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Author: Mattias Thuvander

Research

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Investigation of the Distribution of Phosphorus in Copper

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SSM perspective

Background

Copper alloyed with 30-100 ppm phosphorus (P) is used as the corrosion barrier of the canister which will be used for long term storage of spent nuclear waste for the KBS-3 concept proposed by SKB. The reason to add 30-100 ppm P is its positive effect against creep embrittlement. It have been proposed that the mechanism behind this effect is that P affects the motion of dislocations in the grain boundaries and thus the grain boundary sliding which will reduce the formations of creep cavities. According to the mechanism proposed, the amount of P at the grain boundaries should be significantly higher compared with the bulk analysis of the material. However, no experimental evidence has been presented that support the proposed mechanism.

Objective

The objective of this work is to find experimental support for the proposed mechanism to increase the creep ductility of copper material.

Results

The amount of P in the center of the grains was measured by atom probe tomography (APT). The P concentration was found to be about the same as the bulk concentration of the material. Additionally, the P concentration at the grain boundaries was analyzed using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). No P could be detected at the grain boundaries suggesting that the local grain boundary concentration of P is less than 0.1 at%. If the concentration of P would have been significantly higher, i.e. 10 times, in the grain boundaries compared to the bulk concentration, this would have been spotted in the analysis.

The results of the investigation do not support the proposed mechanism for the effect of P on the creep ductility of P doped copper material.

Need for further research

The performed investigation revealed difficulties with APT analysis of copper. Therefore no APT analysis was carried out for a sample with a grain boundary. Further research is needed to develop the methods for APT analysis of copper material with the goal to be able to perform APT analysis of copper samples containing grain boundaries.

Project information

Contact person SSM: Peter Ekström
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Author: Mattias Thuvander

Department of Applied Physics Chalmers University of Technology

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Content

1. Sammanfattning

Två kopparlegeringar med olika fosforhalt, 6 respektive 80 vikts-ppm, har undersökts i denna studie. Matrisen i båda legeringarna undersöktes med atomsondstomografi (APT). Fosforhalten i matrisen i materialet med 80 ppm uppmättes till ungefär samma som totalhalten, vilket visar att fosfor till största del finns kvar i matrisen. Korngränser i detta material undersöktes med transmissionselektronmikroskopi i kombination med energidispersiv röntgenanalys, men fosfor kunde inte detekteras. Detta visar att fosforhalten i den aktuella volymen vid korngränsen är mindre än ungefär 0,1 atom-%, vilket också kan uttryckas som att korngränsernas täckningsgrad är mindre än en tiondel av ett monolager. Resultaten från denna studie indikerar att mekanismen för fosfors positiva inverkan på kryp-försprödning inte är relaterad till kraftig korngränssegring.

2. Summary

Two copper alloys containing different amounts of phosphorus, 6 and 80 wtppm, respectively, have been investigated. The matrix of both alloys was analysed using atom probe tomography (APT). The matrix P concentration in the 80 wtppm P material was about the same as the bulk concentration and it was therefore concluded that the majority of the P atoms resides in the matrix. Grain boundaries in the alloy containing 80 wtppm P were investigated using transmission electron microscopy and energy dispersive spectroscopy. No P could be detected, suggesting that the local grain boundary concentration should be below about 0.1 at%, or alternatively that the grain boundary coverage is smaller than 1/10th of a monolayer. The results in this study suggest that the mechanism by which P suppresses creep embrittlement is not related to strong GB segregation.

3. Background

This investigation was initiated by the Swedish Radiation Safety Authority (SSM). Two copper alloys, containing different levels of phosphorus, have been studied. The material OFP[1] contained 80 wtppm P, whereas the material OFHC[2] contained 6 wtppm. The chemical composition of the materials is shown in table 1. The OFP material originates from an extruded pipe, whereas the OFHC material comes from a 19 mm bar. Both the matrix and grain boundaries (GBs) should originally be analysed using atom probe tomography (APT). Due to unexpected difficulties to do APT on Cu, the plans were changed. The matrix of both alloys was analysed using APT, but grain boundaries, only in OFP, were analysed using transmission electron microscopy (TEM) and energy dispersive spectroscopy (EDS). One attempt to analyse a GB with APT was made, but failed.

The underlying reason to study P in Cu, is that it has been found that P has a positive effect against creep embrittlement. However, the mechanism behind this effect is still not known.

Table 1: Composition (wtppm, except for Cu) of the two materials, obtained from D-lab.

	OFP	OFHC
Mn	0.5	1.6 ± 0.1
P	80 ± 4	6 ± 0.8
S	7 ± 2	7 ± 2
Cr	4 ± 0.6	7 ± 0.7
Ni	1 ± 0.4	1 ± 0.4
Cu	99.99 ± 0.01%	99.99 ± 0.01%
Co	1.6	1.3
Sn	0.2	0.2
As	1.0	1.0
Pb	4	5 ± 1
Bi	1.0 ± 0.5	1.0 ± 0.5
Fe	4	15 ± 2
O	3	9
Sb	1.0	1.0
Zn	1	1
Zr	1	2
Ag	16 ± 0.8	15 ± 0.8
Cd	0.2	0.1
Te	3.0	2.0
Se	1.1	1.0
H	<0.2	0.3

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[1] OFP = Oxygen Free Phosphorus Doped Copper

[2] OFHC = Oxygen Free High Conductivity Copper

4. Experimental details

Light Optical Microscopy

In order to roughly estimate the grain size using light optical microscopy (LOM), polished samples were etched in a solution of ammonium peroxydisulfate (10 g) in water (100 ml). This etching also made GBs visible when performing specimen preparation for APT and TEM using focused ions beam/scanning electron microscopy (FIB/SEM).

FIB/SEM

Two different FIB/SEM instruments were used; FEI Strata (old) and FEI Versa (new). As the GBs were visible, the samples could be taken from the right region. Figure 1 shows the position of a matrix APT sample in OFP, far from any GB.

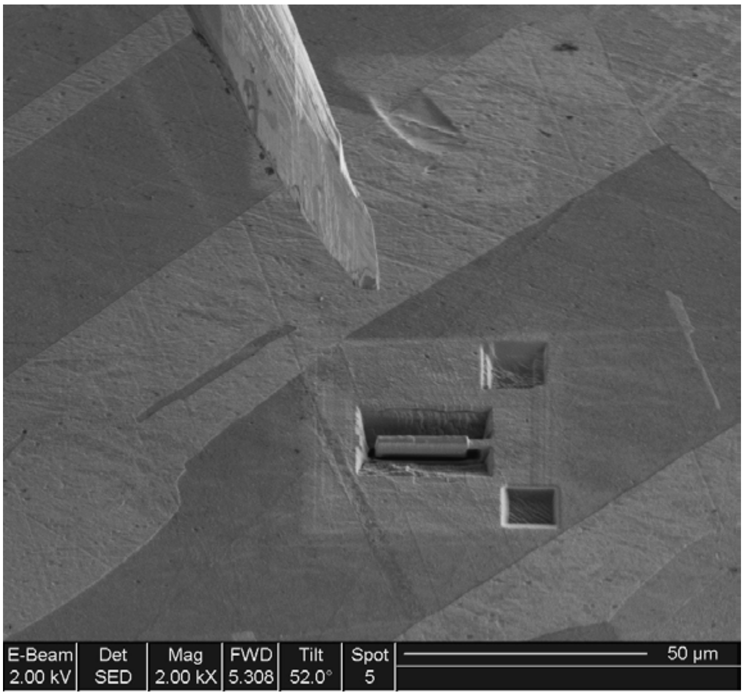

Figure 1. FIB/SEM lift-out sample in the material OFP. The needle seen is the so called omniprobe, which is used to lift out the sample, that can then be sharpened to an APT sample or thinned to a TEM sample.

APT

Copper has been investigated surprisingly little using APT. One would think it should be an easy material to analyse, like for example nickel, which is one of the easiest. However, in this project it was noted that it is very difficult to get good analyses. In laser pulse mode, which can be used to analyse a wide spectrum of materials; most metals, oxides, carbides, semiconductors and even bone, Cu gives a very high background, making it largely impossible to quantify elements of low concentration. In voltage pulse mode the mass spectrum looks much better, but the background (noise) is dependent on the pulse frequency. At the standard pulse frequency of 200 kHz, the background was found to be about 7 times higher than at 10 kHz. Such a low frequency, of course, results in a much longer experiment time. As often in voltage pulse mode, the number of ions detected before specimen fracture is much smaller than when using laser pulse mode.

During this project contact was made with Mr. Hisham Aboulfadl, University of Saarbrücken, and Dr. Francisca Mendez-Martin, University of Leoben. Both these researchers have recently been working on APT of Cu, and they have made similar observations. Apparently, the situation is similar for silver. There are some new theories on the way to explain why laser pulsing does not work well for these materials. The reason why the background when using voltage pulsing is frequency dependent does also not seem to be known. Possibly, slower pulsing leads to more adsorption of hydrogen from the ultra-high vacuum, which somehow could stabilize the evaporation process.

The instrument used in this project was a local electrode atom probe (LEAP) from Imago (now Cameca), model 3000X HR. For the runs giving useful results voltage pulsing was used with a pulse fraction of 20%, pulse frequency 10 kHz, temperature 70 K and evaporation rate 1%. The data was evaluated using the software IVAS 3.6.

TEM/EDS

A TEM/EDS investigation was made using an advanced TEM instrument, FEI Titan, equipped with a monochromator, and it has an aberration-corrected probe. It was operated at 300 kV. Prior to the analysis using Titan, the sample was checked in a standard TEM instrument, FEI Tecnai. Both instruments are equipped with EDS analysers, from Oxford Instruments (Titan) and EDAX (Tecnai), respectively.

5. Results

LOM

Images from LOM are shown in figures 2-3. The grain size of the OFP material was about 200 µm, whereas the grain size of OFHC was much smaller, about 20 µm.

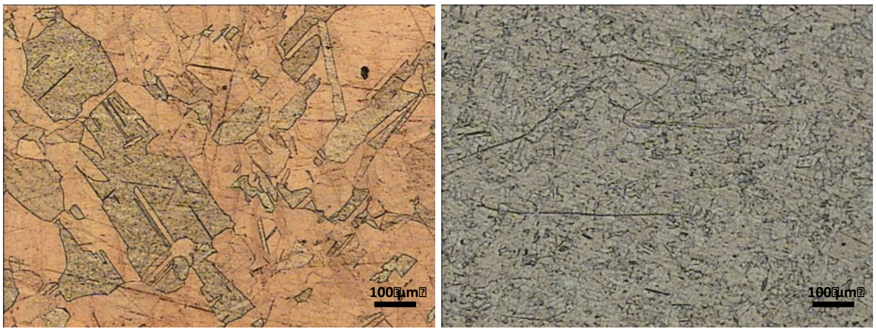

Figure 2. Material OFP to the left, and OFHC to the right. The grain size is much larger in OFP than in OFHC.

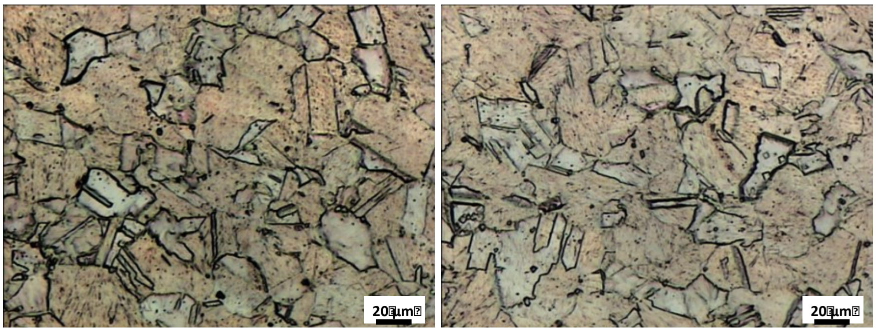

Figure 3. Images at higher magnification of OFHC.

APT

Mass spectra from successful runs of OFP and OFHC are shown in figures 4-5. These were made using voltage pulsing at 10 kHz and both contain about 4 million atoms. In both analyses Cu is detected as Cu+, Cu2+ and CuH2+. In the spectrum from OFP, phosphorus peaks are present as P+ (31 Da), P2+ (15.5 Da) and P2+ (62 Da). In the spectrum from OFHC, on the other hand, no P-peaks can be observed. As the P content in OFHC is very low, this proves that the P-peaks observed in the OFP mass spectrum definitely are phosphorus, and not caused by other ions from some sort of contamination etc.

The following peaks were observed in both spectra; O+, CO+, CO2+, Cl+, CuO+ och CuCl+. The measured composition is presented in table 2. The measured P content in OFP is 140 atppm (about 70 wtppm). This is only marginally lower than the bulk concentration, and considering reasonable errors, the bulk concentration is within the error-bars of the measurement. The conclusion must be that more or less all P is in solid solution in the matrix.

As the amounts of oxygen and chlorine are much higher than expected, these signals probably origin from some sort of contamination or oxidation, or from the vacuum.

The distribution of P atoms in the analysed volume of the OFP material is shown in figure 6. The distribution within this volume is homogeneous. Towards the end of the analysis a region enriched in Si was encountered. The local Si content was about 5 at%. It is not clear what this could be. Another interesting element in the Cu alloys is sulphur. Using APT, low levels of S can hardly be measured, because of overlaps with O2+ and CuH2+.

One additional run was made on the OFP material with the same experimental parameters. This run was short and it was not good enough to allow proper quantification to be made, but it confirmed the presence of P. Also, one attempt was made to make a lift-out sample from a GB. Unfortunately the run was very short, and did not contain any GB. In order to increase the chance of finding a GB some development of the FIB/SEM procedure has to be made; the width of a lift-out is typically 2 μm, and the analysed width is below 100 nm, making the chance of hitting the GB small.

Table 2: The measured composition of the matrix (at% or atppm). For the OFP analysis, the Si-rich region has been excluded. The error bars are judgements from experience.

	OFP	OFHC
O	0.05 ± 0.01%	0.09 ± 0.02%
Cl	0.05 ± 0.01%	0.008 ± 0.002%
P	140 ± 20 ppm	< 20 ppm
N+Si	20 ± 5 ppm	< 20 ppm

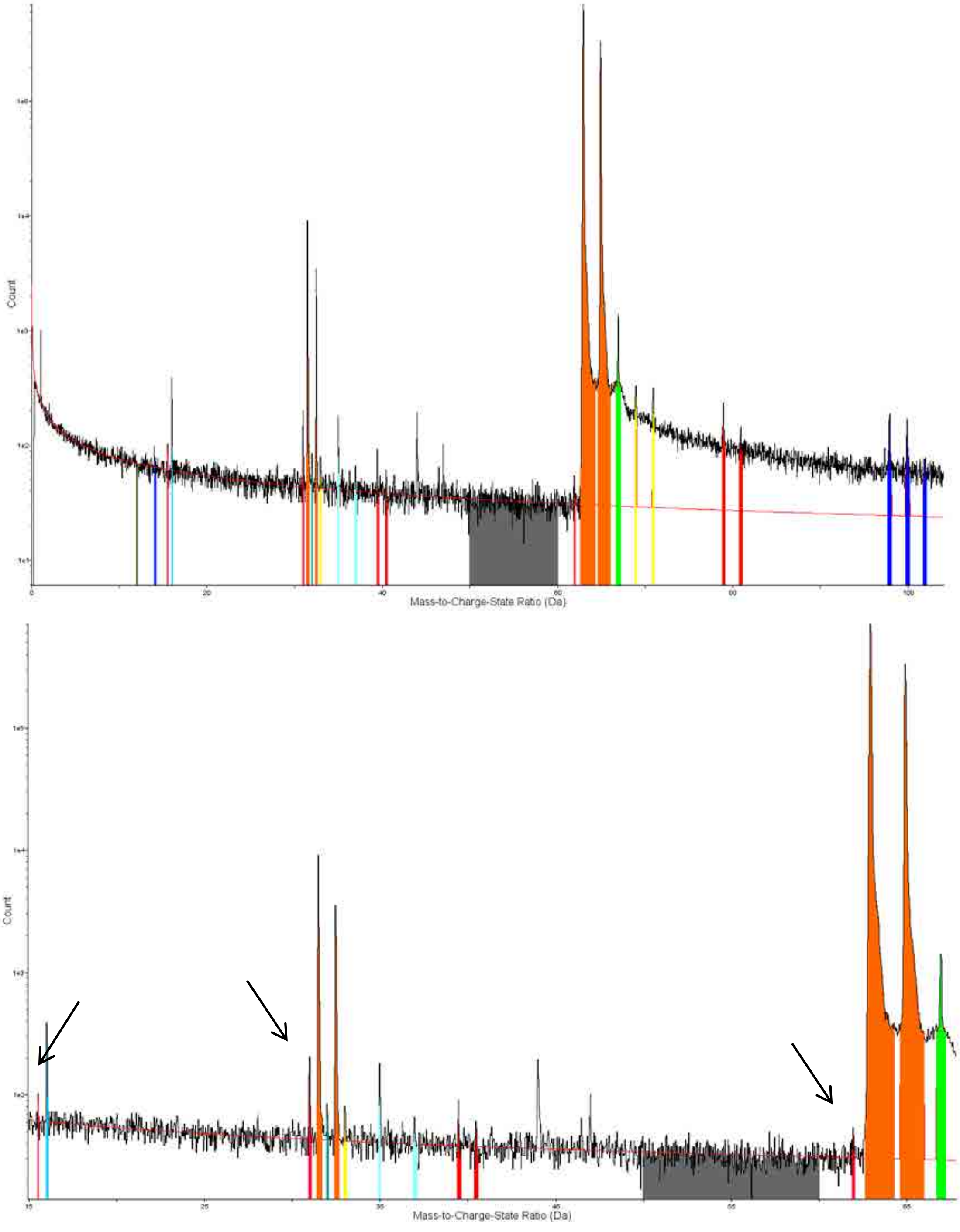

Figure 4. APT mass-to-charge-state spectra from OFP. The upper spectrum shows the range from 0-100 Da. The bottom spectrum shows 15-65 Da. Phosphorus was identified at the masses 15.5 (P^{2+}), 31 (P^{+}) and 62 (P_2^{+}), red peaks marked with arrows. Note that the y-scale is logarithmic.

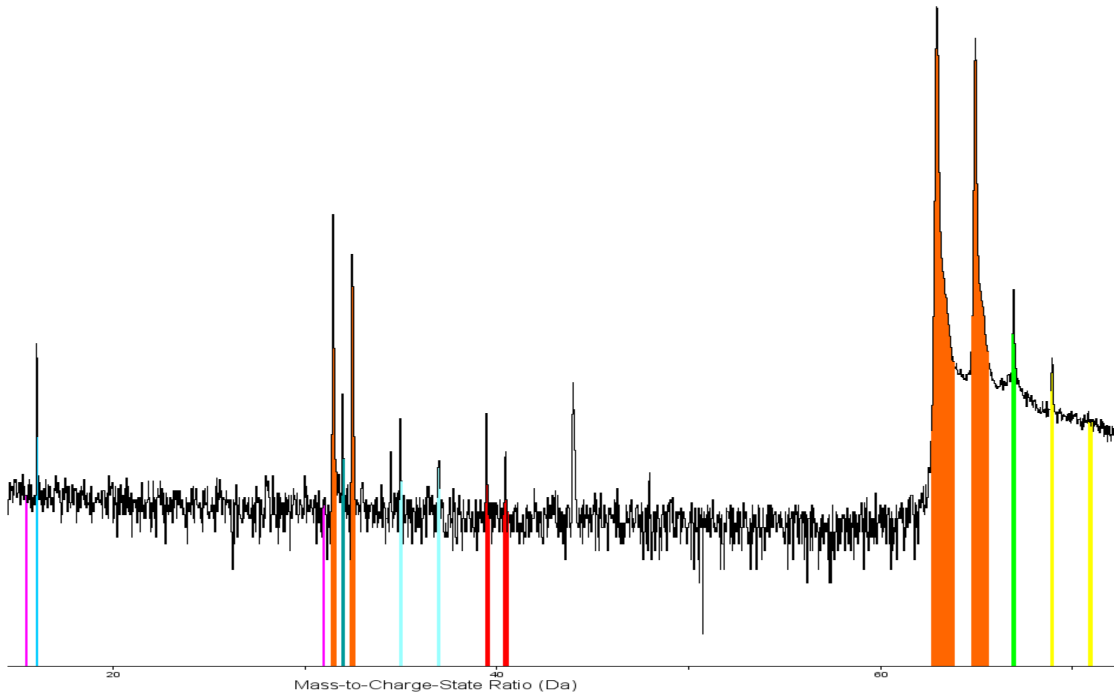

Figure 5. APT mass-to-charge-state spectra from OFHC. There are no peaks that can be assigned to P, compare with figure 4. Note that the y-scale is logarithmic.

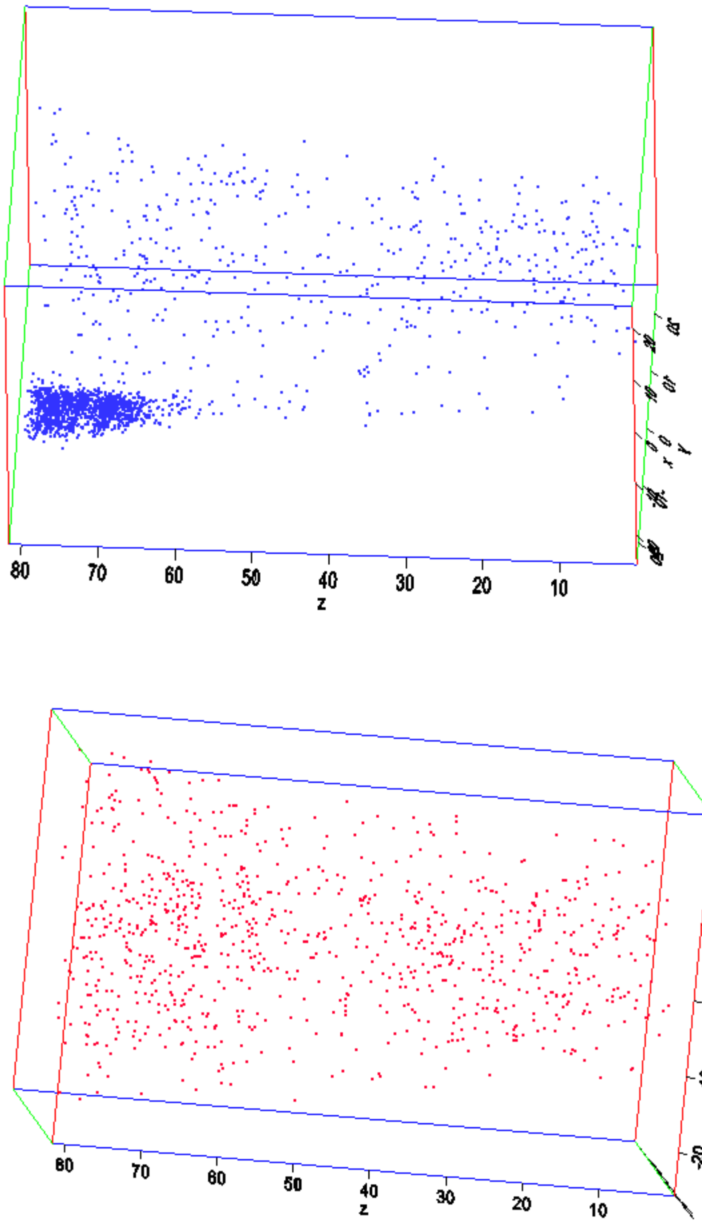

Figure 6. The upper image shows the distribution of Si (and N, which overlaps with Si at 14 Da). The bottom image shows the distribution of P. The axes are labelled in nm. The analysed cube has dimensions 50×50×80 nm^3.

TEM/EDS

TEM images of the OFP material are shown in figures 7-8. The sample was made with FIB/SEM and a region containing a GB was chosen. In fact, the region also contains a triple point, see figure 8. No signs of any precipitation could be seen in the images, also not at the triple point, where the chance of finding precipitates would be greatest. If there were significant P segregation it could happen that some precipitates (Cu3P) would form.

A careful EDS investigation was undertaken using the Titan microscope. Spectra were acquired at several positions in the matrix and at the three GB segments (see figure 8) and at the triple point. Nowhere P could be identified. One example of a spectrum from a GB is shown in figure 9. At the position in the spectrum where a P peak should appear, there is only the background noise present. As a comparison, the segment of the spectrum containing Fe is also shown in figure 9. The clear Fe peak observed was quantified to 0.1 at%, thus providing an estimate of the detection limit. In this case Fe probably does not come from the sample, but from stray radiation (holder, pole piece etc.).

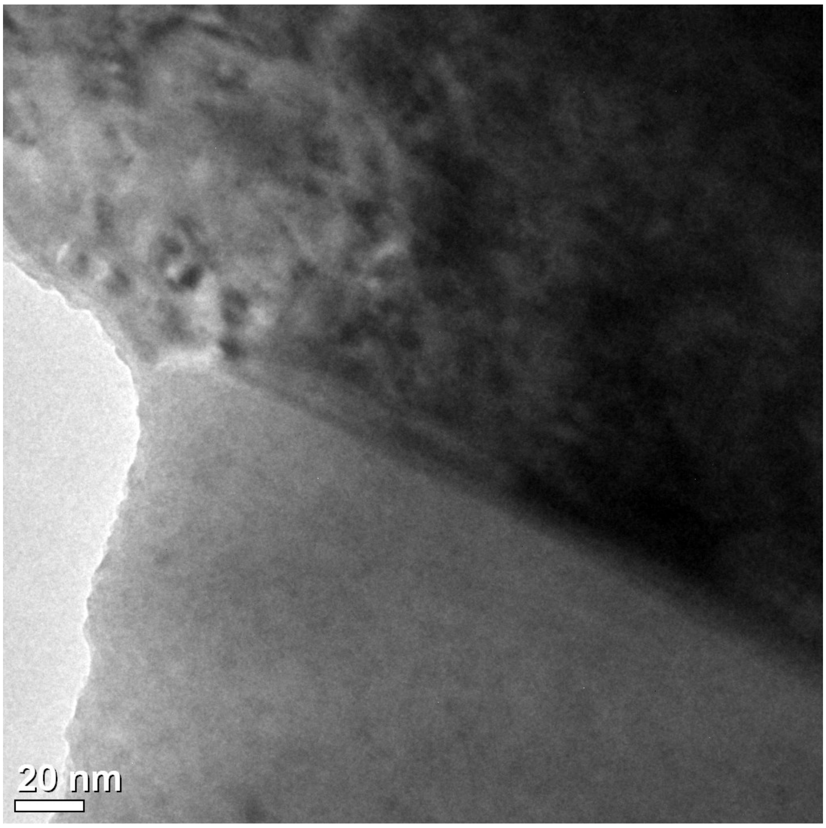

Figure 7. TEM image of a GB in OFP (Tecnai).

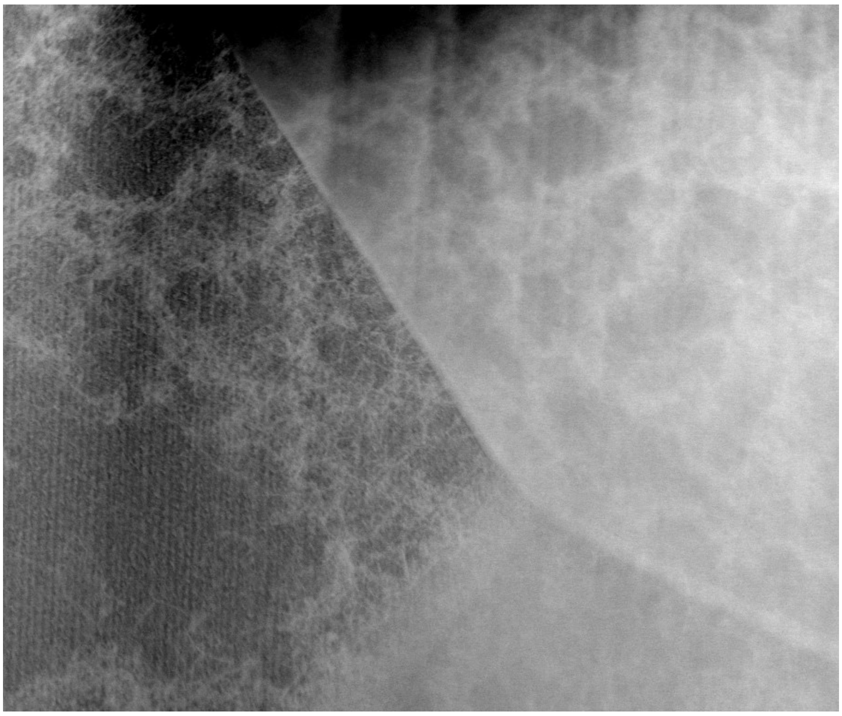

Figure 8. TEM (HAADF) image of three GBs and a triple point in OFP (Titan).

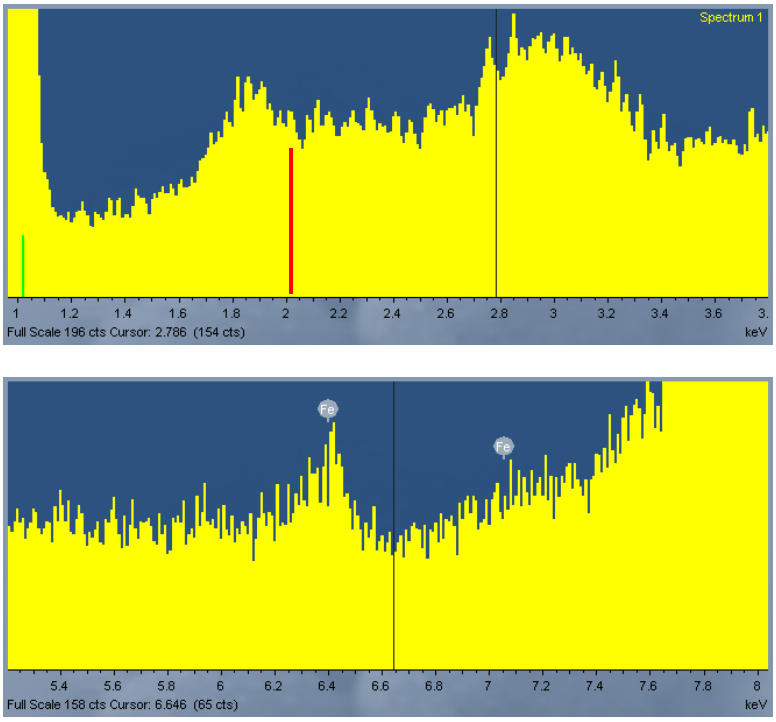

Figure 9. EDS spectrum from a GB in OFP. No P can be measured. P has its main peak at 2.01 keV (red line), but at this energy there is only noise (see upper spectrum). For comparison the Fe peak (6.4 keV) is shown in the bottom spectrum. From this peak the Fe content was determined to 0.1 at%. This signal probably stems from stray radiation, and does not come from the Cu sample.

6. Discussion

The matrix P content of the OFP material measured with APT was almost the same as the bulk concentration. This shows that the matrix has not been significantly depleted, which could have happened if precipitates (Cu3P) had formed. This is the same as to say that the P content of 80 wtppm is below the solubility limit at the relevant temperature. However, from the measurement of the matrix P content it cannot be said that no segregation to GBs takes place. As the grain size is very large in OFP (200 µm) the matrix content would only need to go down by about 2 wtppm to give one monolayer (ML) of segregation. Such a small decrease would require a much higher accuracy in the APT measurement than what is possible to be detected. The concentration of P in the probed volumes in the TEM/EDX investigations is judged to be below 0.1 at%. This value can also be used to estimate an upper limit of the amount of segregation in terms of MLs. If we assume that a ML has a thickness of 0.1 nm and that the average width of the probed volume is 10 nm (which should be a conservative estimate) due to beam broadening in the sample, see figure 10, one ML would result in a measured concentration of 1 at%. Hence, the concentration of 0.1 at% would correspond to a segregation of about 1/10th of a ML. This means that if segregation to GBs is important, the segregation is not strong.

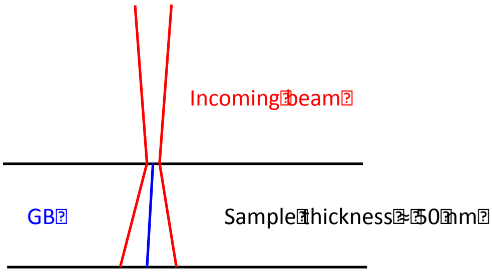

Figure 10. Geometry of TEM/EDX analysis of a GB. The incoming beam is very small (about 0.1 nm), but it gets broadened when it comes deeper into the sample. The average width of the probed volume is expected to be about 10 nm.

7. Conclusion

As the amount of P in the matrix of OFP measured by APT was approximately the same as the bulk concentration, and as no P could be detected at GBs by TEM/EDX, it seems like P resides in the matrix. The positive effect of P regarding creep embrittlement of Cu is probably not governed by strong P segregation to GBs.

8. Acknowledgements

APT lift-out samples were fabricated by Ms. Sabrina Koch, Mr. Gustav Sundell and Dr. Torben Boll. TEM lift-out samples were fabricated by Dr. Samira Nik, who also performed the TEM/EDS investigation together with Dr. Henrik Pettersson. The EDS detection limit was discussed with Prof. Mats Halvarsson. Exchange of valuable information with Mr. Hisham Aboulfadl and Dr. Francisca Mendez-Martin is acknowledged.

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Strålsäkerhetsmyndigheten
Swedish Radiation Safety Authority

SE-171 16 Stockholm
Solna strandväg 96

Tel: +46 8 799 40 00
Fax: +46 8 799 40 10

E-mail: registrator@ssm.se
Web: stralsakerhetsmyndigheten.se