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A study of grain boundary sliding in copper with and without an addition of phosphorus

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ABSTRACT

Copper will be used as a corrosion barrier in the storage of high level nuclear waste. In order to improve the creep fracture properties of the material it will contain 30–50 ppm of phosphorus, OFP copper as opposed to OF copper without P. It has been suggested that the phosphorus impedes grain boundary sliding in copper and recently a quantitative theory based on this idea has shown that there is no risk for creep-brittle fracture of OFP copper under waste storage conditions. In order to verify the basis of this theory grain boundary sliding has been investigated in copper with and without a P addition. The method has been to examine intentionally scratched surfaces of tensile specimens tension tested to plastic strains of 1%, 2% and 4% at 150 and 200 °C. After testing specimen surfaces have been examined in SEM and sliding distances have been measured as in-surface displacement of scratches. The results have been plotted as distribution functions where the fraction of slides smaller than a given value is plotted versus sliding distance. The result is that in most cases the distribution functions for OF and OFP copper overlap. In a small number of cases there is a tendency that less sliding has occurred in OFP copper. The overall conclusion is however that although there may be a slight difference between the materials with regard to grain boundary sliding it is not large enough to explain the observed difference in creep brittleness. Tension tests to fracture in the temperature range 100–200 °C show that the tensile properties of the two copper qualities are more or less identical until intergranular cracking starts in the OF copper. Then the flow stress decreases in comparison with OFP. It is suggested that at least part of the observed differences in creep strength between the two coppers may be due to the effect of intergranular cracking.

1. Introduction

High level nuclear waste in Sweden is planned to be stored underground in large canisters with an outer shell of copper. The size of the canisters is 4850 mm in length and 1050 mm in diameter. The thickness of the copper shell is 50 mm. The purpose of the copper shell is to serve as a corrosion barrier for up to 1 million years. However it also needs to retain its structural integrity from a mechanical point of view for the same period of time. Thus the mechanical properties of copper in the interesting temperature range and in particular the creep fracture properties have been subject to intensive investigations. Early on it was discovered that the oxygen free relatively high purity copper intended for use as copper overpack did not have a sufficiently good creep ductility. Creep tests in the temperature range 180–250 °C resulted in intergranular failure at strains as low as 0.3% [1,2]. However in the same investigation it was shown that copper with an addition of 50 ppm of phosphorus did not fail by intergranular creep failure in tests in the same temperature range. These tests were carried out at slightly higher stresses because the addition of phosphorus apparently also increased the creep strength of the copper. Thus it was necessary to test at higher stress or temperature in order to get a reasonable failure time.

Since these early observations copper with 30–50 ppm P has been shown to always fail in a ductile manner under the test conditions used [3–8]. Based on these results it has been concluded that there is no risk for creep failure of the copper canister under the intended storage conditions [9]. However the present writer has suggested that it is quite possible that the creep brittle mechanism might still be at work in the P-doped copper (denoted OFP as opposed to the OF copper without P) but retarded by the presence of phosphorus so that it is not accessible by creep tests within a reasonable time frame but still important for the time frame of interest for the copper canister [10]. A recently presented theory by Sandström and Wu for the effect of phosphorus on the low temperature creep fracture of copper indicates however that this is not a problem [11]. A prediction of the theory is that OFP copper will be fully ductile at times and temperatures of interest for the waste canister. The theory is based on the idea that a part of the phosphorus content is located in grain boundaries and there serves to retard grain boundary sliding. This will retard nucleation

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of the cavities in the grain boundary which cause the creep brittle failures and to some extent also retard the growth of the cavities.

According to Sandströn and Wu there is a linear relationship between nucleation rate and strain rate:

$$\frac{dn}{dt} = B\dot{\varepsilon}_{ct} \tag{1}$$

Sandström and Wu shows how such a relationship can be derived from a similar relationship between grain boundary sliding distance s_d and creep strain ε_{cr}:

$$s_d = C_s\varepsilon_{cr} \tag{2}$$

where the constant C_s has been assumed to have the value 0.05 μm. In subsequent calculations they use expressions for the strain rate derived by Sandström and Andersson which include the effect of phosphorus [7,8]. The effect of phosphorus on creep strength is taken into account by dividing the strain rate equation for OF copper by a factor f_p which takes on the value 3000 at 75 °C and then decreases continuously with temperature up to 300 °C where it reaches the value 1. In Eq. (1) the expression for strain rate from [7] is modified by calculating it with the applied stress reduced by a grain boundary sliding resistance denoted σ_{break} calculated from the concentration of P and the interaction energy between P and the grain boundary. This leads to a profound reduction in the grain boundary sliding in the presence of phosphorus and a concomitant reduction in the nucleation of cavities. For 35 ppm of P the reduction in sliding at constant overall strain rate is by a factor of about 63,000 at 150 °C at an applied stress of 150 MPa. However because of the effect of P on creep rate only about 131 MPa is needed for the OF copper to reach the same strain rate.

The idea that phosphorus affects the grain boundary sliding and thus the mechanical properties of copper is not entirely new. The present writer suggested that it is the retardation of grain boundary sliding by phosphorus which leads to the increase in creep strength of OFP copper in comparison with OF copper. This idea was tested in a student project by a Swiss guest student at KTH, Gabrielle Pax, in 1998. Under the supervision of the present writer she performed normal and slow strain rate tests of copper at 100 and 200 °C. The tests showed that the OF copper failed with low fracture strains in the slow tests while the tensile properties of OF and OFP copper were virtually identical in tests at normal strain rates. At 200 °C two slow tests, one OF and one OFP, were interrupted at 4% strain and the specimen surfaces were examined for signs of grain boundary sliding. Despite the rather spectacular example of grain boundary sliding in the OF sample shown in Fig. 1, our general, qualitative, impression was that there was no real difference between the materials with regard to the magnitude of the sliding that had occurred in the two materials.

The theory of Sandström and Wu is currently the only theory which can predict the creep fracture behaviour of OFP copper under waste storage conditions. However it rests on the assumption that phosphorus inhibits grain boundary sliding in copper. On the other hand the student project indicated that there was no difference between the materials. This is the background to the present investigation which is an attempt to more quantitatively than before assess the differences in grain boundary sliding between OF and OFP copper.

2. Experimental details

The copper used in the present investigation as well as in the previous student project was originally delivered as two 40 mm thick hot-rolled plates from Outokumpu copper works in Finland. To the material in one of the plates had been added 35 ppm of phosphorus in order to improve the creep ductility. The composition of the two materials is given in the tables below.

The OF copper

Ag	As	Co	Cr	Fe	Ni	O	P	S	Se	Sn
10	<50	<10	<10	<10	<10	n.a.	<10	<10	n.a.	<50
Te	Zr									
n.a.	n.a.									

The OFP copper

Ag	As	Co	Cr	Fe	Ni	O	P	S	Se	Sn
10	<50	<10	<10	<10	<10	n.a.	35	<10	n.a.	<50
Te	Zr									
n.a.	n.a.									

The OFP copper has also been used in previous stress corrosion cracking tests [12]. In connection with those tests it was determined that the texture of the OFP copper was more or less random, meaning that a few weak peaks in intensity existed but these had no relation to the geometry of the plate. A metallographic examination of samples from both plates showed uniform grain structures of well recrystallized grains. The grain size in both samples was about 100 μm as determined by the mean intercept method.

The tension test specimens were fabricated with a 5 mm diameter circular cross section. The gauge length was 37.5 mm with a rounded shoulder transition to the 8 mm diameter and 17 mm long thread at both ends. For the study of grain boundary sliding the traces from the turning were removed by grinding the surface by successively finer emery papers from 120 mesh to 1200 mesh. After grinding about 1–2 μm of material was removed by electropolishing in 50% phosphoric acid. The resulting surface was quite smooth and would not easily permit observations of grain boundary sliding. Therefore the surface was wiped along the length of the specimen by a piece of cloth impregnated with 3 μm diamond paste. This resulted in a number of longitudinal scratches on the

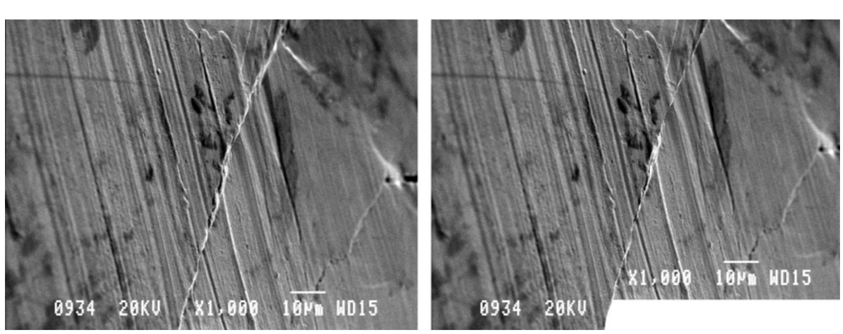

Fig. 1. Example of grain boundary sliding in OF copper after 4% strain. The picture to the left is as it was observed. The picture to the right demonstrates the continuity of surface scratches after that the lower part of the picture has been moved about 10 μm along the grain boundary.

specimens from which the sliding offsets at grain boundaries were easily measured. The observations of grain boundary offsets were performed with a JEOL 820 scanning electron microscope.

The tension testing was carried out in an Instron TT-DM-L screw-driven tensile tester with an electric furnace to keep the specimens at constant temperature. The temperature was monitored continuously with two thermocouples mounted at different locations on the specimen. The temperature differences noted during a test were at most ±2 °C from the set temperature over the test time or over the specimen. The tests were run with extension rates of 1 mm/min, 0.01 mm/min and in a few cases 0.005 mm/min corresponding to strain rates of 4.44×10^{-4}, 4.44×10^{-6}, and $2.22 \times 10^{-6}\ s^{-1}$. The extension rates were not calibrated before testing but the resulting length changes of the test specimens after testing measured with a digital caliper agreed to within 5% with calculated changes based on nominal extension rates.

The load was recorded directly to hard disk via a 24 bit analog-to-digital converter. Before testing the load cell scale factor was determined by loading the cell with calibrated weights from 0 to 30 kg in steps of 5 kg. The load cell scale factor was determined by linear regression of the measured values of output and load. The good linearity of the cell was demonstrated by the value $R^2 = 0.9998$ for the regression analysis. The tests for determination of grain boundary sliding were run to 1%, 2%, and 4% plastic strain. While the tests were running the apparent elastic modulus of the test was determined from the early data of the test. Then the plastic strain for subsequent points could be determined by subtracting the elastic portion of the strain from the total strain. In that way the tests could be stopped at a plastic strain value which at most differed by 1% (relatively) from the intended value.

3. Results

3.1. Tensile properties

In addition to the results obtained in the present project results from the student project are also included in the summary of the results. The stress–strain curves are presented as true stress versus true strain. However this is true only up to some point before the maximum of each curve. After that point necking has started and in the neck the cross-sectional area becomes progressively smaller than the nominal area used to calculate the true stress resulting in an apparently decreasing true stress. For the OF material intergranular cracking also contributes to the decrease in applied load manifested as an apparent decrease in true stress. Fig. 2 shows the stress–strain curves of the OFP material. All the curves indicate a ductility of about 40% before necking and ultimate failure. In particular one test was run at 200 °C at the lowest available strain rate. It is clear from the stress–strain curve of this specimen that there is no tendency for creep brittle failure under those conditions.

In contrast all except two of the stress–strain curves for the OF material indicate a reduced ductility, Fig. 3. At 52 °C a test was run at the lowest available strain rate, $2.22 \times 10^{-6}\ s^{-1}$, and it is clear from the curve that there is no indication of any creep brittleness. At 100 °C a result is available with a strain rate of $4.44 \times 10^{-4}\ s^{-1}$. The resulting stress–strain curve is virtually identical with the stress–strain curve of the OFP material showing that in the absence of intergranular cracking the two materials have more or less identical mechanical properties. This can again be seen for the other stress–strain curves of the OF material with reduced ductility from intergranular cracking. As long as there is no tendency for intergranular cracking the stress–strain curves of the OF material follow the stress–strain curves of the OFP material within the spread that is normally observed in testing of stress–strain properties.

It was unexpected that creep brittleness would show up at the higher strain rates. For the specimen tested at 150 °C with a strain rate of $4.44 \times 10^{-6}\ s^{-1}$ with a fracture strain of 30% the fracture surface was examined in SEM.

3.2. Observations of grain boundary sliding

When two grains which lie in the specimen surface slide relative to each other the displacement can be out of the surface as well as in the plane of the surface. One might even argue that on average the displacement out of the surface will be greater than in the plane of the surface since the constraint to the displacement will be less on the unloaded surface in comparison with the constraint for movement along the surface. In any case a full determination of grain boundary sliding magnitudes would require a full three dimensional determination of the displacement which would be quite work consuming. Therefore in the present case the measurements have been limited to the projection of the displacement vector on the plane of the surface. This measure is thought to be sufficient for detection of any differences in grain boundary sliding propensities of two materials. Fig. 4 illustrates the method used.

It is clearly seen in the figure that part of the sliding is out of plane. However what is measured is the displacement of scratches at the grain boundary. Lines were drawn along a scratch on both sides of the grain boundary. Then the distance between the lines along the direction of the grain boundary was measured. All these operations were done using the freely available image analysis program NIH Image. The length values returned by NIH Image was converted to μm using a scale factor determined from measurement of the scale mark on the micrograph.

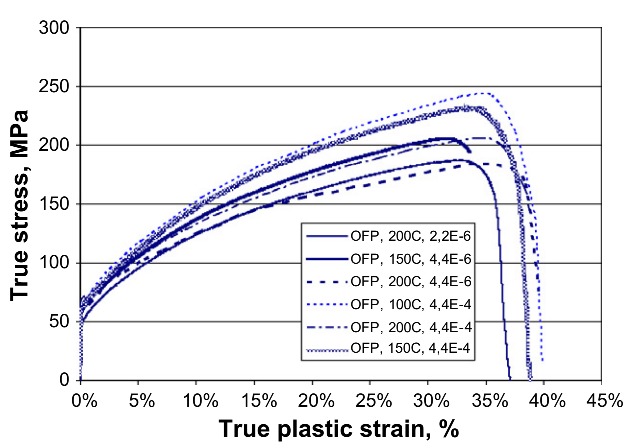

Fig. 2. Tensile properties of the OFP material at different temperatures and strain rates.

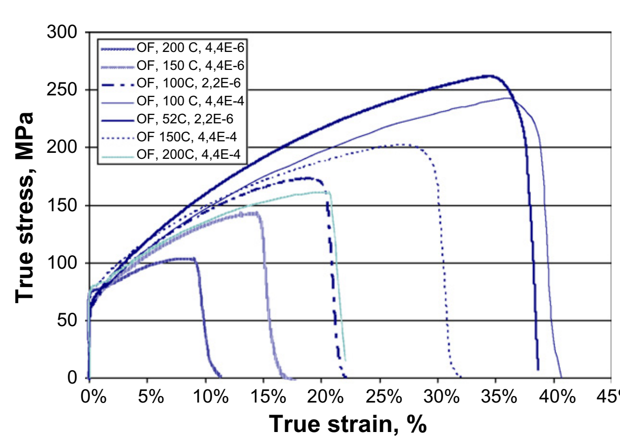

Fig. 3. Tensile properties of the OF material at different temperatures and strain rate.

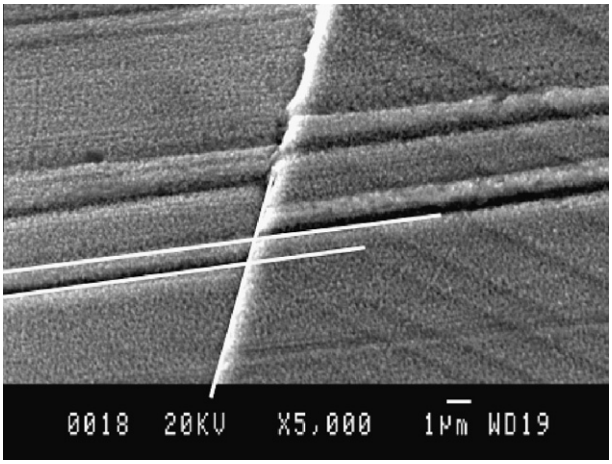

Fig. 4. Picture illustrating how the grain boundary sliding was measured.

In many cases more than one dislocated scratch was available for measurement. In those cases an average of the displacement has been used. It is quite clear from the observations done in the present project that the sliding can vary along a grain boundary. Similar variations have been observed when interferometric methods have been used to study grain boundary sliding [13]. One reason could be interactions with dislocation slip, note the coarse slip lines in Fig. 4. The dislocation slip was quite concentrated in a few slip lines at which scratches were also visibly dislocated although not to the same extent as at grain boundaries.

On the 12 specimens available grain boundary sliding was measured on 10–30 boundaries. The results have been plotted as a type of distribution functions showing the fraction of observed slip distances lower than a given value. The results are plotted in Figs. 5–10.

There seems to be slightly less sliding in the OFP material but the overall impression is that the difference is small with total overlap of the distribution curves in most cases.

For each sliding distribution it is possible to evaluate a mean value. This value has been plotted as a function of strain in Fig. 11.

The mean sliding distances observed at 150 °C do not follow a logical pattern. At 200 °C on the other hand there seems to be a reasonably linear relationship between mean sliding distance and strain for both the OF and OFP materials. Evaluations of the slopes of the trend lines result in 54 μm for the OF material and 52 μm for the OFP material. In both cases there is a small positive intercept at zero strain. The observations at 200 °C confirm the linear relationship between sliding and strain expressed in Eq. (2). However the proportionality factor observed is about 1000 times higher than the value assumed by Sandström and Wu in their theoretical calculations. Since the observed sliding is only the projection of sliding on the specimen surface the actual proportionality factor is even greater.

A feature frequently observed when examing surfaces for sliding was an intergranular crack. An example is shown in Fig. 12. These cracks were observed both in OF and OFP material at low strains. The mechanism for opening of these cracks must be different from that which leads to the creep brittle failures since they seem to be about equally frequent in OF and OFP material although no quantitative evaluation has been attempted. The cracks open at low strains and do not grow. They can be observed on the surfaces of OFP specimens deformed to fracture. They are then very open indicating that they have formed at low strains.

The fracture surface of the OF specimen tested at the higher strain rate at 150 °C was examined in SEM in order to confirm that

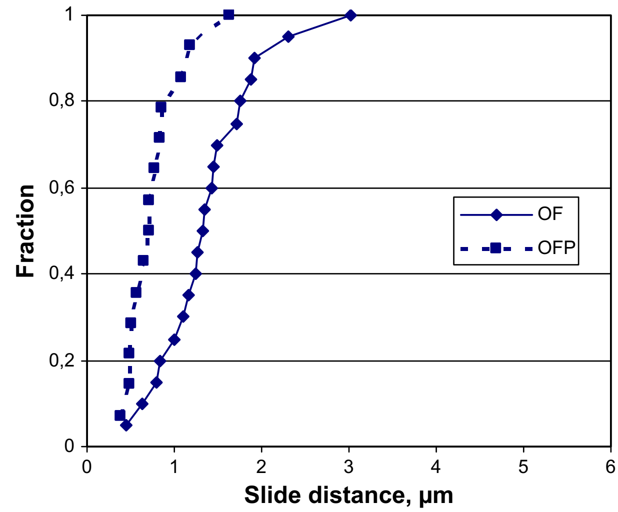

Fig. 6. Observed sliding distances at 2% plastic strain at 150 °C. Number of measured distances 20 in OF and 14 in OFP.

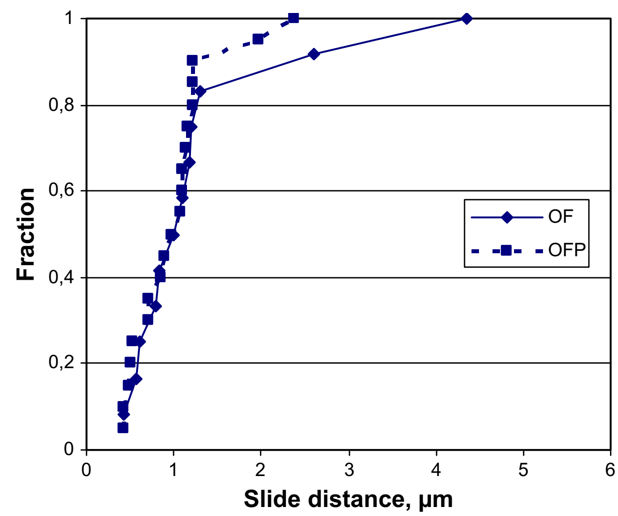

Fig. 7. Observed sliding distances at 4% plastic strain at 150 °C. Number of measured distances 12 in OF and 20 in OFP.

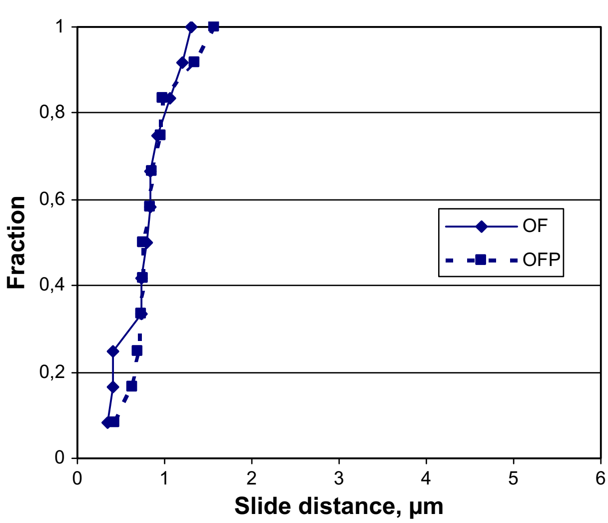

Fig. 5. Observed sliding distances at 1% plastic strain at 150 °C. Number of measured distances 12 in each material.

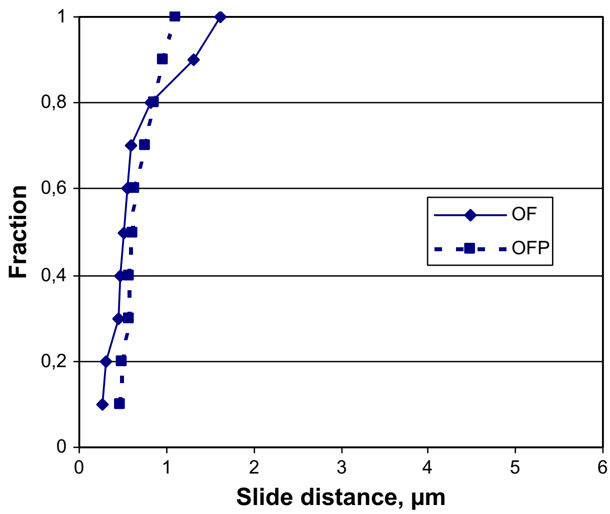

Fig. 8. Observed sliding distances at 1% plastic strain at 200 °C. Number of measured distances 10 in each material.

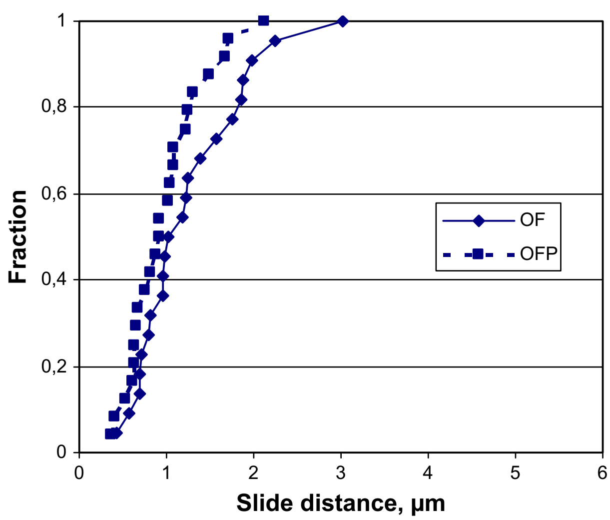

Fig. 9. Observed sliding distances at 2% plastic strain at 200 °C. Number of measured distances 22 in OF and 24 in OFP.

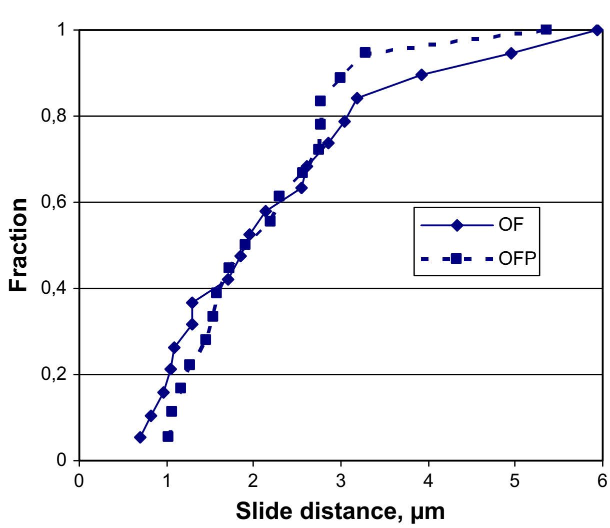

Fig. 10. Observed sliding distances at 4% plastic strain at 200 °C. Number of measured distances 19 in OF and 18 in OFP.

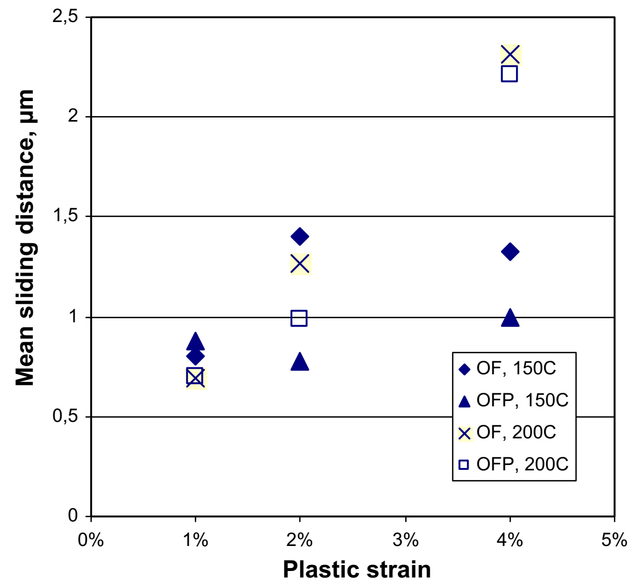

Fig. 11. Mean sliding distance as a function of strain.

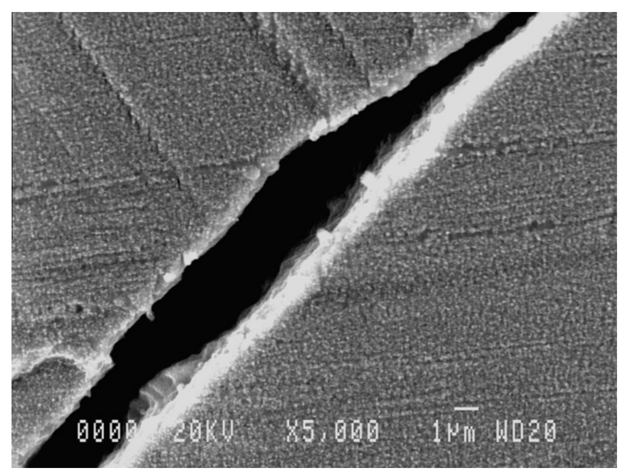

Fig. 12. Intergranular crack observed in OFP material deformed 4% at 200 °C.

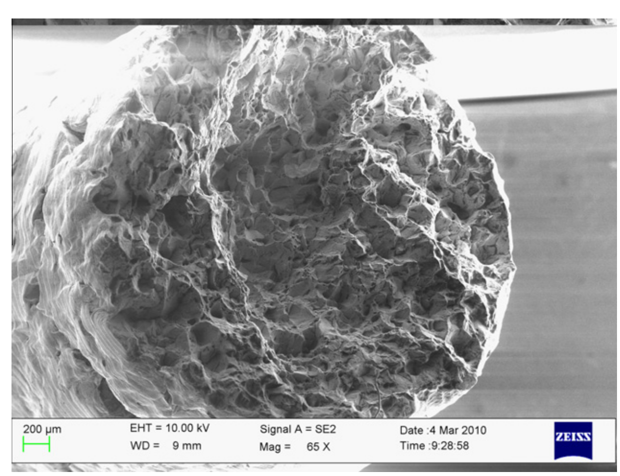

Fig. 13. Fracture surface of OF specimen tested at 150 °C with a strain rate of $4.4 \times 10^{-4}\ s^{-1}$.

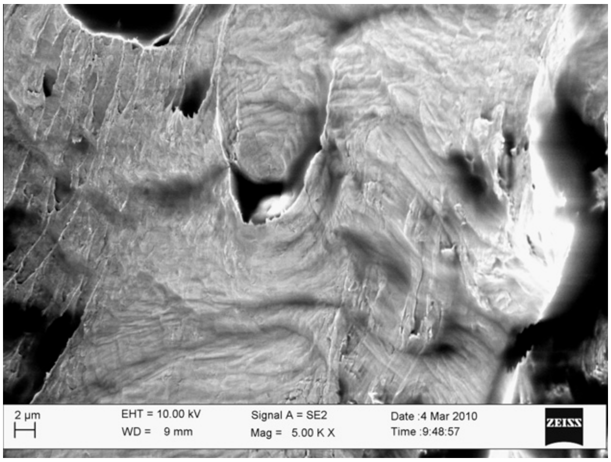

Fig. 14. Intergranular facet. No cavities seem to have formed.

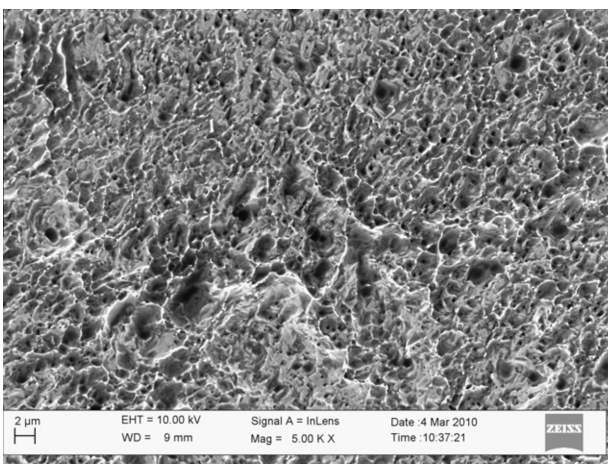

Fig. 15. Intergranular facet. The surface is covered with dimples formed when the presumably cavitated boundary has separated.

the reduction in ductility compared to OFP was caused by intergranular fracture. As can be seen in Fig. 13 the fracture surface has a clear intergranular character despite the fact that the fracture strain is as high as about 30%. A few of the intergranular facets were examined in more detail. Some of them had a fairly featureless appearance as can be seen in Fig. 14 which is in contradiction to the proposed mechanism of cavity nucleation and growth as the cause of intergranular fracture.

Other facets on the other hand had an appearance fully consistent with the cavity nucleation and growth mechanism as can be seen in Fig. 15. The intercavity distance seems to be of the order of about 1 µm, the same order of magnitude as in the calculations by Sandström and Wu [11].

4. Discussion

The tensile test results of the OF specimens show a clear trend as can be seen in Fig. 3. Both an increase in temperature and a decrease in strain rate reduces the fracture strain. At 52 °C there is no observable creep embrittlement. These results can be compared to theoretical predictions by the Sandström–Wu model. The predictions by the model can be summarized very simply. According to the model all OF specimens should have failed with 23% strain, a fracture strain which increases slightly from 52 to 200 °C. The reason is that the model includes two components for growth of cavities. The first expresses the influence of diffusion on cavity growth and is dependent only on stress and temperature. The other expresses the influence of plastic strain on cavity growth and is proportional to cavity radius and strain rate. At the temperatures and strain rates investigated in the present project the second component dominates and this gives the effect that all tests should have resulted in the same fracture strain.

According to Sandström and Andersson the effect of phosphorus on creep of copper is that it locks dislocations requiring an extra stress increment to move [8]. This hypothesis leads to a model for creep rate where the creep of OFP copper in comparison with OF copper is reduced by a factor f_p which takes on a value of 950 at 100 °C and decreases to 32 at 200 °C for the temperature range studied in the present project. This difference should show up in the tensile properties. If one uses the Sandström–Andersson expression for strain rate it requires an about 15% increase in stress to achieve the same strain rate in OFP as in OF material in the temperature range 100–200 °C. This is not seen in the present tensile test results where the tensile properties seem more or less identical for OF and OFP until intergranular cracking starts. The present results rather indicate that the difference in creep strength observed might be due to weakening of the OF material by intergranular cracking. It is clear that many of the creep test results might be interpreted in the same way since intergranular fracture conceivably has occurred quite soon after the minimum creep rate has been obtained [3]. Therefore the effective stress at the minimum creep rate might have been significantly higher than the nominal value.

The study of grain boundary sliding has shown conclusively that there are no large differences if any in the sliding behaviour of OF and OFP copper. Therefore other reasons for the effect of phosphorus on the creep brittleness of copper must be sought. The conclusions of the Sandström–Wu model that creep brittleness will be absent in OFP copper under waste storage conditions are no longer credible. It still remains a possibility that creep brittleness may be present under conditions which cannot be reached by experiments for which only limited time periods are available.

5. Conclusions

The results of the project including the previous student project can be summarized by the following conclusions:

- The tensile properties of OF and OFP copper are almost identical in the temperature range 100–200 °C.
- The stress level in OF copper is reduced when intergranular cracking starts which is the difference between OF and OFP copper with regard to tensile properties.
- Plastic deformation in both materials is accompanied by similar amounts of grain boundary sliding. The component of sliding parallel with the specimen surface is about 50 µm/unit of strain in both materials at 200 °C.
- There is currently no credible theory available which explains the effect of phosphorus on the creep-brittle fracture of copper.

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