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# Phosphorus in creep tested copper – Studies in Auger electron spectroscopy and Transmission Electron Microscopy

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# **Phosphorus in creep tested copper – Studies in Auger electron spectroscopy and Transmission Electron Microscopy**

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Swerim AB

This report concerns a study which was conducted for Svensk Kärnbränslehantering AB (SKB). The conclusions and viewpoints presented in the report are those of the authors. SKB may draw modified conclusions, based on additional literature sources and/or expert opinions.

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## Summary

In Sweden it is planned to use canisters (containers) with an outer shell of 5 cm copper for final disposal of spent nuclear fuel. In the assessment of copper as a barrier for one million years in the repository, it is important for the copper to maintain its high ductility. It has long been known that small additions of phosphorus increase the creep ductility and creep strength of copper, and it has been modelled to be in good agreement with observations (Sandström 2018), but the mechanism for this remains uncertain. If phosphorus is present as particles, it should be possible to discover them by using electron microscopy, electron spectroscopy and electron diffraction techniques. In this work, 20 samples of copper were imaged and analysed using scanning electron microscopy, transmission electron microscopy, Auger electron spectroscopy and energy dispersive X-ray spectroscopy. Copper containing between 0 and 105 weight-ppm phosphorus was studied. The studied material was of different conditions, having either been mechanically tested using creep testing, slow strain rate tensile testing, or not mechanically tested at all. Using these techniques, phosphorus particles was only found in phosphorus-containing copper that had been creep strained. Using Auger spectroscopy and observations in scanning electron microscopy, phosphorus was found on the fracture surface as small particles, ca 0.1 to 0.5  $\mu\text{m}$  in size. Using transmission electron microscopy and energy dispersive X-ray spectroscopy, phosphorus was found as particles in samples that had been creep tested. The present work shows that phosphorus is agglomerated into particles in deformed copper and provides insight to the elusive question of the role of phosphorus in copper creep ductility.



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# 1 Introduction

It has long been known that small additions of phosphorus increase the creep ductility and creep strength of copper, and it has been modelled to be in good agreement with observations (Sandström 2018), but the mechanism for this remains uncertain. Ever since the research on creep of copper containing phosphorus started it has been difficult to ascertain where the phosphorus is found in relation to the surrounding copper. For a full history of the research the reader is directed to the most recent overview publication (Andersson-Östling 2020).

Thermodynamic calculations show that phosphorus should be in solid solution in pure copper (Magnusson and Frisk 2013a). At 25 °C the solubility limit can be as low as 386 ppm. However, this content is much higher than the 50 to 55 ppm that is the most common content in the coppers studied in this investigation. If phosphorus is present as particles, it should be possible to discover them by using high-resolution electron microscopy, electron spectroscopy and electron diffraction techniques. The main difficulty in identifying where the phosphorus is found in the copper matrix is that when energy dispersive X-ray spectroscopy (EDS) is used in scanning electron microscopy (SEM), phosphorus contents on the order of parts per million, as is found in Cu-OFP, are below the detection limits. Furthermore, if phosphorus is present in grain boundaries, it cannot be seen in SEM, and it is also difficult to perform analysis on very small particles (below 50 to 100 nm) in SEM. However, in transmission electron microscopes (TEM) the interaction volume – the volume in the sample that the electron beam interacts with – is smaller than in SEM, so very small particles and grain boundaries can be studied and EDS can be employed since the interaction volume is smaller.

Another spectroscopy technique, Auger electron spectroscopy (AES) is much more sensitive to the surface phenomena than EDS. A spectrometry technique, Time-of-Flight secondary ion mass spectrometry (ToF-SIMS), is suitable for qualitative surface analysis. Another combined spectrometry and microscopy technique, atom probe tomography (APT), can also be used to provide tomographic and compositional measurements.

For these reasons, TEM has previously been used to study particles in copper with various contents of phosphorus (Magnusson and Bergqvist 2018, Bergqvist and Gordon 2018), ToF-SIMS was used to study the distribution of phosphorus in copper grains (Andersson-Östling et al. 2018), Auger microscopy was used to study fracture surfaces in Cu-OFP (Sundström et al. 2020) and atom probe tomography has also been used (Thuvander 2015) to investigate the distribution of phosphorus in copper.

In the one investigation in TEM (Bergqvist and Gordon 2018) material from Minican 4 was studied (Gordon et al. 2017), both deformed (pre-cracked wedge open load specimen) and not deformed, but it was concluded that the sample preparation methods may have influenced the results: electrolytic preparation using phosphoric acid and focused ion beam preparation where platinum sputtering is used. Phosphoric acid could cause corrosion products containing phosphorus to form on the surface of the prepared sample, and the X-ray energy peak for platinum overlaps with that of phosphorus in energy dispersive X-ray spectrums, making it difficult to analyse small quantities of phosphorus. Argon milling was also used to remove corrosion products and platinum from the surface.

A subsequent investigation (Magnusson and Bergqvist 2018) used different preparation methods and found no phosphorus agglomeration in the four different Cu-OFP grades that were studied, including creep tested Cu-OFP (125 °C, 155 MPa, 5 395 hours). Based on analysis with ToF-SIMS in another work (Andersson-Östling et al. 2018) which also included creep strained material, it was concluded that all the phosphorus was in solid solution. Work with atomic probe tomography (APT) and TEM on OFP copper (not creep strained) (Thuvander 2015) did not find phosphorus segregated to grain boundaries.

However, in the Auger electron spectroscopy studies of fracture surfaces (Sundström et al. 2020) structures appeared that looked like wakes. In the centre of the wakes, phosphorus containing particles were found in creep strained material. In the present work, AES and TEM was used to further study these particles: AES was used on fracture surfaces and TEM was used on the interior of the material. In this work, 20 samples of copper were imaged and analysed using scanning electron microscopy,

transmission electron microscopy, Auger electron spectroscopy, energy dispersive X-ray spectroscopy and selected area electron diffraction. In Sundström et al. (2020) only creep-strained material had been studied, and TEM was not used in that work. The present work contains TEM analysis and includes additional material conditions: as-received material, to see if the particles could be found before creep straining, and material that had been subjected to identical temperature conditions as the creep strained material, but without any deformation. Such comparisons were made to differentiate the effect of temperature and strain on the formation of these particles.

The results from Sundström et al. (2020) were inconclusive because phosphorus-containing particles were found at the fracture surface of one sample in one lab (Chalmers), but not in another sample in another lab (Högskolan Dalarna). They differed in two aspects: at Högskolan Dalarna, samples could be broken in a vacuum chamber, preventing any reaction at the surface with elements present in lab air, mainly oxygen. The Chalmers equipment had a lower detection limit in AES for elements. The samples used in Sundström et al. (2020) were taken from previously creep tested specimens (Mannesson and Andersson-Östling 2014). The material came from a tube with the SKB identity T58. In the present study, the lab at Chalmers is used for the AES and since the lab in Högskolan Dalarna could no longer perform such work. Four different samples were studied at Chalmers.

The testing methodology was the same as in the previous study (Sundström et al. 2020): a miniature sample that had been cut out from copper material with wire electric discharge machining (W-EDM) was fractured with a hammer in lab air (as was done at the Chalmers lab in the previous study) and then brought into the electron microscope to study the new fracture surface. The four samples studied at Chalmers had phosphorus contents ranging from zero to 105 parts per million (ppm). Only one of the four samples was taken from the gauge length part of a creep tested specimen, so that was the only sample that had undergone creep strain. This creep strained sample had a phosphorus content of 50 ppm and it was the sample in which phosphorus was found. This replicated the results from the Chalmers lab in Sundström et al. (2020) where phosphorus was found in creep strained material.

Based on these results, transmission electron microscopy was used to different copper materials and conditions at Swerim. The copper was taken from copper used in previous SKB projects at Swerim, either from mechanical testing specimens or from as-received material. The copper had been used in projects that were performed at Swerim from the late 1990's until 2022. The transmission electron microscopy (TEM) studies, totalling 12 TEM samples of which 8 were taken from the gauge length of creep tested specimens, also showed that phosphorus was only found in creep strained material.

This work shows that phosphorus is agglomerated into particles in creep strained Cu-OFP, and the implications of this finding are discussed since it could give insight into the mechanisms which form the particles and the causes of increased ductility in Cu-OFP.

## 2 Method

### 2.1 Material conditions

In the present study, material was taken from different types of SKB copper: phosphorus contents ranging from 0 to 105 ppm, from different parts of the canister or as-received material, from welded parts, and material with elevated levels of impurities. Note that in the tables shown in this report, the designation “T58” refers to a specific extruded tube from SKB. The copper had been used in projects that were performed at Swerim from the late 1990’s until 2022.

These different types of materials can be further divided into different categories, which differ mainly in whether they have been subjected to elevated temperatures and/or deformation. Of these categories, those studied in AES and SEM at Chalmers included material from categories 1, 3 and 4. The samples have also been noted with a sample number in Table 2-1 and Table 2-2 which are also mirrored in Table 3-1 and Table 3-2. The sample numbering is not related to the category numbering.

Some sample numbers are reoccurring because these samples were studied both in TEM and AES. Note that in all tables, the stress, strain rate, temperature and duration of the mechanical tests is given regardless of whether the sample was taken from the gauge length (deformed) or the gripping area (non-deformed) of the mechanical test specimen. The gripping area is only subjected to the elevated temperature, no stress or strain.

A brief note on terminology used in this report: in general, “specimen” refers to a mechanical testing specimen used for example in creep testing or slow strain rate tensile testing. “Sample“ refers to samples that were taken from these mechanical testing specimens and it also refers to samples that were taken from copper that had not been mechanically tested. These samples were studied using electron microscopy techniques described below. The samples are assigned a sample number based on order of appearance in the tables in this report.

For instance, two different samples can be taken from the same mechanical testing specimen: one from the gripping head, and one from the gauge length, and are then assigned different numbers. Some samples were studied both in AES and TEM. In cases where both samples were taken from the same part of the same specimen, they have been given identical numbers.

The materials are divided into four different categories:

- 1) Creep tested at elevated temperature. It has thus been subjected to elevated temperatures and deformation simultaneously. The temperatures that the creep tested specimens were subjected to was 75 or 175 °C, at stresses from 130 to 170 MPa. All creep tested material was creep-strained at elevated temperature for times ranging from 29 to 15 000 hours.

Creep tests can be divided into different stages, and the strain rate is highest at the beginning and end of a creep test (if it ruptures). The minimum creep rate (MCR), or minimum strain rate, is found in between and it is at this strain rate which the specimen spends most of its time in a test. This strain rate is shown where applicable in the tables in this report, but it is called minimum strain rate rather than minimum creep rate.

These samples were taken from within 10 to 15 mm of the necking or fracture region of creep tested specimens.

- 2) Slow-strain rate tested at elevated temperature. As with creep tested material, it has been subjected to elevated temperatures and deformation simultaneously. However, it has undergone testing at strain rates that are higher than those found in creep testing but lower than those found in tensile testing. The time duration of such tests is on the order of a few hours to hundreds of hours: the specimen studied in this project had a duration of 167 hours.

As with creep tests, slow strain rate tests can also be described with a minimum strain rate which the specimen experiences.

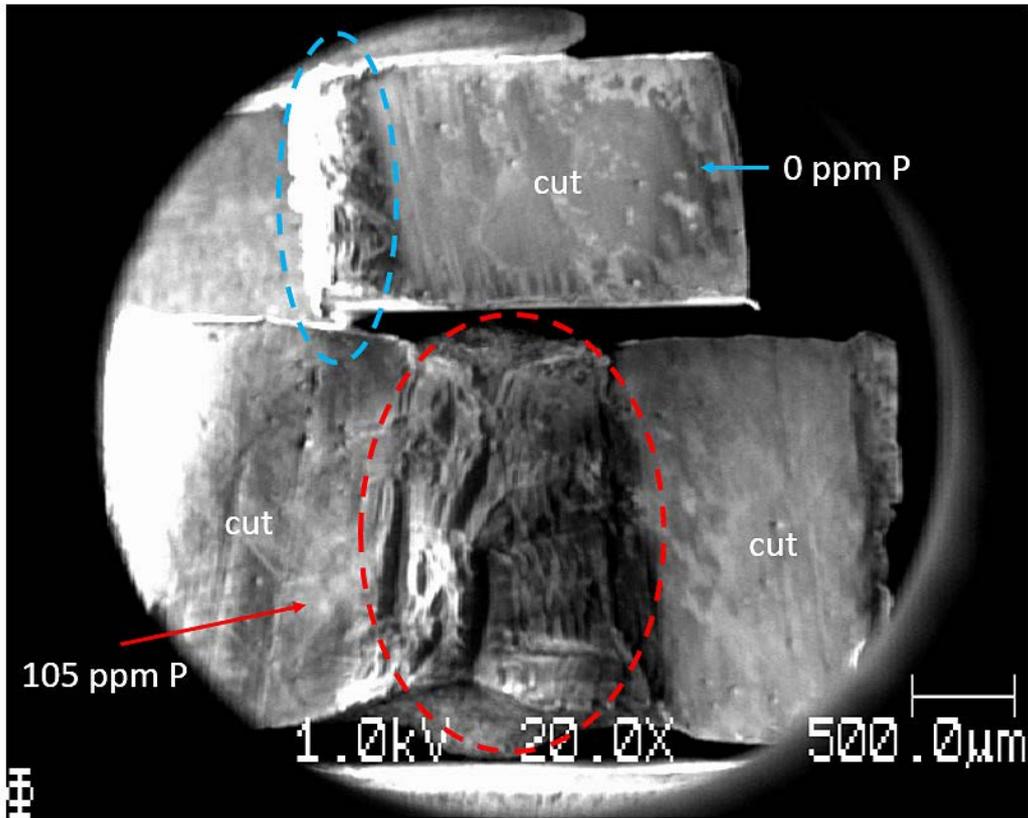
- 3) Material that had sustained elevated temperatures but no deformation. This material has been subjected to 75 °C or 175 °C for times ranging from 29 to 15 000 hours. These samples were taken from the gripping area of the specimens which were creep tested or slow strain rate tested. Since it is taken from the gripping area, this material has not been subjected to any stress. They serve as a comparison to the slow strain rate and creep tested material.
- 4) Material that was in a virgin condition, taken directly from copper that had been delivered by SKB (“as-received”).

## 2.2 Auger electron spectroscopy and scanning electron microscopy

Scanning electron microscopy (SEM) can be used to study the surface of metallic materials by using a focused electron beam which scans the metallic sample, causing electrons and X-rays to be emitted from the sample. The electrons originate from different depths in the sample and are of different energies: some are of lower energy and originate from the surface, while some are of higher energy and originate from deeper within the material. Electrons can also be transmitted through the sample, which is used in transmission electron microscopy (TEM) where thin foil samples are made, allowing for transmission of electrons through it. These different electrons can be used for both imaging at very high magnifications, chemical analysis (spectroscopy) as well as diffraction to determine crystallographic properties. There are different types of spectroscopies, the most common being energy dispersive X-ray spectroscopy (EDS) and wavelength dispersive X-ray spectroscopy (WDS). When EDS or WDS is used in scanning electron microscopy (SEM) phosphorus contents on the order of parts per million, as is found in Cu-OFP, are below the detection limits. EDS can however be used in TEM to study phosphorus particles because the interaction volume, the volume in the sample that the electron beam interacts with, is smaller in TEM.

Auger electron spectroscopy (AES) is especially attuned to the study of surfaces using Auger electrons which originate from the near-surface region of the sample, on the order of nanometres, and the electrons have lower energies. A sample is subjected to a focused electron beam and the amount of emitted Auger electrons is then measured.

Copper does not exhibit a ductile to brittle transformation when cooled as steels do but remains ductile at lower temperatures. This means that it is difficult in copper to obtain a fracture surface by shearing that has not been heavily plastically deformed. By using the necking region from the creep specimens, which has already been weakened by the creep rupture process, a more brittle fracture can be achieved, with a surface that could contain weakened grain boundaries and that can be studied with AES. In this manner it should be possible to study the grain boundaries and find out if phosphorus is present there. The testing methodology is described in detail in Sundström et al. (2020). The instrument used in the present study is PHI 700 Scanning Auger Nanoprobe. The accelerating voltage of the electron beam is 10 kV, and its beam current is 10 nA. In the present study, samples studied in AES were taken from material categories 1, 3 and 4, (see Section 2.1): creep tested material from gauge length and gripping area, and as-received material. The samples’ surfaces were measured with AES at multiple sites for each sample, with acquisition times ranging from 1 to 30 minutes. On average, a sample spent about 2 hours being examined in the chamber, including the time taken to create and eliminate the vacuum inside the microscope chamber. Multiple images were taken of the same sample at different locations on the fracture surface. Each row in Table 2-1 corresponds to a single sample that was studied: there were not multiple samples made for each row in Table 2-2, so a total of 5 samples were studied in AES, four in this study and one in the previous study (Sundström et al. 2020). That sample is also included in Table 3-1. An overview of two samples being studied inside the SEM is shown in Figure 2-1. A samples’ fracture surface was large, about 1.5 mm × 1.2 mm (ca 2 mm<sup>2</sup>) but the imaged areas were much smaller and varied in size since the imaging was done at many different magnifications: 20 times magnification for the overview image (Figure 2-1) while the images used for analysis ranged from 1 000 (imaged area 400 μm<sup>2</sup>) to 100 000 times magnification (imaged area 0.8 μm<sup>2</sup>), with spectroscopy being performed on spots in images taken at magnifications ranging from 8 000 to 100 000 times magnification. Most of the spectroscopy was performed at magnifications from 12 000 to 50 000 times magnification. Information about the samples is summarized in Table 2-1 showing e.g., type of material and phosphorus content.



← Force

*Figure 2-1. Overview of two samples in the SEM, which were examined with AES. One sample with 0 ppm phosphorus is seen above another sample with 105 ppm phosphorus. Areas labelled “cut” indicates areas that were cut with a saw before the hammer blow. Force arrow indicates direction of hammer blow.*

Table 2-1. AES sample matrix.

Sample	Material	Phosphorus (ppm)	Material batch or type	Original specimen name or material label	Material category and type	Deformed/not deformed	Stress (MPa)	Temperature (°C)	Time (hours) and minimum strain rate (%/h)	Report reference	Date of study in AES
1	OFP	105	Extruded Ø 16 mm rods from Outokumpu Poricopper OY.	4K	3 Disrupted creep test (no necking on gauge length)	No, from gripping area	160	175	6200 h 0.00002 %/h	TR-99-39	2020-10, present study
2	OFP	50	Lid material from FSW project, material unaffected by weld.	64 deg	4 From lid, as-received material	No	n/a	RT	n/a	Posiva SKB Report 10	2020-10, present study
3	OF	0	G221	OF4 G221	4 Taken from copper rod approx. 50 mm diameter.	No	n/a	RT	n/a	n/a	2020-10, present study
4	OFP	50	T58	Prov 9	1 Creep test	Yes, from gauge length of creep specimen	170	75	148 h 0.054 %/h	R-17-19	2020-10, present study
5	OFP	50	T58	n/a	1 Creep test	Yes, from gauge length of creep specimen	Not known	75	Not known	R-14-31	2018, previous study (Sundström et al. 2020)

## 2.3 Transmission electron microscopy

Electron microscopy can be used to study the surface of metallic materials by using a focused electron beam on the sample, causing electrons and X-rays to be emitted from the sample. The electrons originate from different depths in the sample and are of different energies: some are of lower energy and originate from the surface, while some are of higher energy and originate from deeper within the material.

Electrons can also be transmitted through the sample, which is used in transmission electron microscopy (TEM) where thin foil sample are made, allowing for transmission of electrons through it. This makes it possible to image and use spectroscopy on very fine details, such as small particles or grain boundaries.

Transmission electron microscopy (TEM) was used to study materials from categories 1 to 4 (see Section 2.1). The full sample matrix is shown in Table 2-2.

On creep tested specimens, TEM samples were taken approximately 10–15 mm from the necking region or fracture. If samples had been taken closer to the necking region, only deformed microstructure would be seen in the TEM images, yielding no valuable information about the presence or not of phosphorus in the matrix. If they had been taken farther away, there was a risk that an insufficient amount of deformation was present. The test matrix already had non-deformed material taken from the specimen heads as a reference and since TEM samples require extensive preparation work, the authors did not want to risk cutting out material from creep tested specimens only to find that a spot with insufficient deformation had been chosen. For these reasons, 10 to 15 mm was considered appropriate as a distance where it was possible that the matrix was uniaxially strained while still retaining some of the original structure visible.

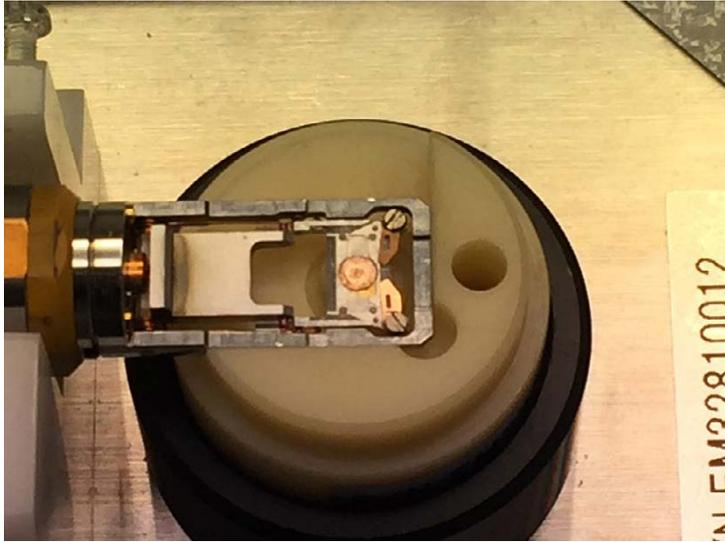
The samples were studied during about 1 year, from beginning of 2021 to beginning of 2022. One operator performed all the work, and it was done in the same machine and the samples were prepared in the same way throughout the project.

After the initial 5 samples had been studied in AES (number 1 to 5 in Table 2-1, of which sample 5 was studied in a previous project (Sundström et al. 2020), the results were reviewed, and further materials were selected for study in TEM. These new samples are numbered from 6 to 15 (Table 2-2) and were studied in the same ways as the previous materials. Two of the samples studied in AES were also studied in TEM, sample 4 and 5.

To prepare the TEM samples sulphuric acid was used instead of phosphoric acid which had been used in a previous study (Bergqvist and Gordon 2018). This was done to eliminate the risk of contamination from the sample preparation, a risk which a previous study had identified (Bergqvist and Gordon 2018). This means that all phosphorus found during the TEM studies are present in the material before the study, and none have come from the preparation stage. This can however not be said for sulphur. TEM samples are very small: circular discs with a diameter of 2 to 3 mm and a single imaged area being 2 to 9  $\mu\text{m}^2$  for images in this project. Multiple images were taken of the same sample and different locations of the sample were studied.

TEM thin foil samples were prepared from the copper material by jet-electropolishing. The material was thinned down by grinding to approximately 150  $\mu\text{m}$  and a 3 mm diameter disk was punched out from the material. Jet-electropolishing was done using a TenuPol-3 (Struers) to perforation of the material, and analysis in the TEM was done on areas around the hole at material thicknesses up to approximately 150 nm (see Figure 2-2). The electrolyte used was a water solution containing 20 vol% ethanol, 10 % 1-propanol, 10 % (conc)  $\text{H}_2\text{SO}_4$  and 5 g urea and with a 25 V applied potential. TEM and STEM imaging and EDS analysis was done in a JEM 2100-F TEM (JEOL) that is equipped with X-Max 80  $\text{mm}^2$  TLEN SDD energy dispersive X-ray detector (Oxford Instruments).

This method can be compared with the previous TEM work where electrolytic preparation (phosphoric acid) and focused ion beam preparation combined with argon milling was used (Bergqvist and Gordon 2018), and where only grinding, polishing and argon milling was used (Magnusson and Bergqvist 2018), without any acid. In the present work, phosphoric acid was not used to make sure that phosphorus observed did not originate from sample preparation and focused ion beam was not used to prevent contamination from platinum. In addition, argon milling was not used because previous work had concluded (Magnusson and Bergqvist 2018) that it caused crystalline defects in the sample to appear.



**Figure 2-2.** Transmission Electron Microscopy sample in holder. The disc is ca 3 mm diameter and 150  $\mu\text{m}$  thick with an area in the centre that is much thinner; 150 nm. This is the area studied in TEM.

Table 2-2. TEM sample matrix.

Sample	Material	P (ppm)	Material batch or type	Original specimen name or material label	Material category and type	Deformed during testing?	Stress (MPa)	Temperature (°C)	Time (hours) and minimum strain rate (%/h)	SKB reference	Date of study in TEM
4	OFP (T58) (Prov 9)	50	T58	Prov 9	1 Creep tested	Yes, from gauge length of creep specimen	170	75	148 h 0.054 %/h	R-17-19	2021-01
5	OFP (T58)	50	T58	Not known	1 Creep tested	Yes, from gauge length of creep specimen	Not known	75	Not known	R-14-31	2021-01
6	Forged lid	50	Forged lid	LID75-2	3 Creep tested	No, from gripping area	170	75	14 287 h, 0.0005 %/h	TR-07-08	2021-03
7	Forged lid	50	Forged lid	LID75-2	1 Creep tested	Yes, from gauge length of creep specimen	170	75	14 287 h, 0.0005 %/h	TR-07-08	2021-03
8	OFP (T58)	50	As-received		4 As-received tube material	Not a mechanical test specimen	0	RT	n/a	n/a	2021-03
9	HAZ	50	Heat affected zone	HAZ75-2	3 Creep tested	Yes, from gauge length of creep specimen	170	75	360 h, 0.00085 %/h	TR-07-08	2021-05
10	WMI	50	Weld metal, inner	WMI75-2	3 Creep tested	Yes, from gauge length of creep specimen	170	75	2 200 h, 0.00132 %/h	TR-07-08	2021-05
11	OF	0	OF	CuP0_300_1N	3 Creep tested	Yes, from gauge length of creep specimen	130	175	29 h, 0.0687 %/h	TR-99-39	2021-05
12	OFP-ZnBiTe	67 (also elevated levels of Zn, Bi, Te)	OFP	CuZnBiTe-75-2	2 Slow-strain rate tested	Yes, from gauge length of SSRT specimen	n/a (33 % strain)	75	167 h, 0.19 %/h	SKBdoc 1917201	2021-05
13	WMI	50	WMI	WMI75-2	1 Creep tested	No, from gripping area	170	75	2 200 h, 0.00132 %/h	TR-07-08	2021-10
14	OFP	105	OFP	OFP (4K)	1 Disrupted creep test (no necking on gauge length)	Yes, from gauge length of creep specimen	160	175	6 200 h, 0.00002 %/h	TR-99-39	2021-10
15	OFP-ZnBiTe	67 (also elevated levels of Zn, Bi, Te)	CuZnBiTe 2 LOT#117130-1	Cu-ZnBiTe 7.2.1	1 Disrupted creep test	Yes, from gauge length of creep specimen	130	175	1 079 h, 0.00562 %/h	SKBdoc 1975930	2021-10



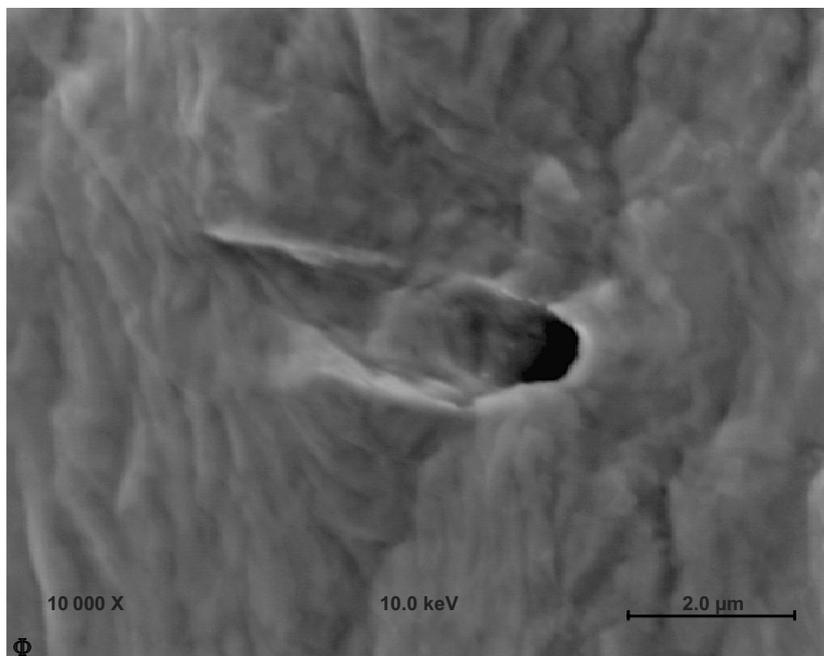
## 3 Results

### 3.1 Auger electron spectroscopy

The results for the studied samples have been summarized in Table 3-1. The results for each sample are described in detail with images and results from spectroscopy in the following paragraphs. Sample 5 from the previous work (Sundström et al. 2020) is not shown in this report. As in the previous work (Sundström et al. 2020), so-called ‘wakes’ or U-shaped regions are found with particles that contain phosphorus (sample 4: Figure 3-12, Figure 3-14) or sulphur (sample 1: Figure 3-4) or neither (sample 2: Figure 3-7). In sample 3, no such regions were found (Figure 3-9).

#### 3.1.1 Sample 1: OFP, 105 ppm P, from gripping area of a creep test

Several U-shaped regions were found (Figure 3-1). Three U-shaped regions were measured with spectroscopy, but no phosphorus was found (Figures 3-2 and 3-3). Sulphur was found in one particle (Figure 3-4).



*Figure 3-1. A U-shaped region found in sample 1.*

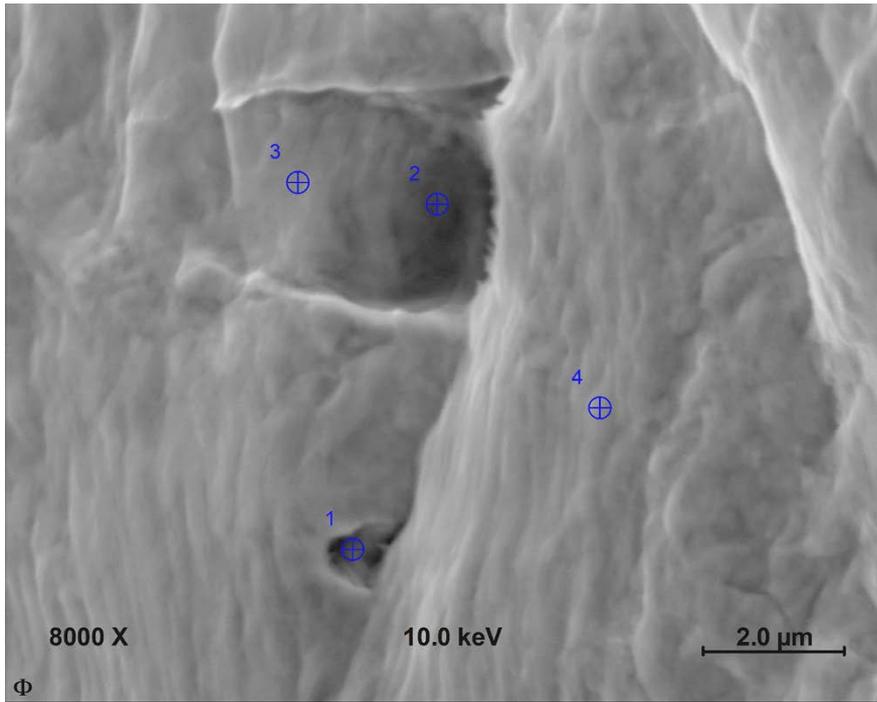


Figure 3-2. A region measured with spectroscopy in sample 1.

Cu 2020-10-20.103.spe: 30.0 eV-1530.0 eV, Register	Chalmers
2020 Oct 20 10.0 kV 10 nA FRR	4.1755e+004 max
Sur1/Area1/4 (Der5)	1.96 min
	RSF

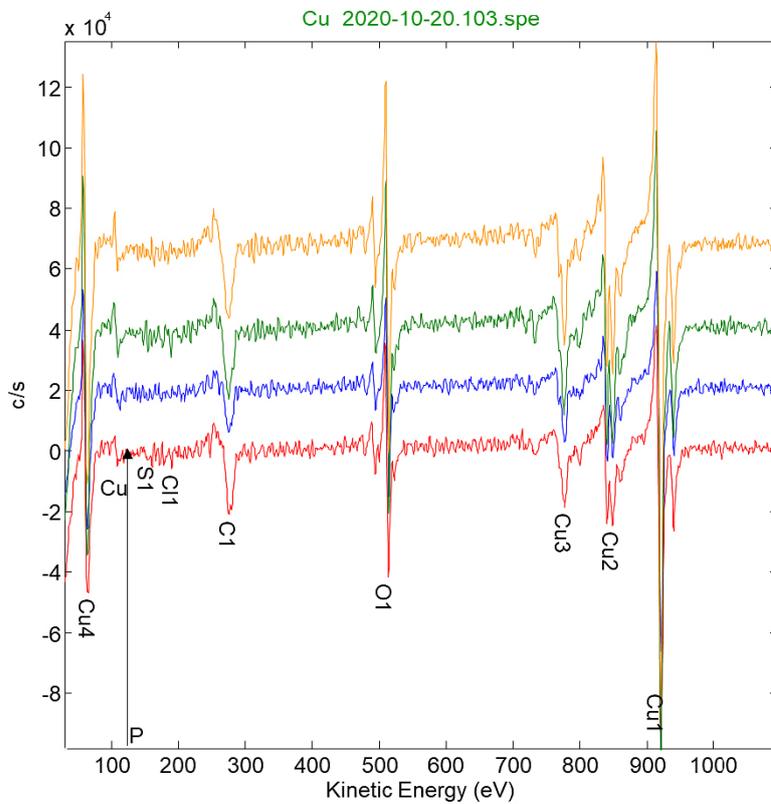
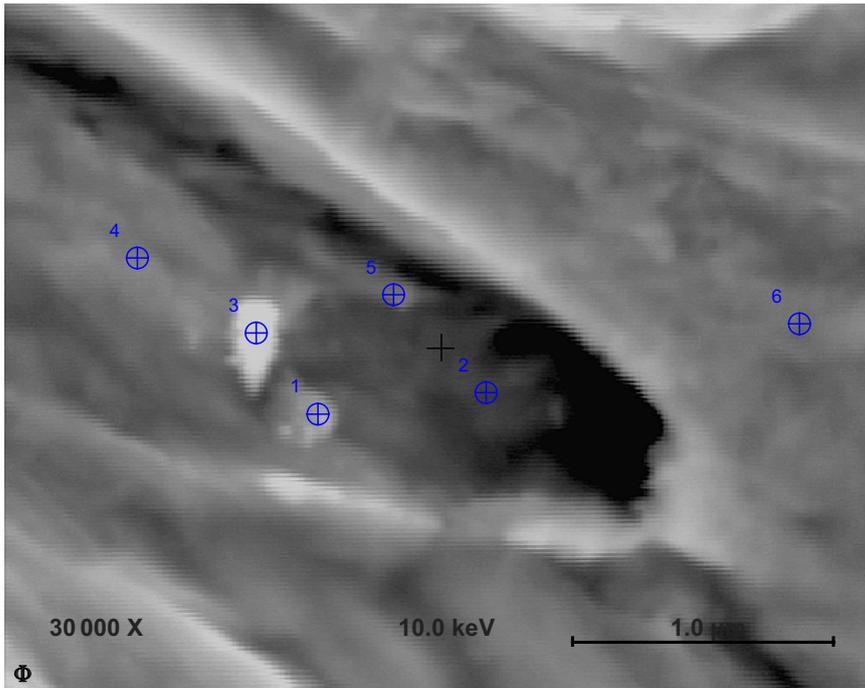


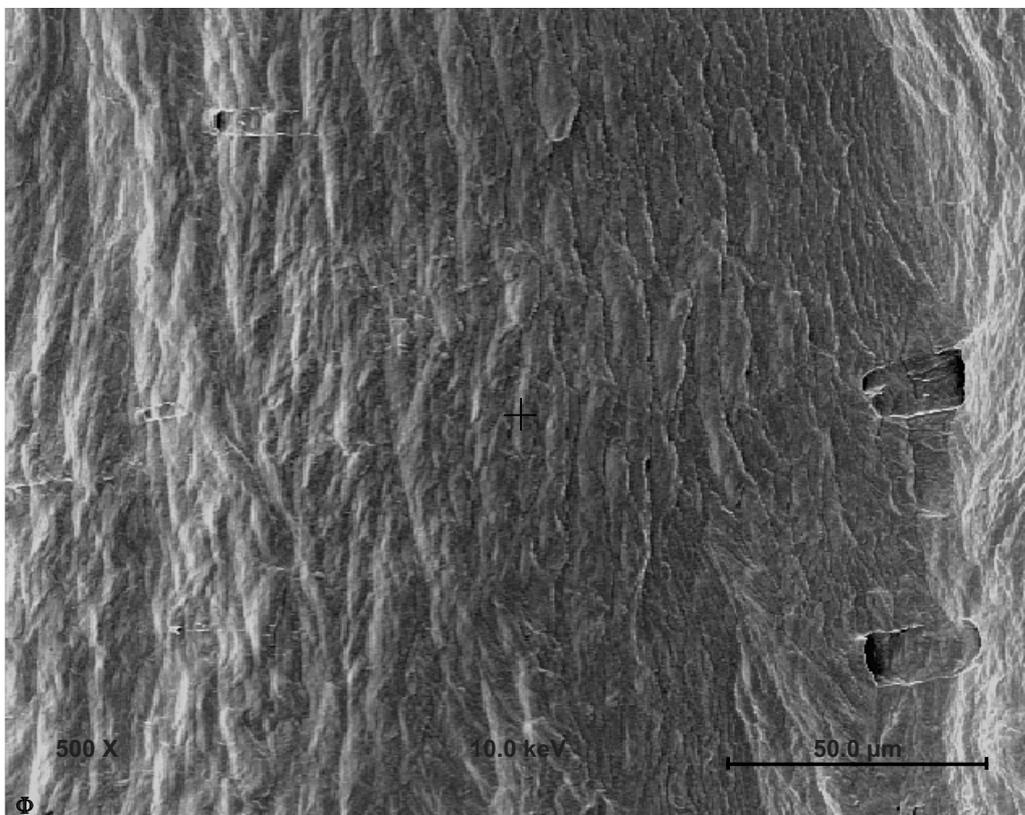
Figure 3-3. Spectroscopy of sample 1 of sites in Figure 3-2. The black arrow shows where the peak of phosphorus would appear if the measurements would have shown phosphorus.



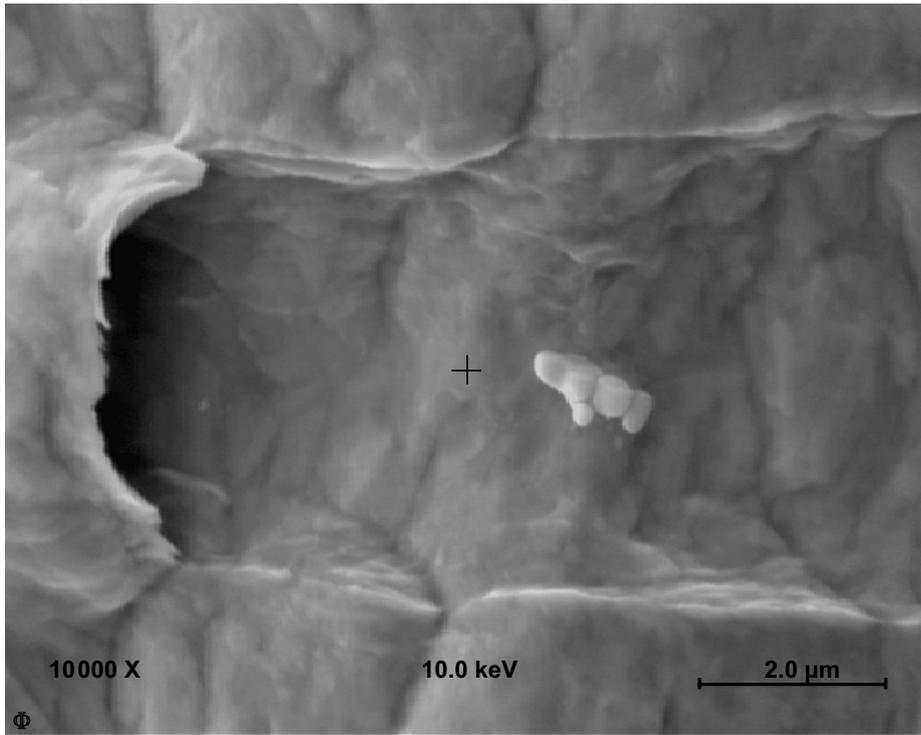
*Figure 3-4. Particle in sample 1 found to contain sulphur when measured with spectroscopy.*

### **3.1.2 Sample 2: OFP, 50 ppm, from as-received material**

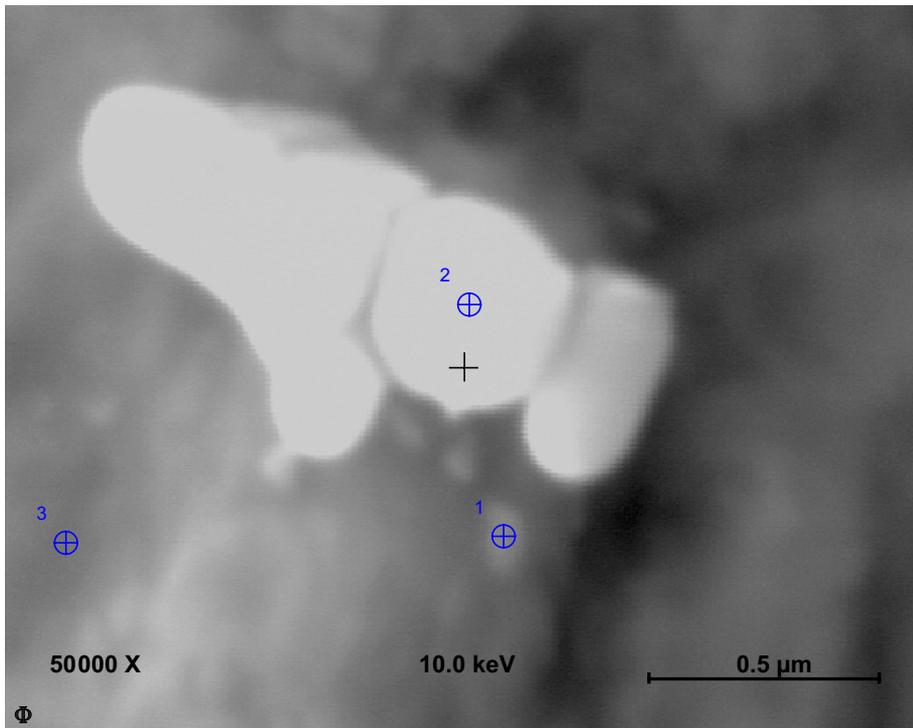
A few U-shaped regions were found in this specimen (Figures 3-5 to 3-7). No phosphorus or sulphur was found in spectroscopy when measured on particles that were found (Figure 3-8).



*Figure 3-5. U-shaped regions in sample 2.*

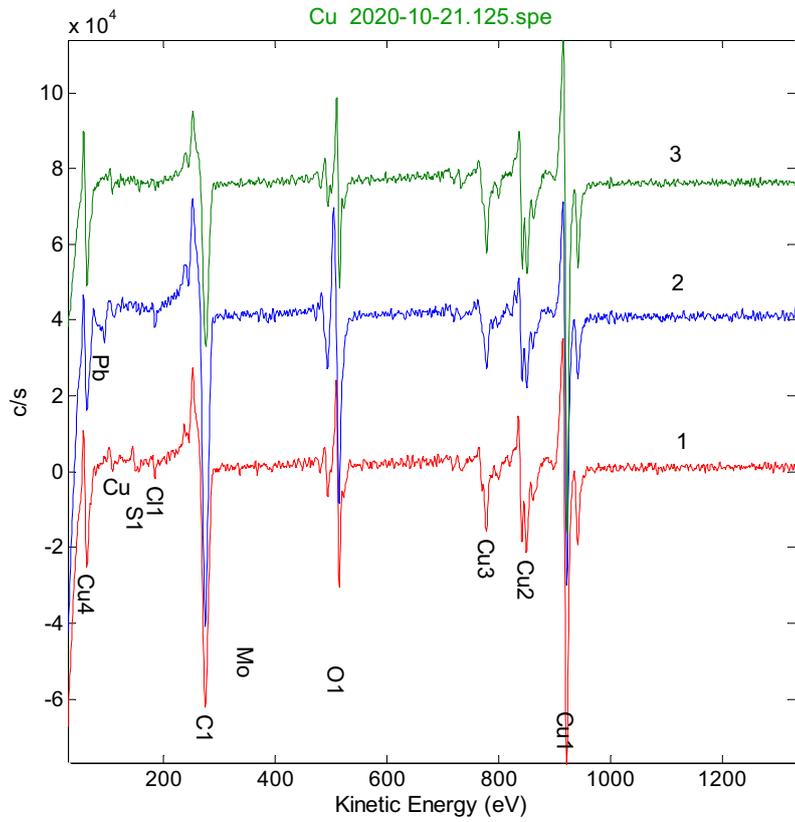


**Figure 3-6.** Magnification of upper left corner in previous image (Figure 3-5) in sample 2.



**Figure 3-7.** Magnification of centre-right region in previous image (Figure 3-6). Sites for measuring with AES marked with blue cross in circle.

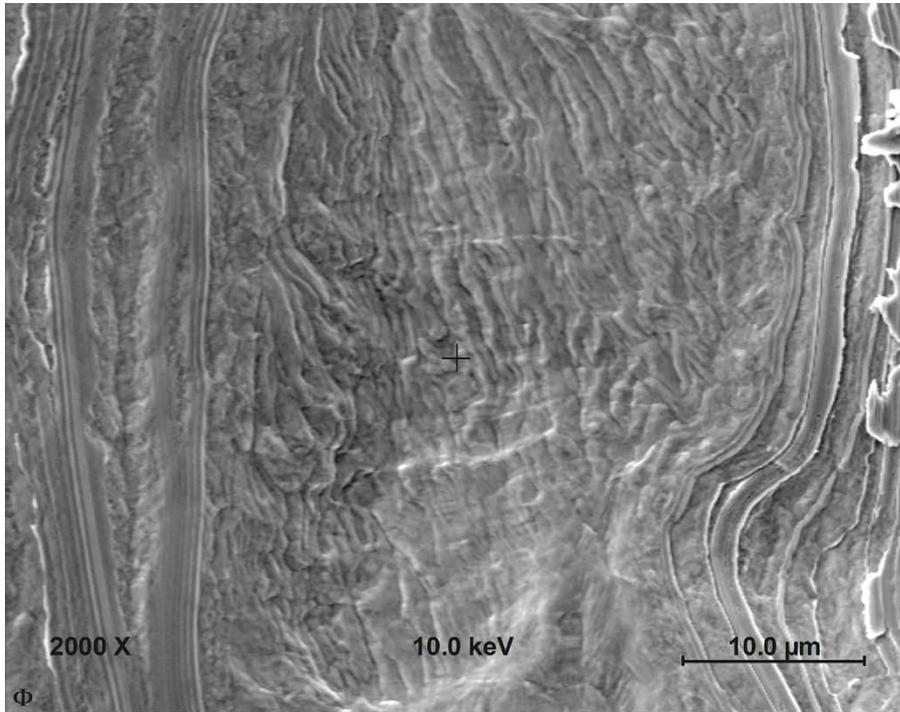
Cu 2020-10-21.125.spe: 30.0 eV-1330.0 eV, Register	Chalmers
2020 Oct 21 10.0 kV 10 nA FRR	10.84 min
3.5221e+004 max	RSF
Sur1/Area1/1 (Der5)	



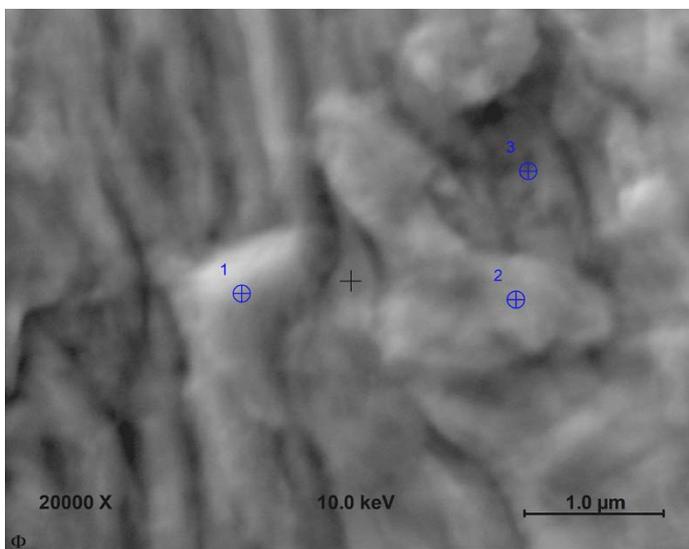
**Figure 3-8.** Spectroscopy of previous image (Figure 3-7) for sample 2.

### 3.1.3 Sample 3: OF, 0 ppm P, from as-received material

U-shaped regions were not found in this sample 3. The fracture surface showed ridges (Figure 3-9). Some regions were measured but no phosphorus was found (Figures 3-10 and 3-11).



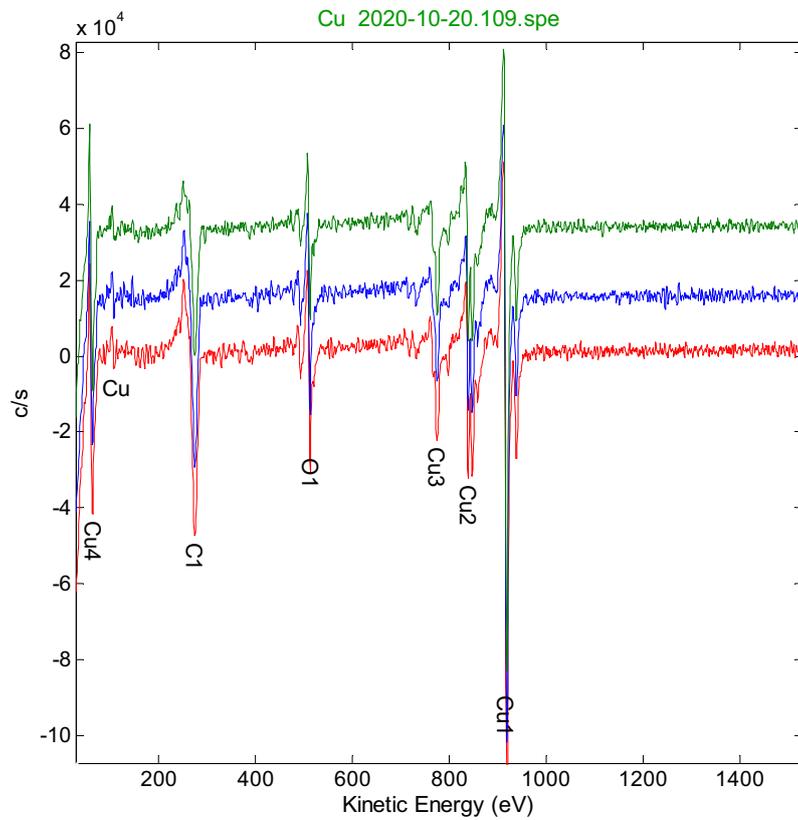
*Figure 3-9. Ridges on fracture surface of sample 3.*



*Figure 3-10. Region with measuring sites for AES in sample 3.*

Cu 2020-10-20.109.spe: 30.0 eV-1530.0 eV, Register  
2020 Oct 20 10.0 kV 10 nA FRR 5.1033e+004 max  
Sur1/Area1/1 (Der5)

Chalmers  
5.25 min  
RSF

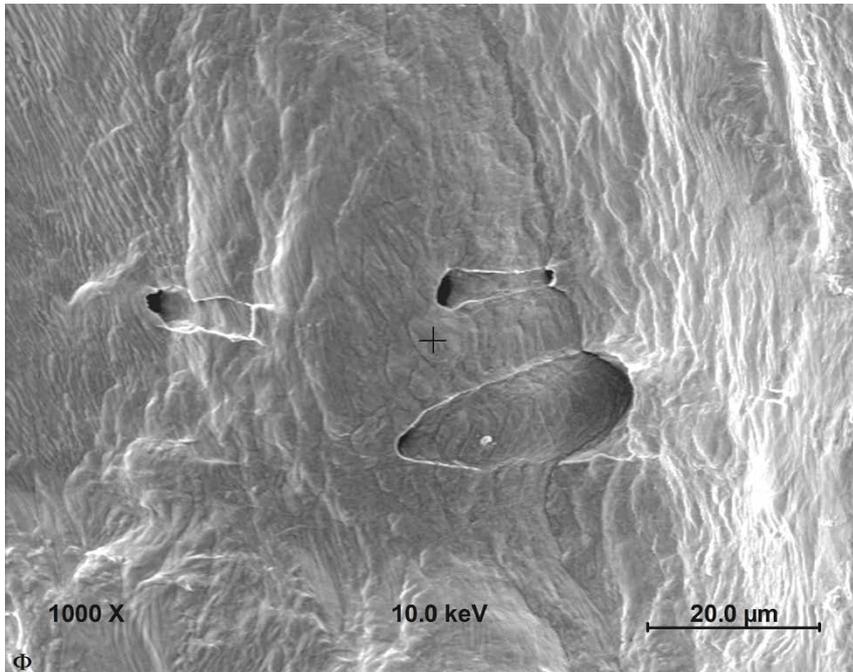


*Figure 3-11. Spectroscopy for previous figure for sample 3 (Figure 3-10).*

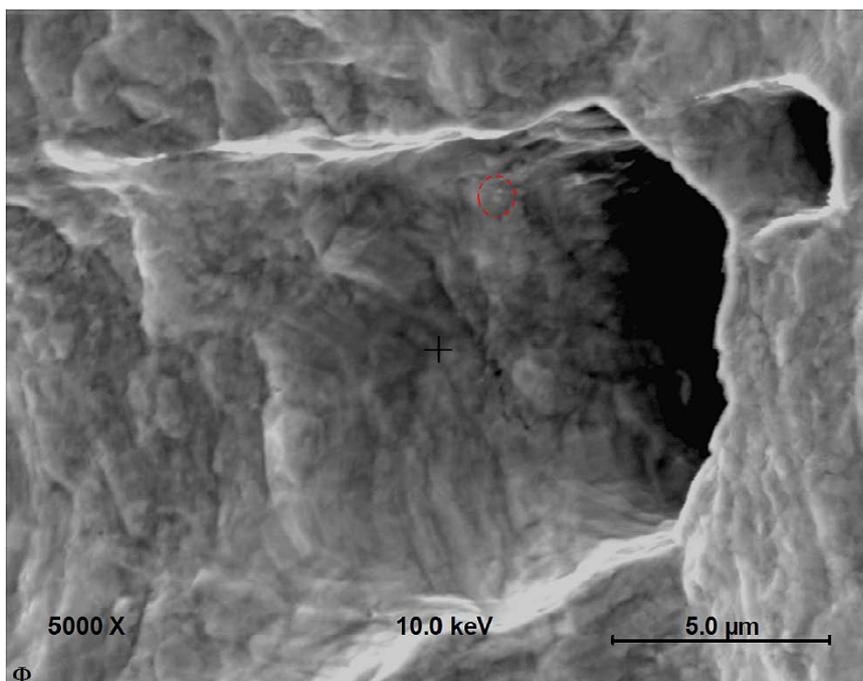
### 3.1.4 Sample 4: 50 ppm P, from gauge length of creep test

Several U-shaped regions were found in this sample (Figure 3-12). One region was measured with spectroscopy and phosphorus was found in 2 particles (Figures 3-13 to 3-15).

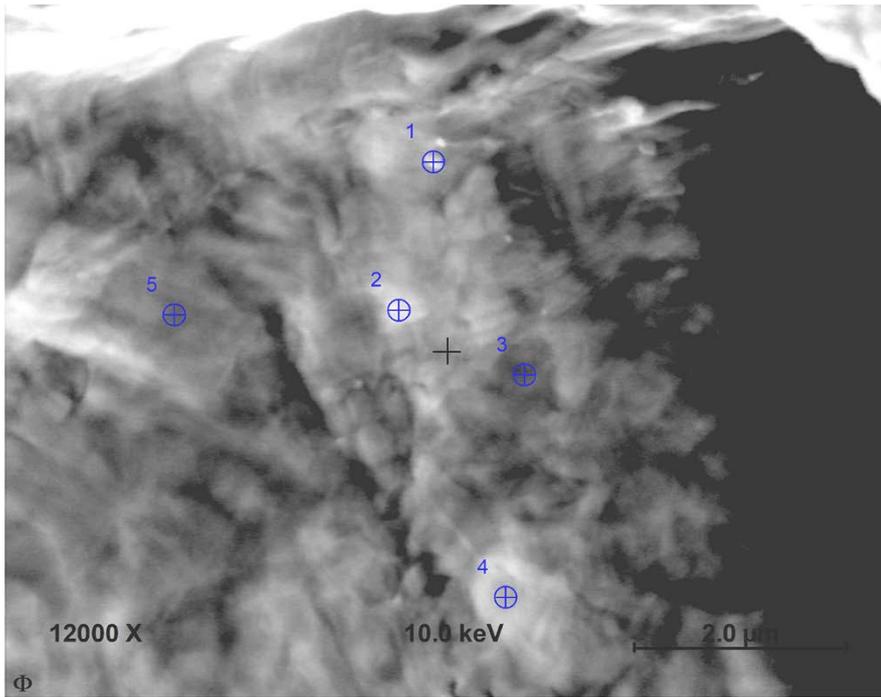
Spectroscopy showed that the particles in Figures 3-16 and 3-17 consisted of carbon (likely pollution from environment, 55 at%), oxygen (15 at%), phosphorus (3 at%), and copper (27 at%). In weight %, the contents were about 8 wt% oxygen, 4 wt% phosphorus, 60 wt% copper and 25 % carbon. In Figure 3-18, only select parts of the electron volt-spectrum were studied to reduce the time for analysis.



*Figure 3-12. U-shaped region found in sample 4.*

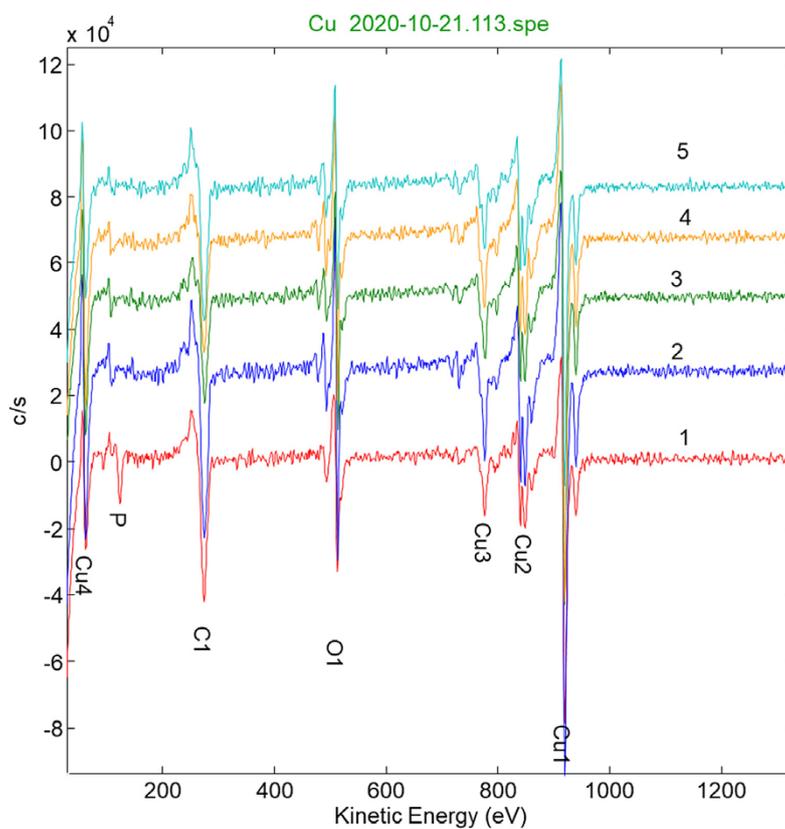


*Figure 3-13. U-shaped region with a smaller region with particles circumscribed in red circle, found in sample 4.*

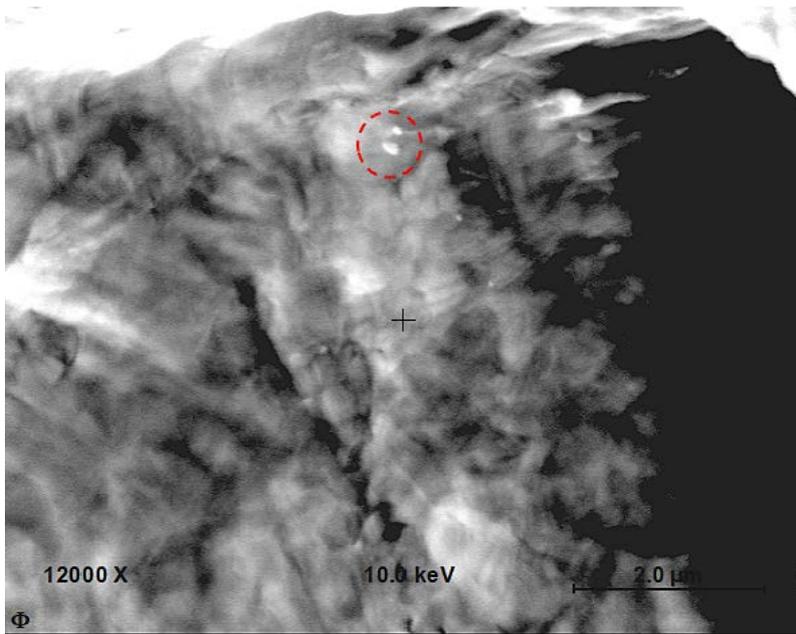


**Figure 3-14.** Region from previous figure (Figure 3-13) in further magnification. Measurement point 1 was found to contain phosphorus.

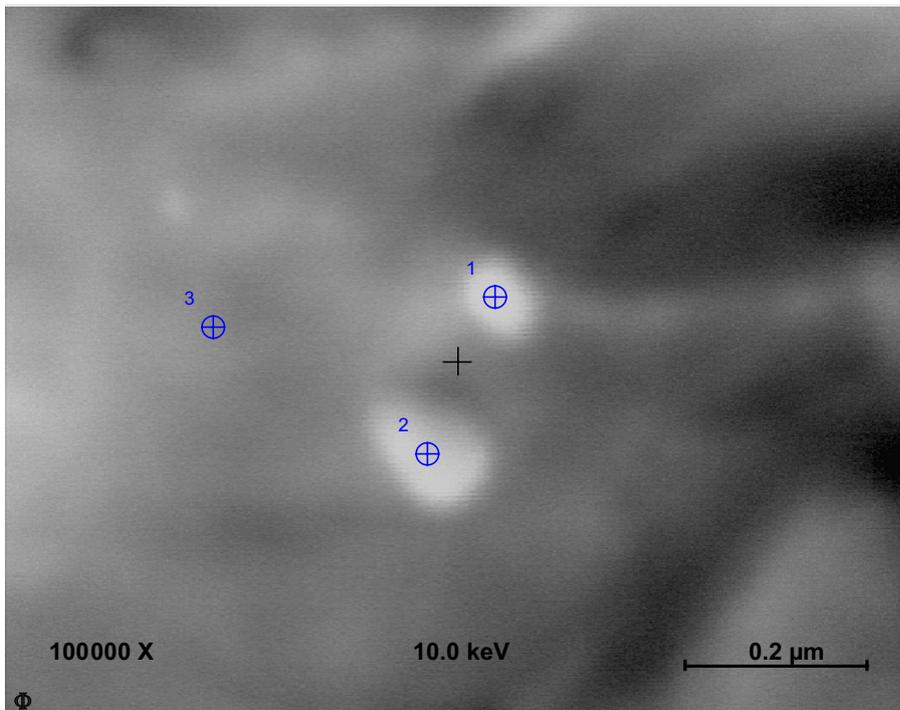
Cu 2020-10-21.113.spe: 30.0eV-1330.0eV, Register	Chalmers
2020 Oct 21 10.0 kV 10 nA FRR	1.2157e+005 max
Sur1/Area1/5 (Der5)	4.34 min
	RSF



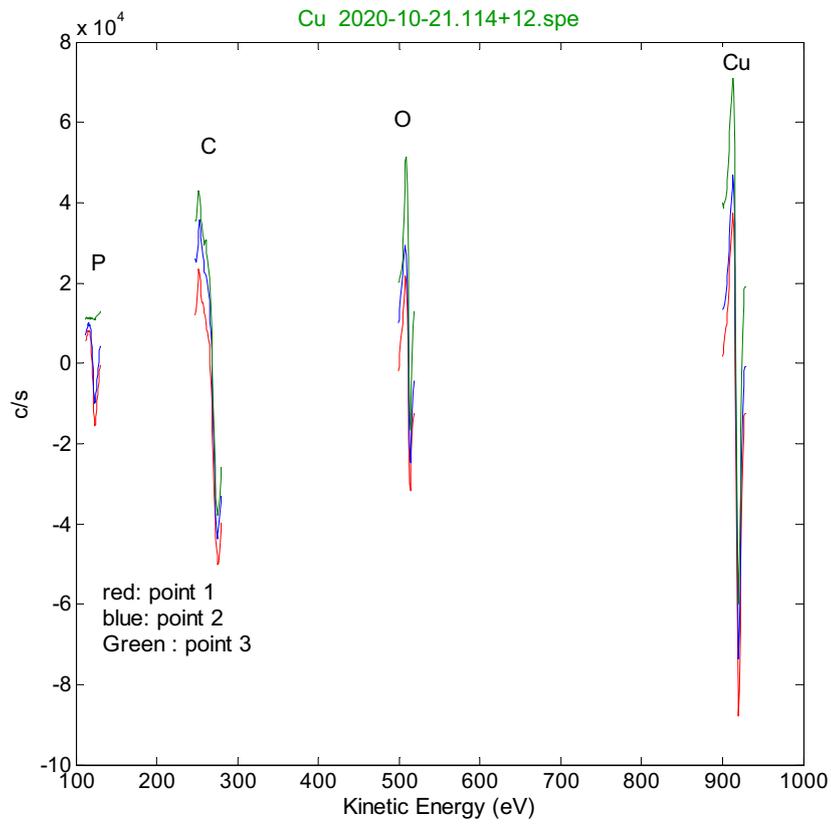
**Figure 3-15.** Spectroscopy for previous figure, Figure 3-14. Measurement point 1 contains phosphorus.



**Figure 3-16.** Region in Figure 3-14 without measurement sites marked out.



**Figure 3-17.** Red-circumscribed region from previous figure (Figure 3-16) in further magnification. Both site 1 and 2, two different particles, were found to contain phosphorus when measured with AES.



**Figure 3-18.** Spectroscopy for previous figure for sample 4 (Figure 3-17).

Table 3-1. Results from AES.

Sample	Material	Phosphorus (ppm)	Material batch or type	Original specimen name or material label	Material category and type	Deformed/not deformed	Stress (MPa)	Temperature (°C)	Time (hours) and minimum strain rate (%/h)	Report reference	Date of study in AES	Comment
1	OFP	105	Extruded Ø 16 mm rods	4K	3 Disrupted creep test (no necking on gauge length)	No, from gripping area	160	175	6 200 h 0.00002 %/h	TR-99-39	2020-10, present study	Phosphorus not found. Sulphur found.
2	OFP	50	Lid material from FSW project, material unaffected by weld.	64 deg	4 From lid, as-received material	No	n/a	RT	n/a	Posiva SKB Report 10	2020-10, present study	Phosphorus not found.
3	OF	0	G221	OF4 G221	4 Taken from copper rod approx. 50 mm diameter.	No	n/a	RT	n/a	n/a	2020-10, present study	Phosphorus not found.
4	OFP	50	T58	Prov 9 (Id nr: 9)	1 Creep test	Yes, from gauge length of creep specimen	170	75	148 h 0.054 %/h	R-17-19	2020-10, present study	Phosphorus found.
5	OFP	50 ppm	T58	n/a	1 Creep test	Yes, from gauge length of creep specimen	Not known	75	Not known	R-14-31	2018, previous study (Sundström et al. 2020)	Phosphorus found previously, see Sundström et al. 2020.

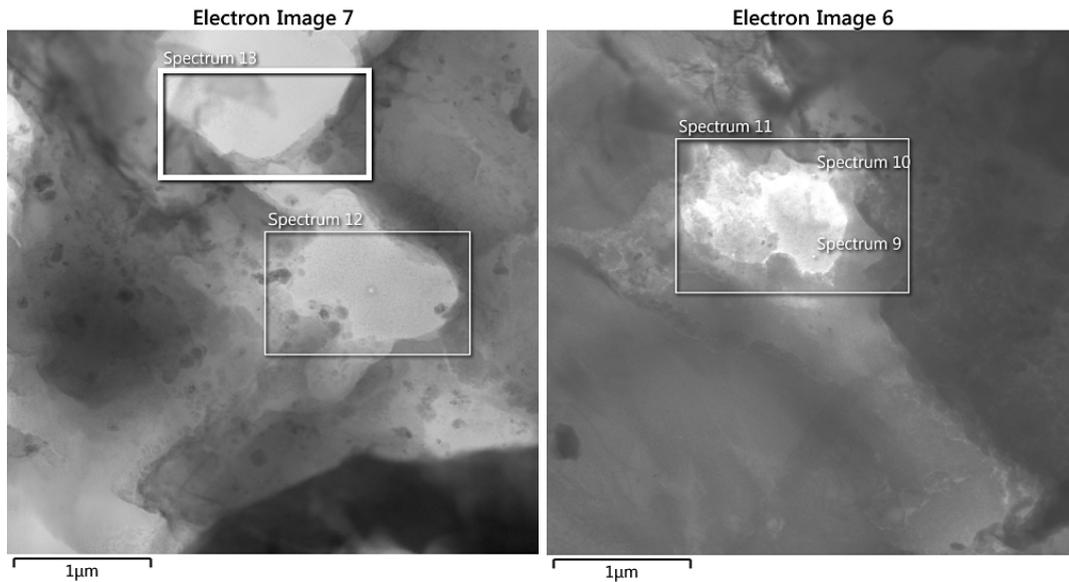
## **3.2 Transmission electron microscopy (TEM)**

The results from the TEM study can be found in Table 3-2. The results show some trends. No phosphorus was found in OF materials (sample 11). No phosphorus was found in undeformed OFP material: in material from the gripping end of the creep specimen (sample 6, sample 13), from a gauge length on an unruptured creep specimen (sample 14) or from as-received (not deformed) material (sample 8). Sample 14 was taken from a specimen that had not ruptured during the creep testing, so there was no necking and had been strained only 0.57 %. It was not as severely deformed as the other creep tested specimens in Table 2-1. The gripping area of this specimen was also studied in AES (sample 1 in Table 3-1) where no phosphorus was found. No phosphorus was found in a slow strain rate tested material (sample 12). But phosphorus was found in material taken from the gauge length of creep tested materials (sample 4, sample 5, sample 7, sample 9, sample 10, sample 15). In sample 5, phosphorus was only found in AES, not in TEM. Examples from the TEM micrographs and the accompanying spectrographs as well as a diffraction pattern can be found in Figure 3-19 to Figure 3-22.

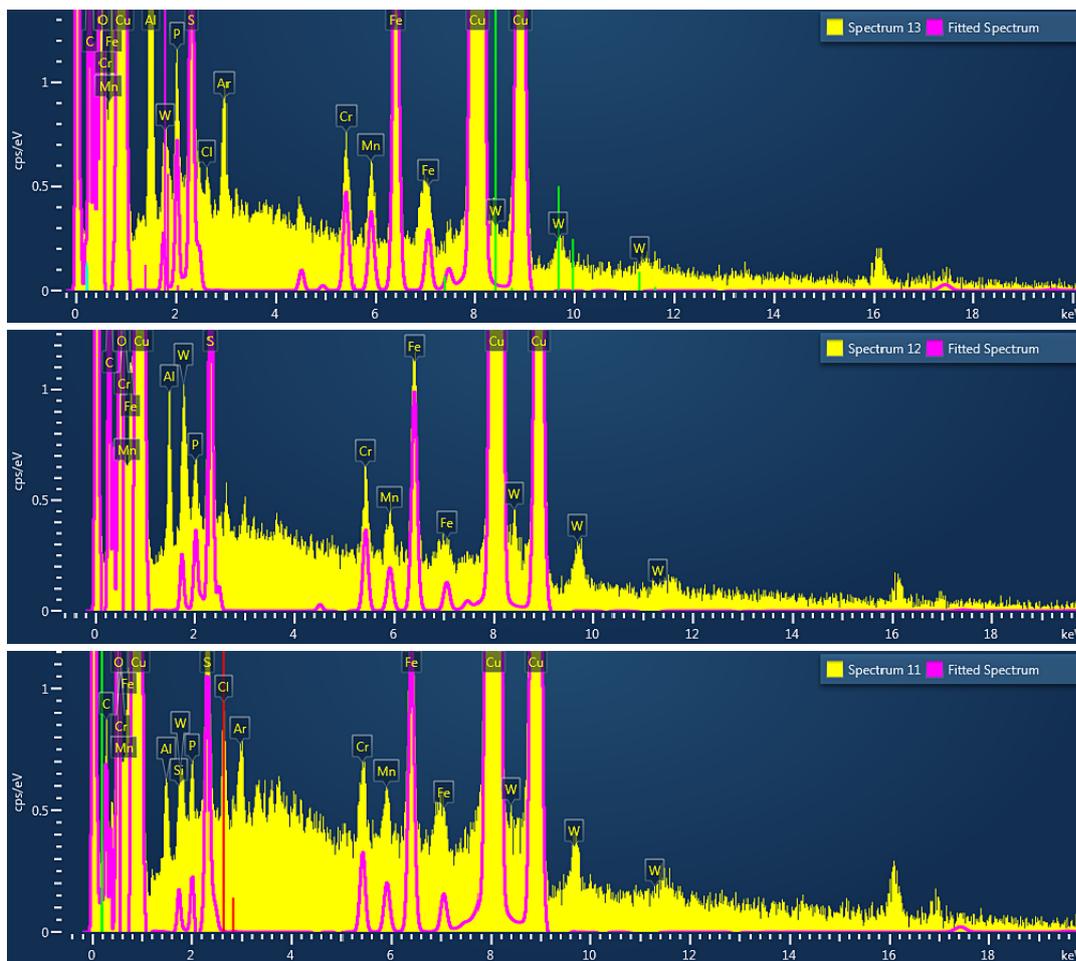
Table 3-2. Results from TEM.

Sample	Material	P (ppm)	Material batch or type	Original specimen name or material label	Material category and type	Deformed during testing?	Stress (MPa)	Temperature (°C)	Time (hours) and minimum strain rate (%/h)	SKB reference	P found (Yes/No)	Notes
4	OFF (T58) (Prov 9)	50	T58	Prov 9	1 Creep tested	Yes, from gauge length of creep specimen	170	75	148 h 0.054 %/h	R-17-19	Yes	Particle containing sulphur and phosphorus coherent with Cu-matrix (Figure 3-22).
5	OFF (T58)	50	T58	Not known	1 Creep tested	Yes, from gauge length of creep specimen	Not known	75	Not known	R-14-31	No	Phosphorus found using AES.
6	Forged lid	50	Forged lid	LID75-2	3 Creep tested	No, from gripping area	170	75	14287 h, 0.0005 %/h	TR-07-08	No	Compare to sample 7. This is non-deformed material taken from grip of the same specimen (original specimen name "LID75-2").
7	Forged lid	50	Forged lid	LID75-2	1 Creep tested	Yes, from gauge length of creep specimen	170	75	14287 h, 0.0005 %/h	TR-07-08	Yes	Compare to sample 6. This is deformed material taken from gauge length of same specimen as 6 (original specimen name "LID75-2"). Sulphur also found.
8	OFF (T58)	50	As-received		4 As-received tube material	Not a mechanical test specimen	0	RT	n/a	n/a	No	
9	HAZ	50	Heat affected zone	HAZ75-2	3 Creep tested	Yes, from gauge length of creep specimen	170	75	360 h, 0.00085 %/h	TR-07-08	Yes	
10	WMI	50	Weld metal, inner	WMI75-2	3 Creep tested	Yes, from gauge length of creep specimen	170	75	2200 h, 0.00132 %/h	TR-07-08	Yes	
11	OF	0	OF	CuPO_300_1N	3 Creep tested	Yes, from gauge length of creep specimen	130	175	29 h, 0.0687 %/h	TR-99-39	No	Sulphur found

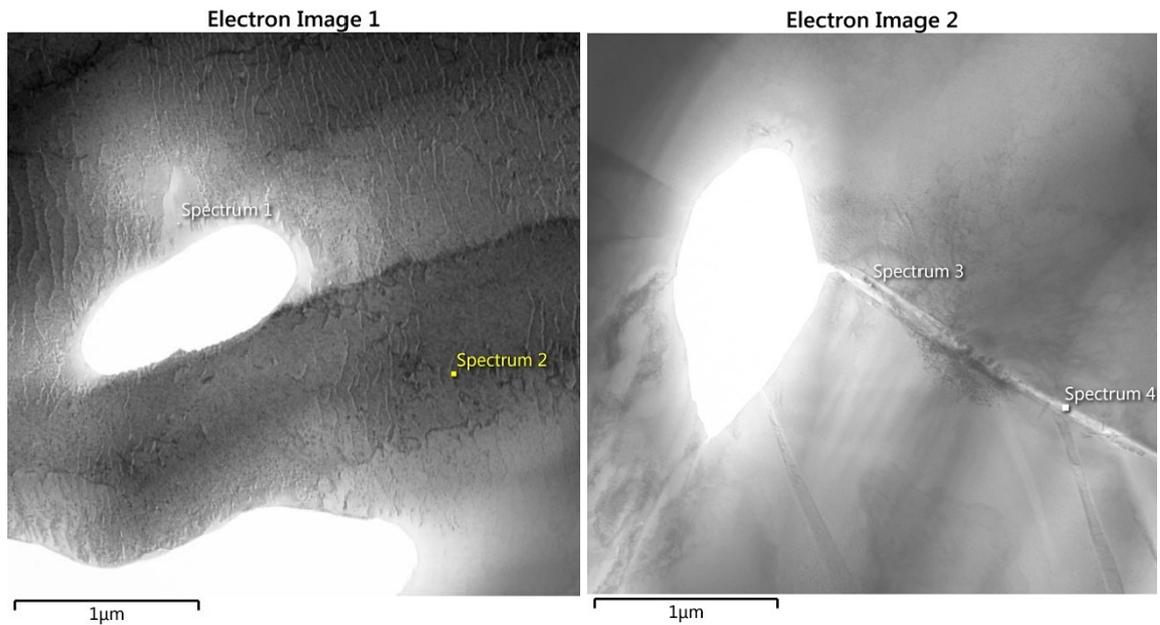
12	OFP-ZnBiTe	67 (also elevated levels of Zn, Bi, Te)	OFP	CuZnBiTe-75-2	2 Slow-strain rate tested	Yes, from gauge length of SSRT specimen	n/a (33 % strain)	75	167 h, 0.19 %/h	SKBdoc 1917201	No	
13	WMI	50	Weld metal,inner	WMI75-2	1 Creep tested	No, from gripping area	170	75	2200 h, 0.00132 %/h	TR-07-08	No	Compare to sample 10. This is material taken from the grip from the same specimen as that in sample 13 (original specimen name "WMI-75-2").
14	OFP	105	OFP	OFP (4K)	1 Disrupted creep test (no necking on gauge length)	Yes, from gauge length of creep specimen	160	175	6 200 h, 0.00002 %/h	TR-99-39	No	Compare to AES sample 1 (Table 3-1). The Auger sample was taken from the gripping area, while the TEM sample was taken from the gauge length.No phosphorus found using TEM.
15	OFP-ZnBiTe	67 (also elevated levels of Zn, Bi, Te)	CuZnBiTe 2 LOT#117130-1	Cu-ZnBiTe 7.2.1	1 Disrupted creep test	Yes, from gauge length of creep specimen	130	175	1079 h, 0.00562 %/h	SKBdoc 1975930	Yes	Compare to sample 12. In the creep test phosphorus was found, but not in SSRT.



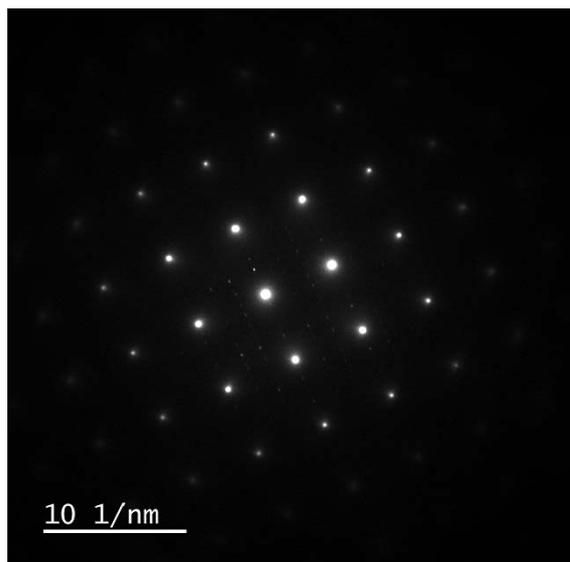
**Figure 3-19.** Sample 15, TEM images with analysis points marked.



**Figure 3-20.** Sample 15, spectrograms from the analysis shown in Figure 3-19. A distinct phosphorus peak can be found in all the spectrograms.



**Figure 3-21.** Sample 13. No phosphorus has been found in this sample. The bright white structure in the left image is a natural hole made during the sample preparation of the TEM foil.



**Figure 3-22.** Electron diffraction patterns from measurements of a particle in sample 4 (Table 3-2), showing that it is coherent with the Cu matrix.



## 4 Discussion

### 4.1 Previous work

Previous studies with ToF-SIMS (Andersson-Östling et al. 2018) have shown that both non-deformed and creep strained copper grains contain phosphorus in solid solution. However, Andersson-Östling et al. (2018) did not find any phosphorus in grain boundaries and no variation of phosphorus content within the grains. No phosphorus containing particles were found. It was concluded that phosphorus was present in solid solution in the copper matrix, although the presence of a monolayer of phosphorus atoms in the grain boundary could not be ruled out using ToF-SIMS. Work with atomic probe topography and TEM (Thuvander 2015) on OFP copper (not creep strained) concluded that there was no segregation of phosphorus to grain boundaries.

While this study does find what appears to be phosphorus-containing particles, it should at the same time be emphasised that most of phosphorus must be in solid solution, partly because of results from previous studies (Andersson-Östling et al. 2018) and thermodynamic considerations (Magnusson and Frisk 2013a) but also since the number of particles found in this study are too few to bind up the amount of phosphorus present in SKB copper (50 ppm phosphorus). Furthermore, both as-received Cu-OFP and creep strained Cu-OFP has been studied in TEM before (Magnusson and Bergqvist 2018) and no accumulation of phosphorus was found in creep strained copper, although 1 of 6 spectrums in the as-received Cu-OFP showed elevated levels of phosphorus, and this spectrum was located at a boundary consisting of dislocations in the material (Magnusson and Bergqvist 2018). That study also used different sample preparation methods than the present work, using either only grinding and polishing or grinding, polishing and argon milling. In both the ToF-SIMS work (Andersson-Östling et al. 2018) and the previous TEM work (Magnusson and Bergqvist 2018), it is not known from where on the creep specimen the strained material was taken. It is possible that it was taken from the gripping area.

The previous work with AES (Sundström et al. 2020) did observe the presence of phosphorus particles on fracture surfaces of creep strained Cu-OFP, but no confident conclusion could be made because two samples were studied at two different labs, and phosphorus particles were only found in one lab. In summary, the previous work shows that the evidence for phosphorus particles, or other kinds of agglomeration, in Cu-OFP is weak and was only observed in one sample using one spectroscopy method (AES), but it must be emphasized that the total number of creep-strained Cu-OFP samples (where phosphorus particles might be expected) in all the studies was low: in total four. One in ToF-SIMS (Andersson-Östling et al. 2018), one in TEM (Magnusson and Bergqvist 2018), and two in AES (Sundström et al. 2020). In the present study, a larger number of samples were studied.

### 4.2 Current work

While the previous studies to some extent contradict the findings of this study, what must be emphasized here is the higher number of samples and the consistency in the findings in the present work, which will be expounded on below. Some discrepancies are also brought up.

In AES, four new samples were studied in the present work. Out of the total of five samples, including the one from previous work (Sundström et al. 2020), phosphorus was found in two samples, both of which were creep strained OFP material taken from gauge length of creep strained specimens (sample 4: Figure 3-12 to Figure 3-18, and sample 5: see Sundström et al. 2020 for images), but it was not found in as-received OFP material (sample 2: Figures 3-5 to 3-8) or as-received OF material (sample 3: Figures 3-9 to 3-11) or in OFP material taken from the gripping area of a creep strained specimen (sample 1: Figures 3-1 to 3-4). As in the previous work (Sundström et al. 2020), so-called 'wakes' or U-shaped regions are found with particles that contain phosphorus (sample 4: Figure 3-12, Figure 3-14) or sulphur (sample 1: Figure 3-4) or neither (sample 2: Figure 3-7). In sample 3, no such regions were found (Figure 3-9).

In the previous work with AES (Sundström et al. 2020) it was shown that the particles contained approximately equal parts phosphorus and oxygen (20–30 at%) and the remainder being copper and small amounts of sulphur (a few at%). Carbon was excluded from that analysis. When carbon was included in the analysis, the proportions were still similar. In the present work, spectroscopy showed that in Figure 3-17, the particles consisted of carbon (55 at%), oxygen (15 at%), phosphorus (3 at%), and copper (27 at%). In weight %, the contents were about 8 wt% oxygen, 4 wt% phosphorus, 60 wt% copper and 25 % carbon. Carbon was not excluded in this analysis. The content of oxygen is extremely low in Cu-OFP but oxygen might have been introduced during sample preparation, both for TEM and AES samples in this study.

In TEM, 15 samples were studied in the present work. 8 of the samples were taken from the deformed part of the gauge length of specimens that had been mechanically tested: 7 of these 8 specimens had been creep tested and 1 of them had been SSRT tested (sample 12, Table 3-2). 1 of the creep tested specimens did not have any necking on the gauge length (sample 14, Table 3-2) but the remaining tests had necking. The remaining 7 samples were taken from either as-received material or the gripping area of creep tested specimens. Among the creep strained material studied in TEM, there was only one sample where phosphorus was not found, sample 14 in Table 3-2. This sample was taken from a creep specimen used in a study performed in 1999 and did not have any necking on the gauge length since it was a creep test that was interrupted because it was evident that it would take very long time to reach rupture, since it had been tested for 6200 hours and only reached 0.57 % total strain and a minimum creep rate of 0.00002 %/h. This could indicate that for the particles to form, enough strain is required.

It is an interesting observation that phosphorus was not found in the SSRT specimen, since SSRT tests usually have a higher strain rate than creep tests but slower than tensile tests. The difference here was about 30 times higher strain rate in the SSRT test (sample 12) compared to a creep test of identical material, although tested at different temperatures (sample 15). However, more SSRT samples would be needed to fully justify this distinction.

One additional observation in the present work is contradictory to the general trends of phosphorus particles being present in creep strained material. One specimen was studied both in AES (sample 5, Table 3-1) and TEM (sample 5, Table 3-2), although in AES it is a new fracture surface being studied while in TEM it is a slice of the interior of the material. With both methods, the sample was taken from a region close to the necking on the specimen. In this specimen, phosphorus was found only in the previous AES work (Sundström et al. 2020) but it was not found in the present work using TEM. This could be pure chance: the particles are small and appear to be few and TEM samples are very small, circular discs with a diameter of 2 mm and a single imaged area being 2 to 9  $\mu\text{m}^2$  for images in this project. The size of the particles in TEM and AES were similar, on the order of 0.1 – 1  $\mu\text{m}$  in size (irregularity in shape means it is misleading to describe them as having a diameter). It also shows that TEM can only reliably show the presence of phosphorus, not the absence of it. For that reason, while it is reasonable that phosphorus is not found where it is not expected such as in Cu-OF (sample 11, Table 3-2 and sample 3, Table 3-1), this discrepancy between the TEM and AES observation decreases the confidence in the ability of TEM to reliably show absence of phosphorus. At the same time, there was one specimen (sample 4) where phosphorus was found both in AES and TEM. Thus, there is one observation that is replicated with both methods, and one observation which is not.

In summary, it seems that the particles only appear in creep strained material. They do not appear in the two samples of Cu-OF that were studied. No phosphorus particles are expected in Cu-OF since that material does not contain phosphorus. Phosphorus acid was not used in the sample preparation for TEM, and no sample preparation is made for Auger since it is the fracture surface being studied there. This means that they are unlikely to be an artifact from the sample preparation. They do not appear in as-received material, nor in the grip ends of the specimens. The grip ends have experienced the same temperature for the same duration (i.e., being in the oven in which the mechanical testing is performed) as the gauge length, but without the creep strain. They are only observed in the gauge length of creep deformed material. This is a consistent trend in this work with a high number of observations in TEM: 7 out of 8 creep strained materials, with one discrepant observation not having an obvious explanation (sample 5). In AES, 2 out of 3 creep strained materials showed presence of phosphorus, and the discrepant result is possibly explained, since that specimen had not ruptured and experienced very little strain.

### 4.3 Suggested mechanism for particle formation and increased ductility

It is always difficult to get an overview of the placement of particles in a TEM study since the samples and imaged areas are so small, but from the micrographs taken in the present work, it seems like the particles are contained in grain boundaries or twin boundaries. They are furthermore not distinct separate particles but more like amorphous structures. Diffraction studies in the TEM shows no difference in the diffraction pattern from the surrounding copper. At the same time, it is possible to make spectroscopy (EDS) on the particles, Figure 3-22, and phosphorus and sometimes sulphur is present in the particles.

Based on the findings, some speculation can be made on the mechanism of formation for the particles observed in the present work.

Phosphorus is probably concentrated into particles that form in microvoids in the material, formed by phosphorus moving along diffusion pipes (see Love 1964 for a description on dislocation pipe diffusion) and being collected at microvoids already present there, or microvoids whose formation is caused by the transport of phosphorus to the site. These are not crystalline particles but rather an agglomeration of sulphur and phosphorus into amorphous globules that can be observed in TEM. The term “particle” has been used throughout the report, but it does not indicate a discrete crystalline phase globular in shape that can be distinguished from the surrounding matrix using diffraction techniques. The “particles” are instead amorphous irregular or globular structures that appear as bright features of 0.1 to 1  $\mu\text{m}$  in size in electron microscopy.

If the voids form first and the particles then fill the voids, or if the formation of the particles creates the voids is not known. One can find voids without particles but not particles without traces of voids. The voids without particles could result from particles falling out during sample preparation. The particles exhibit signs of being amorphous, not crystalline. Sulphur is also present in the particles, sometimes only sulphur but most often a mix of sulphur and phosphorus. This should not be taken as evidence for a much higher concentration of sulphur since the detection limit for sulphur is much lower than for phosphorus. The analysis is qualitative, not quantitative regarding detected amounts of sulphur and phosphorus. Sulphuric acid was also used during sample preparation in TEM (but not in AES), which makes it difficult to draw conclusions about sulphur.

Furthermore, it is known that the general diffusion rate for phosphorus in pure copper is extremely low at room temperature and slightly elevated temperatures (below circa 200 °C) (Magnusson and Frisk 2013b). This statement only concerns the general diffusion rate, not grain boundary diffusion (see Magnusson and Frisk 2013b for a description of grain boundary diffusion) and pipe diffusion (Love 1964) where the pipe could be a collection of dislocation lines (a bundle of dislocations). What the diffusion rate could be for these mechanisms in creep strained Cu-OFP is not known to the author, but diffusion distances for phosphorus in non-strained copper were calculated in Magnusson and Frisk 2013b based on a literature review. At elevated temperatures (above 500 °C, far higher than what has been used for creep testing of Cu-OFP and Cu-OF), grain boundary diffusion of phosphorus in copper is 140 times faster than self-diffusion of copper in grain boundaries. It is also known that the diffusion rate of phosphorus can be increased by a much higher rate by straining (Sandström 2018), which is known as strain induced diffusion. This could very well explain why P-particles only appear in creep deformed material.

Phosphorus should thermodynamically be in solid solution (Magnusson and Frisk 2013a) at the amounts and temperatures studied (room temperature to 175 °C, 0 to 105 ppm P). It is however important to note that in the presence of oxygen, copper phosphate particles could appear (Cu-P-O) (Magnusson 2017, Magnusson and Frisk 2013a). The content of oxygen is extremely low in Cu-OFP but oxygen might have been introduced during sample preparation, both for TEM and AES samples in this study.

When all the evidence obtained from the present study is summarised, the following mechanism for formation of phosphorus particles is proposed. Phosphorus at the content levels found in Cu-OFP stay in solid solution from the initial manufacturing of the material, through the mechanical and heat treatments of the material and during the specimen manufacturing process. When the material is then creep tested the creep deformation opens diffusion pipes for phosphorus to diffuse along and the result

is the formation of phosphorus and sulphur containing particles. The same particles are then likely active in the creep process and contribute to the increase of the creep ductility to 30–50 % compared to the common 2–5 % for non-phosphorus containing copper. This is a combination of an empirical statement (creep testing properties of Cu-OFP) and a microstructural observation statement (phosphorus containing particles). The suggested mechanism for the increase in ductility would be that the particles stabilize grain boundaries, preventing the grain boundaries from becoming brittle which increases the ductility. More work is needed to provide evidence for this proposed mechanism. Work that could elucidate this would be calculations on diffusion rates of phosphorus in creep tested copper, which is being performed in a new project.

## 5 Summary

Previous work with high-resolution microscopy (TEM, SEM), spectroscopy (EDS) and spectrometry (ToF-SIMS, APT) techniques showed that:

- Studies using TEM, EDS, ToF-SIMS and APT have not shown the presence of phosphorus-containing particles or other kinds of phosphorus agglomeration in deformed Cu-OFP or non-deformed Cu-OFP (Magnusson and Bergqvist 2018, Bergqvist and Gordon 2018, Andersson-Östling et al. 2018, Thuvander 2015).
- A study using Auger spectroscopy (Sundström et al. 2020) showed the presence of phosphorus containing particles on fracture surfaces of creep strained Cu-OFP. Two samples were studied in two different labs, one sample for each lab. It was only observed in one of the two labs that performed the work.

Present work with high-resolution spectroscopy (AES, EDS) and microscopy (SEM, TEM) shows that:

SEM and AES

- On fracture surfaces in creep strained Cu-OFP, phosphorus containing particles were observed in SEM. Presence of phosphorus in the particles was shown using AES. These particles were only found in creep strained Cu-OFP: in one sample from the present project, and one from the previous project (Sundström et al. 2020). The particles are of size 0.1 to 0.5  $\mu\text{m}$  and irregular or globular in shape.

TEM

- TEM studies show amorphous particle-like structures containing phosphorus in the microstructure in creep strained Cu-OFP. The structures are irregular in shape and 0.1 to 1  $\mu\text{m}$  in size. A total of 15 samples were studied, of which 8 were taken from the deformed part of the gauge length of specimens that had been mechanically tested: 7 of these had been creep tested and 1 of them had been slow strain rate tested. Among the creep strained Cu-OFP samples studied in TEM, there was only one sample where phosphorus was *not* found, which was possibly explained by the low amount of creep strain it had experienced.
- No phosphorus containing particles were found in non-creep strained Cu-OFP material.
- TEM studies show no phosphorus containing particles in the one slow strain rate tested specimen.
- Additionally, phosphorus was not found in a Cu-OFP creep specimen which had a low amount of strain and low strain rate.

Mechanisms for particle formation and effect on ductility

- This study supports the hypothesis that phosphorus is agglomerated into particles in deformed copper.
- The mechanism for formation of these particles is not known, but some speculation can be made based on the present work. It is likely driven by diffusion mechanisms which increase the diffusion rates of phosphorus in copper. Since there is no data known on the diffusion rates of phosphorus in creep strained phosphorus containing copper material, it is currently difficult to find support for this. A new project is under way to estimate such diffusion rates from experiments.
- The particles could be instrumental in the transformation of the creep properties of copper with and without phosphorus content. The suggested mechanism for this would be that the particles stabilize grain boundaries, preventing the grain boundaries from becoming brittle. This would increase the creep ductility of Cu-OFP.



## 6 Conclusions

- This study shows evidence of agglomeration of phosphorus into particles in creep deformed copper.



## References

SKB's (Svensk Kärnbränslehantering AB) publications can be found at [www.skb.se/publications](http://www.skb.se/publications). SKBdoc documents will be submitted upon request to [document@skb.se](mailto:document@skb.se).

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**Bergqvist H, Gordon A, 2018.** TEM analysis of grain boundaries in copper samples from MiniCan 4. Swerea KIMAB. SKBdoc 1628820 ver 1.0, Svensk Kärnbränslehantering AB.

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