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Technical Note

2012:13

A review of the creep ductility of copper for nuclear waste canister application

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SSM perspektiv

Bakgrund

Strålsäkerhetsmyndigheten (SSM) granskar Svensk Kärnbränslehantering AB:s (SKB) ansökningar enligt lagen (1984:3) om kärnteknisk verksamhet om uppförande, innehav och drift av ett slutförvar för använt kärnbränsle och av en inkapslingsanläggning. Som en del i granskningen ger SSM konsulter uppdrag för att inhämta information i avgränsade frågor. I SSM:s Technical note-serie rapporteras resultaten från dessa konsultuppdrag.

Projektets syfte

Uppdraget är en del i SSM:s granskning av SKB:s ansökan om slutförvaring av använt kärnbränsle. Uppdraget avser granskning av SKB föreslagna krypbrottmekanismer för koppar som används som korrosionsbarriär i kapseln.

Författarens sammanfattning

SKB har inte presenterat tillräckligt med bevis för att rättfärdiga deras position att OFP kopparmaterialet i kapsel har en tillräcklig krypduktillitet. Det stora experimentella underlaget som SKB tagit fram visar endast att OFP kopparen har tillräcklig krypduktillitet under betydligt kortare tidsintervall än vad som gäller i slutförvarssammanhang. För att kunna göra trovärdiga extrapoleringar av krypduktilliteten behöver en trovärdig teori för orsaken till krypsprödhet tas fram. Den av SKB framlagda teorin för krypsprödhet kan i nuvarande utseende inte användas för trovärdiga extrapolationer av krypsprödhet. Alternativt måste SKB presentera en förklaring till effekten av fosfor på koppars krypduktillitet och att fosfortillsatsen säkerställer frånvaron av krypsprödhet i OFP koppar.

Det är intressant att notera att SKB har presenterat experimentella bevis för att interkristallin sprickor kan bildas i OFP material vid brottmekanisk provning. Kanske är det möjligt att mer systematiskt undersöka bildning och tillväxt av interkristallina sprickor med brottmekaniska undersökningar av OFP koppar.

Projektinformation

Kontaktperson på SSM: Peter Ekström
Diarienummer avrop: SSM2011-2024
Aktivitetsnummer: 3030007-4101

SSM perspective

Background

The Swedish Radiation Safety Authority (SSM) reviews the Swedish Nuclear Fuel Company's (SKB) applications under the Act on Nuclear Activities (SFS 1984:3) for the construction and operation of a repository for spent nuclear fuel and for an encapsulation facility. As part of the review, SSM commissions consultants to carry out work in order to obtain information on specific issues. The results from the consultants' tasks are reported in SSM's Technical Note series.

Objectives of the project

This project is part of SSM:s review of SKB:s license application for final disposal of spent nuclear fuel. The assignment concerns review of creep mechanisms for copper material used as a corrosion barrier in canisters for final disposal of nuclear fuel in Sweden.

Summary by the author

SKB has presented insufficient evidence to justify their position that the OFP copper has an adequate creep ductility during long term storage. Their large body of experiments only serves to prove that the creep ductility is sufficient for much shorter time spans than the intended storage times. There is a clear need for a credible theory of creep brittleness of OFP copper which will permit extrapolations to long term storage. The theory presented by SKB does not in its present state permit credible extrapolations. Alternatively SKB needs to find an explanation to the effect of phosphorus on the creep ductility and that it ensures the absence of creep brittleness in OFP copper.

It is interesting to note that SKB has presented experimental evidence that intergranular cracks can form in OFP material tested in cracked specimens. Perhaps it is possible to more systematically study formation and growth of intergranular cracks in specimens of OFP copper with cracks.

Project information

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Technical Note 2

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Content

1. Background

The copper used as the corrosion barrier of the canisters which will be used for long term storage of nuclear waste in Sweden is a pure copper with an addition of 30-100 ppm of phosphorus (P). The purpose of the addition of phosphorus is the ensure that the copper will have an adequate creep ductility[1] under the conditions of long term storage. Early experiments with copper without the addition of P showed that this material had a very low creep ductility when tested in the temperature range 180 - 215 ˚C [1]. Since there was no guarantee that this would not also occur at the lower temperatures of waste storage it was necessary to find a copper material with better creep ductility. It turned out that copper with an addition of about 50 ppm P appears to be such a material [1]. After an extensive testing programme which seemingly confirmed the high creep ductility of P doped copper it has been chosen by the Swedish Nuclear Fuel and Waste Management Company (SKB) as the material for the corrosion barrier of their planned waste canisters.

2. Objective of the review.

The purpose of the present review is to determine if the findings by SKB in relation to the creep ductility of P doped copper are sufficient to ensure the ductility under waste storage conditions. The justification for a review is that all experiments have been performed at higher temperatures than the storage temperature. Thus the conclusion by SKB rests on the possibility to extrapolate material properties from higher to lower temperature. This is not unique for production of creep data for many technological applications. What is unique to the SKB case is the extrapolation in time by five to six orders of magnitude.

3. SKB's position.

SKB's position on the creep ductility issue is expected to be found in three recent technical reports:

1. Design, production and initial state of the canister, TR-10-14, December 2010.
2. Design analysis report for the canister, TR-10-28, April 2010.
3. Fuel and canister process report, TR-10-46, December 2010.

In the summary of 1 creep ductility is listed as one of the most important properties of the canister in order to perform its barrier function   In the report it is stated that in order to obtain the required creep ductility it is necessary to add 30 -100 ppm of P to the material and to keep the sulphur content below 12 ppm. The required creep ductility is listed as > 15 %. It is not exactly clear how this number has been determined, it should probably come out as a result of the Design analysis report but it is nowhere to be found in that report. The process report contains many interesting

[1] Creep ductility can be defined as strain to final fracture in a creep test.

discussions of failure mechanisms for both insert and shell but no discussion of low creep ductility. This is presumably because SKB feels that the extensive experimental programme on creep fracture of P doped copper has demonstrared beyond any doubts that it has a high creep ductility under all conceivable conditions related to storage. The experimental programme is largely summarized in a report by Andersson-Östling and Sandström [2]. To summarize the SKB position: The copper used for the canister needs to have a creep ductility > 15 % and that requirement is fulfilled by the highly pure copper (>99.99 %) with 30–100 ppm P and less than 12 ppm S.

4. Evaluation and analysis of SKB's position.

The problem with SKB's position that the highly pure copper with a P addition, OFP copper, has been shown to have an adequate ductility for long term nuclear waste storage has been discussed in a previous SKI Report [3]. The basis for the discussion is a plot of results from the original report [1] where copper without the P addition, OF copper, was found to have a very low ductility compared to OFP copper. The plot shown as Figure 1 shows the time to failure as a function of stress.

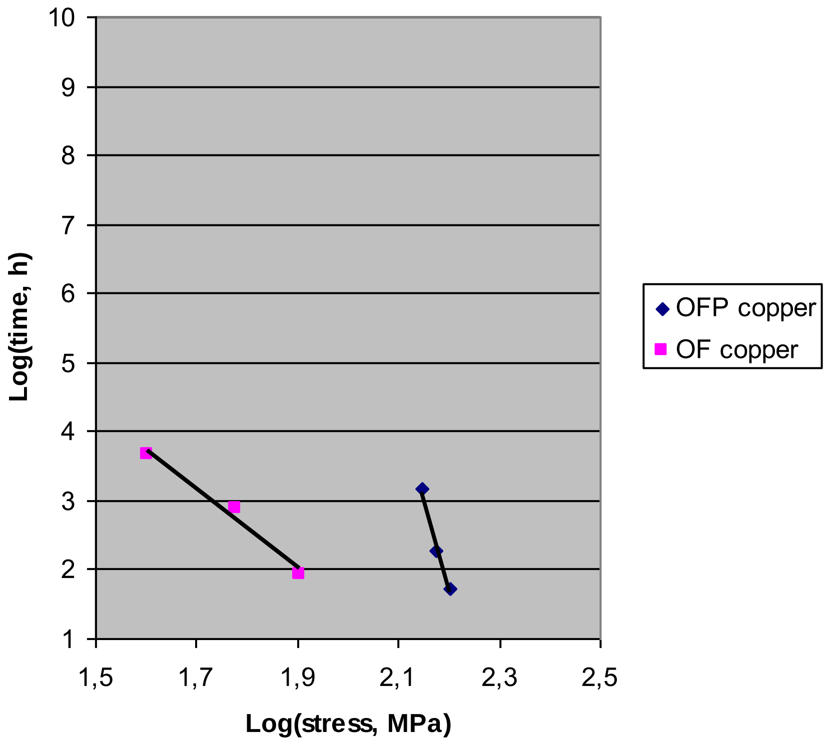

Figure 1. Time to failure in creep tests of OF and OFP copper at 215 ˚C.

It is clear that the stress dependence of the time to failure is different in the two materials. This is not very surprising since the processes leading to failure are different for the two materials. In the OF material failure starts by the nucleation of small cavities in the grain boundaries. These cavities grow and when a certain fraction of the boundary is covered with cavities the grains separate from each other. When a sufficient fraction of the grains have separated the specimen fails by creep brittle failure. Observations in the SKB experiments show that the failure strains can be < 1 % [1].

In the OFP material the specimens fail by thinning down as a result of the creep strain until no load bearing area remains. Initially the specimen is thinned down uniformly along the specimen as the deformation increases. However at some stage a neck of localized higher deformation than elsewhere on the specimen will form. In the type of creep experiment performed by SKB, creep under constant load, it may be shown theoretically that the neck starts to form at the inflection point of the creep curve which is also the point of minimum creep rate during a constant load creep experiment. It should be noted that many of the creep experiment performed by SKB are such that the thinning down of the specimen has a notable effect on the applied stress. In many cases the minimum creep rate occurs after about 10-20 % strain and the true stress is therefore 10-20 % higher than the initially applied stress.

The slopes of the stress dependencies in Figure 1 reflect how the two different failure processes depend on stress. In the case of OFP it will be the negative of the stress exponent for the creep rate while for OF it will be a so far unknown quantity. It is probable that the creep brittle process depends on tensile stress while the deformation induced failure process in OFP depends on shear stress.
Despite attempts to explain the effect of P on creep brittleness [1, 4] it is probably fair to say that the cause of the effect is not fully understood. In the absence of any understanding we can do the following thought experiment. Let us assume that the effect of P is to decelerate the creep brittle process by a factor of 10000. This gives one of the thin lines in Figure 2. The other thin line is an extrapolation of the OFP results.

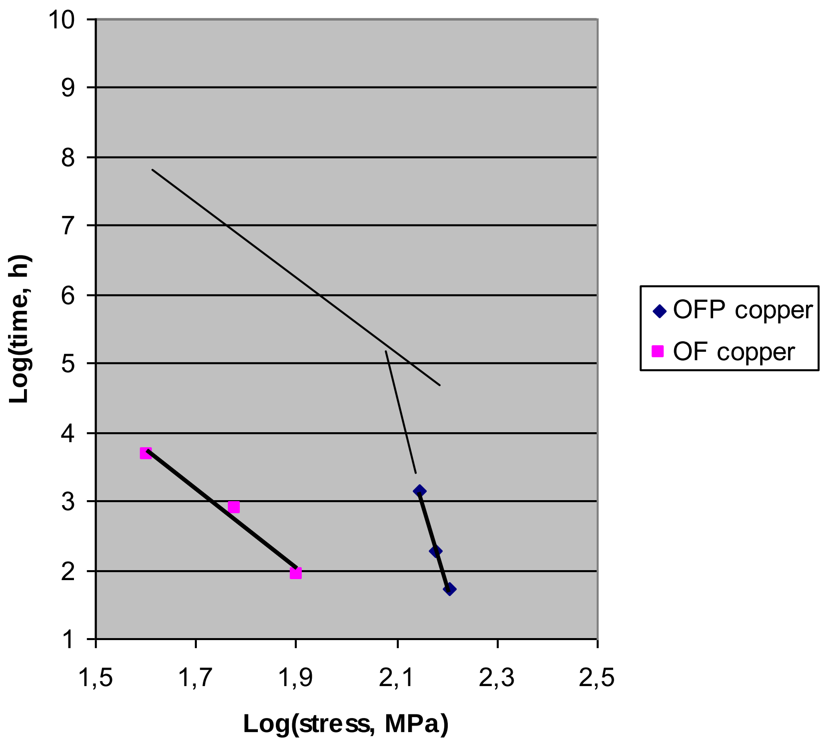

Figure 2. Time to failure in creep tests of OF and OFP copper at 215 ˚C. The line parallel to the OF results represent a hypothetical situation where P decelerates the creep brittle process by a factor of 10000.

The two thin lines cross at slightly less than 100 MPa giving a ductile failure time of just over 100000 h or about 12 years. Since none of the SKB creep tests have gone on for such a long time it is clear that the large volume of creep experiments performed by SKB would have told us nothing of a possible creep brittleness of OFP if such a creep brittleness had the properties represented by the thin line in the Figure. But that would still be a creep brittleness of concern for long-term storage.

The discussion around Figure 2 was first presented in 2006 [3]. A few months later SKB issued a theoretical analysis of the creep brittleness of OF and OFP copper by Sandström and Wu [4]. One of the basic premises for the analysis was that part of the phosphorus content of OFP is located in the grain boundaries. The presence of P in the grain boundaries impedes grain boundary sliding which was postulated to cause nucleation of cavities in the grain boundaries. Thus there will be much less nucleation of cavities in OFP and therefore no creep brittleness. Another interesting result of the theory was that at low temperature there would be no creep brittleness in neither of the two materials. It should be noted that SKB does not rely on this theory in their license application. The statements on creep ductility are besed solely on results from creep experiments run for periods which are 5 to 6 orders of magnitude shorter than the intended storage time.

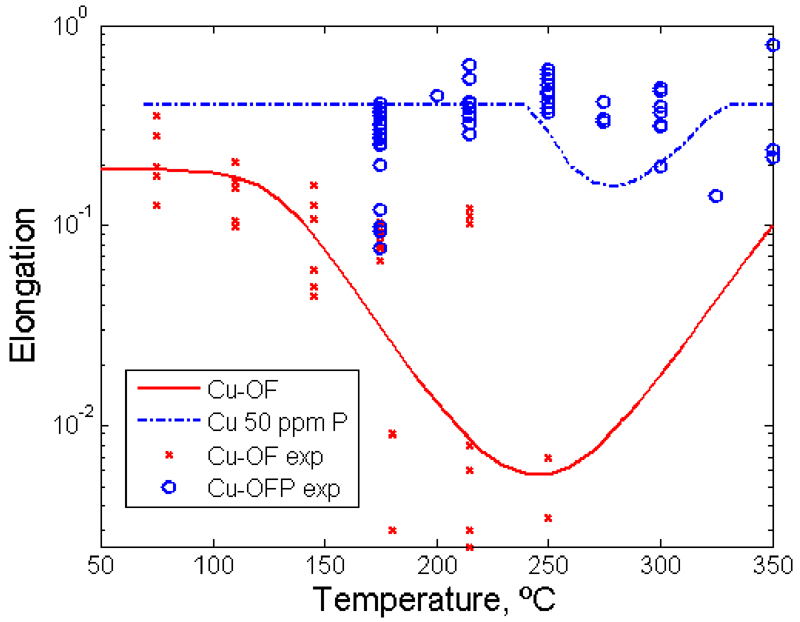

Figure 3. Theoretical evaluation of the creep brittlenes of OF and OFP copper by Sandström and Wu. The curves show predictions by the theory and the plotted points are experimental results.

As can be seen in the Figure both OF and OFP has an adequate ductility at low temperature. A credible theory of the type presented by Sandström and Wu would alleviate the concerns raised in connection with Figure 2.

However there is a problem with the Sandström-Wu theory. About ten years earlier the present writer hypothesized that P in the grain boundaries would impede grain boundary sliding and thus explain why OFP was more creep deformation resistant than OF. The idea was tested in a small student project where observations on grain boundary sliding was compared between OF and OFP after tensile testing at 100 and 200 ˚C to low strain. The results were too few to allow any certain conclusions but the general impression was that there was no difference between the materials with regard to grain boundary sliding. These observations justified a more extensive investigation of grain boundary sliding in OF and OFP copper.

This investigation was carried out with financing from SSM and the results were published in 2010 [5]. The main result of the investigation was that there was no significant difference in the grain boundary sliding in OF and OFP copper when the materials had been deformed to the same strain. This was true both at 100, 150 and 200 ˚C. Thus the basic premise of the Sandstöm-Wu theory has been shown to be incorrect.

A few other interesting observation were done in the project. As long as no cracking has occurred there is no difference at all in the mechanical properties of OF and OFP copper. But as soon as cracking started the OF material deformed at a lower stress than the OFP material. This observation indicates that much, if not all, of the difference in creep strength between the OF and OFP materials may be a result of creep cracking in the former.

In both materials it was observed that a few intergranular cracks open at low strains. How these cracks form is not understood. Perhaps a few grain boundaries are inherently weak. The significance of the observation is that the presence of a few intergranular cracks in OFP cnn not be taken as proof that a general intergranular cracking process is at work in OFP.

Despite the problems with the Sandström-Wu theory it may be of some interest to see how well it fits with some experimental results. This is done in order to emphasize that a basic requirement for a theory is that it can reproduce known experimental data.

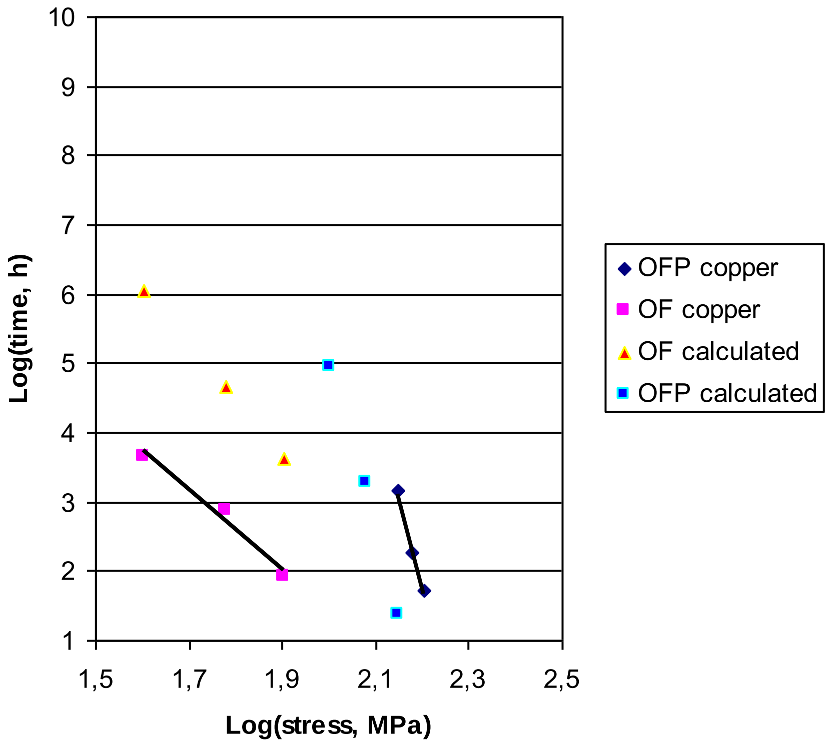

Figure 4. Time to failure as a function of stress. Experimental results compared to predictions of the Sandström-Wu theory.

Figure 4 shows a comparison between the theory and experimental results at 215 ˚C. Not surprisingly the curves for ductile failure are parallel since the calculated points depend on a theory which has been calibrated with these experimental results. The agreement is actually complete if one takes into account that the experimental results are plotted as a function of nominal or engineering stress while the true stress in the experiments have been typically about 15 % higher since much of the deformation has taken place after a plastic strain of 10 - 20 %. The lifetime of OF material seems to be overestimated by about two orders of magnitude and the stress dependence is steeper than for the experimental results. This is clearly indicative of a further problem for the theory in addition to the problem with a basic premise for the theory.

In the theory report [4] most calculations have been carried out for a creep life of 10 000 h or about 1 year. However in one figure ductility results are calculated for a life of 1000 000 h or about 117 years. This figure is reproduced as Figure 5.

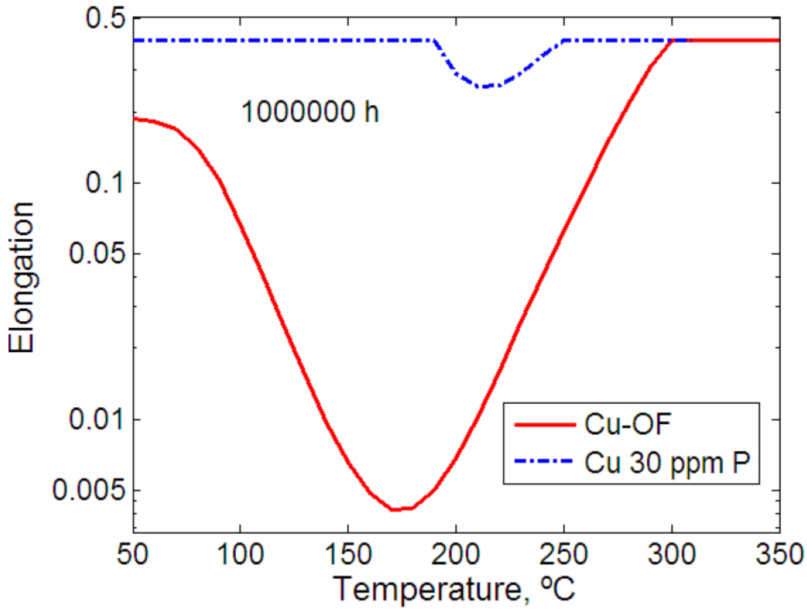

Figure 5. Ductility predictions of the Sandström-Wu theory for a creep life of 1,000.000 h.

In comparison with Figure 3 the ductility minimum for the OF material is deeper and occurs at lower temperature. On the other hand for the OFP material the ductility minimum is reduced but as for the OF material it occurs at a lower temperature. In fact when the same calculation is repeated for 10 000 000 h the ductility minimum for OFP disappears completely. This is of course extremely advantageous for the SKB position on OFP copper creep ductility. However as long as the theory is in doubt there is little value in this information.

There is a way to experimentally approach the problem of a possible formation of intergranular cracks in OFP copper. As mentioned above plastic deformation is controlled by shear stresses while formation and growth of intergranular cracks are controlled by tensile stresses. By using a multiaxial stress state it is possible to keep shear stresses on a low level while the tensile stresses are high. One such situation is the region ahead of a crack tip. Auerkari et al. has calculated that the tensile stress level in the region ahead of a crack tip can be about 3.5 - 4 times the yield strength of copper [6]. It is thus possible to accelerate the formation of intergranular cracks in OFP by testing cracked specimens. Such testing has in fact been performed by SKB with the purpose of observing if creep crack growth would occur [7].

Tests performed with standard size CT specimens at 175 and 215 ˚C did result in some creep crack growth of about 10 mm before the specimens failed by overload since they were both tested at relatively high loads. Post-test metallography showed that intergranular cracks had opened in both specimens. The authors themselves write “Extensive creep damage in terms of cavities and microcracks are visible several mm from the crack, see Figures 3-11c and 3-11d”. And these figures do indeed show creep damage in the form of intergranular cracks although perhaps not so much as to justify the word “extensive”. What is important however is that under the right conditions intergranular creep cracks form in OFP material and it is thus difficult to feel sure that they would not form at a much lower stress given enough time. The times these two crack growth experiment were run were 121 h at 215 ˚C and 812 h at 175 ˚C. Tests were also run at high loads at 22 and 75 ˚C. These tests were not run to failure and were interrupted after 13000 h for the 22 ˚C test and after

5000 and 9000 h for the two 75 ˚C tests. The post-test metallography showed heavily deformed grains close to the crack tip and a few intergranular cracks. It seems possible that those cracks are of the same type as those observed in OFP samples in the grain boundary sliding tests, intergranular cracks which form in low numbers early during a test in ínherently weak grain boundaries.

5. Conclusions

SKB has presented insufficient evidence to justify their position that the OFP copper has an adequate creep ductility during long term storage. Their large body of experiments only serves to prove that the creep ductility is sufficient for much shorter time spans than the intended storage times. There is a clear need for a credible theory of creep brittleness of OFP copper which will permit extrapolations to long term storage. The theory presented by SKB does not in its present state permit credible extrapolations. Alternatively SKB needs to find an explanation to the effect of phosphorus on the creep ductility and that it ensures the absence of creep brittleness in OFP copper.

It is interesting to note that SKB has presented experimental evidence that intergranular cracks can form in OFP material tested in cracked specimens. Perhaps it is possible to more systematically study formation and growth of intergranular cracks in specimens of OFP copper with cracks.

6. References

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   Low temperature creep of copper intended for nuclear waste containers.
   Swedish Institute for Metals Research, IM-2780, Oct 1991

2. Andersson-Östling, H. C. M. and Sandström, R.
   Survey of creep properties of copper intended for nuclear waste disposal.
   SKB, TR-09-32, December 2009

3. Pettersson, K.
   Development of a constitutive model for the plastic deformation and creep of copper and its use in the estimate of the creep life of the copper canister.
   SKI, SKI Report 2007:12, Dec 2006

4. Sandström, R. and Wu, R.
   Origin of the extra low creep ductility of copper without phosphorus.
   SKB, TR-07-02, February 2007

5. Pettersson, K.
   A study of grain boundary sliding in copper with and without an addition of phosphorus.
   Journal of Nuclear Materials, 405(2010), pp. 131-137.

6. Auerkari, P., et al.
   Uniaxial and multiaxial creep testing of copper.
   VTT, SKI Report 2003:06,

7. Wu, R., et al.
   Creep crack growth in phosphorus alloyed oxygen free copper.
   SKB, SKB R-11-11, January 2011

APPENDIX 1

Coverage of SKB reports

The list below covers the SKB reports reviewed in order to find information on SKB's position regarding creep ductility of copper and the the reports forming the basis for that position. No particular sections of the reports can be

Table 1:1

Reviewed report	Reviewed sections	Comments
TR-10-14		
TR-10-28		
TR-10-46		
TR-09-32		
TR-07-02		
R-11-11		

APPENDIX 2

Suggested needs for complementary information from SKB

1. A credible extrapolation of creep ductility of OFP copper based on observations of creep brittle behaviour of the material or alternatively a demonstration, theoretical of experimental, that creep brittleness never occur in OFP copper.

2012:13

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