameter whisker root areas. The result turned out to be that both types of whisker roots show underlying localized attacks.

The small diameter whisker “islands” were already in the preparation steps easily seen to be areas covered with localized attacks on the under-laying metal. In the case of small diameter whiskers the attacks could be referred to the original root position. The attacks were also correspondingly smaller, but still, they were related to the roots and thus the whiskers.

In the large diameter case the whisker root area was large and there were several localized attacks in conjunction with the whisker root. The attacks were less easy to characterize because of preparation problems. The same type of attacks was also found in areas immediately between large diameter roots. Therefore there seems to be no significant difference between large diameter whisker roots and their immediate surroundings concerning localized attacks on the underlying metal. This is also a distinct difference compared with small diameter whiskers.

The natures of the two different types of whisker growth are obviously quite different. This is indicated in several ways. Both by the results from the optical post investigations as well as by results from corrosion monitoring and potential measurements performed during the experiment. As it falls outside the scope of the present investigation to look into this, the question of detailed whisker growth mechanisms should be addressed separately.

The main objective of this investigation has been fulfilled as it was possible to show a direct correlation between whisker growth and localized attack on the under-laying copper metal. This finding could have a direct implication on the integrity of the copper lining of the waste canister and possible release of radionucleii to the repository environment. The seriousness of this question is related to the ability of whiskers to grow from the copper surface out into the surrounding pressurized bentonite. It has been suggested that growth of a sulphide containing whisker could propagate at the tip rather than at the root. Such a mechanism could cause a continuation of whisker growth through pores in the bentonite and cause a simultaneous continuation of the localized attack in the underlying copper metal. However, whiskers are very fragile and easily detached, which could inhibit the continuation of such an attack.

An experimental study should be performed in a bentonite environment in order to conclude the seriousness of the whisker growth mechanism for canister integrity.

Conclusions

The following conclusions can be drawn from the results presented here:

- Again whiskers have been grown on copper in a water environment containing sulphide and other chemical components found in actual ground waters.

- Whiskers are very fragile and complicated techniques have had to be developed to be able to verify whisker position (roots) with the type of attack on the underlying metal. The fragility of whiskers has also been observed in previous experiments.

- In this case two types of whiskers have been observed. One thread/hair like type with a small diameter and another type with a much larger diameter. They are very different and obviously have different origins.

- In both cases a localized type of attack can be attributed to the root of a whisker. It was the main objective of this work to show or contradict this phenomenon.

- In the small diameter case this attribution is quite clear and distinct. The root and the underlying attack are in the same position.

- In the large diameter case there are several attacks within the root area and also outside of it. Those attacks are less easy to characterize.

- The results could have a direct implication on the integrity of the copper lining of the waste canister and possible release of radionucleii to the repository environment. The seriousness should be evaluated by a study of whisker growth on copper in a bentonite environment.

References

1. Hermansson, H-P., and Engman, U., *Korrosion av kopparmaterial för inkapsling av radioaktivt avfall – En litteraturstudie,* SKI Rapport 94:6, Statens kärnkraftinspektion, SKI, April 1994.

2. Hermansson, H-P., and Engman, U., *Some Properties of Copper and Selected Heavy Metal Sulfides – A limited Literature review,* SKI Report 95:29, Swedish Nuclear Power Inspectorate, SKI, June 1995.

3. Hermansson, H-P., and Beverskog, B., *Gropfrätning på kopparkapsel,* SKI Rapport 96:25, Statens kärnkraftinspektion, SKI, Februari 1996.

4. Hermansson, H-P., and Eriksson, S., *Pitting Corrosion of Copper in Nuclear Waste Disposal Environments,* SKI Report 98:2, Swedish Nuclear Power Inspectorate, SKI, 1998.

5. Hermansson, H-P., and Eriksson, S., *Corrosion of the Copper Canister in the Repository Environment,* SKI Report 99:52, Swedish Nuclear Power Inspectorate, SKI, December 1999.

6. Hermansson, H-P., and König, M., *Galvanic and Stress Corrosion of Copper Canisters in Repository Environment,* SKI Report 01:38, Swedish Nuclear Power Inspectorate, SKI, February 2001.

7. Hermansson, H-P., Tarkpea, P., and Holgersson, S., *Composition of Whiskers Grown on Copper in Repository Environment,* SKI Report 01:45, Swedish Nuclear Power Inspectorate, SKI, November 2001.

www.ski.se

STATENS KÄRNKRAFTINSPEKTION
Swedish Nuclear Power Inspectorate

POST/POSTAL ADDRESS SE-106 58 Stockholm
BESÖK/OFFICE Klarabergsviadukten 90
TELEFON/TELEPHONE +46 (0)8 698 84 00
TELEFAX +46 (0)8 661 90 86
E-POST/E-MAIL ski@ski.se
WEBBPLATS/WEB SITE www.ski.se