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Recrystallization of copper with phosphorus and Auger microscopy studies of the phosphorus content

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Update notice

The original report, dated November 2020, was found to contain both factual and editorial errors which have been corrected in this updated version. The corrected factual errors are presented below.

Updated 2024-06

Location	Original text	Corrected text
Page 9, Chapter 2, paragraph 1, first sentence	...study on the effect of indentations on creep of copper (Mannesson et al. 2013).	…copper canister lid (SKB id TX219).

Summary

This study aims at investigating recrystallization behaviour for oxygen free phosphorus doped copper and if the presence of phosphorus can be detected on fracture surfaces.

The recrystallization part of the study used copper specimens extracted from a lid. They were annealed and cold-rolled and then aged at six different temperatures for durations ranging from one day to twelve months. The temperatures can be divided into two categories: low-temperature (75, 125, 175 °C) and high-temperature (250, 350, 450 °C). As reference, one specimen that was only annealed and one that was annealed and cold-rolled were also analyzed. Hardness measurements were made, and a statistical one-way analysis of variance was conducted with the objective of understanding if there was a statistically significant (at a level of 0.05) difference in mean hardness between different durations and temperatures.

The study found that the hardness for 75, 125, 175 °C had large variation within specimens, making it hard to distinguish any trends between hardness, temperature and ageing durations. Statistical analysis revealed that when comparing mean hardness values between different durations within these temperatures only 75 and 175 °C had cases where such variation was significant. However, there was no pattern to the differences nor could they be related to changes in microstructure. Furthermore it could not be concluded that mean hardness of all ageing durations for 75, 125 and 175 °C were different from each other at a significant level. The mean hardness was close to that of the rolled specimen, which also displayed large variation. These results indicate little to no change in the microstructure, or at least little or no recrystallization, which would lower the hardness. This agreed with the metallographic investigations, where recrystallization is not observed for any of the low-temperature specimens. There were however some signs of recovery evident in the metallography.

For the high-temperature specimens, the variation within specimens was lower, as was the variation for the annealed specimen. A specimen aged for 1 day at 250 °C was clearly distinguished from all other high-temperature specimens by having a higher hardness. The other specimens had a lower hardness close to that of the annealed specimen. These hardness results correlated well with the metallographic investigation, where it was observed that the specimen aged for 1 day at 250 °C had just begun recrystallizing. After 1 week at 250 °C, complete recrystallization had nearly been achieved and all other specimens were fully recrystallized. The microstructure of 350 °C and 450 °C is fully recrystallized starting already from the first ageing duration of one day. The 250 °C specimens are fully recrystallized after more than one week of annealing. The grain sizes of the low-temperature specimens did not change throughout ageing, while the grain sizes of the high-temperature specimens increased as time progressed. There were some significant variations in hardness between different durations: for 250 °C and 450 °C there was a significant increase in hardness at 6 months which persisted for the remaining ageing durations. However, this increase could not be related to any developments in the microstructure and the causes of it require further investigation.

The Auger microscopy part of the study used miniature specimens cut from creep test specimens that had been creep tested to just before final fracture. Thus, the microscopy specimens had a weakness in the centre of the specimens that could be used to fracture the specimen in a sideways impact just before Auger spectroscopy.

Two different labs conducted the Auger studies. At one lab, small particles containing phosphorus was detected at the fracture surfaces. These particles were associated with a “wake”-like structure that had previously been found at creep testing of copper with high amounts of creep and plastic deformation. The particles found need to be further investigated to evaluate the density and size of the particles. However, at the other lab no phosphorus at all was detected at the surfaces.

Sammanfattning

Denna studie syftar till att undersöka rekristallisationsbeteendet hos syrefri fosfordopad koppar (Cu-OFP) och om fosforn i kopparn går att finna på brottytor.

Rekristallisationsstudierna använde sig av koppar som tagits från ett kapsellock. Denna koppar glödgades, kallvalsades och åldrades vid sex olika temperaturer under tidsförlopp som löpte från 1 dag till 12 månader. Temperaturerna kan delas in i två kategorier: lågtemperaturprover (75, 125, 175 °C) och högtemperaturprover (250, 350, 450 °C). Som referens studerades även ett prov som endast hade glödgats, och ett som hade glödgats och kallvalsats. Hårdhetsmätningar gjordes på den åldrade kopparn och referensproverna. Hårdhetsmätningarna analyserades statistiskt för att ta reda på om det fanns signifikanta skillnader i medelhårdhet mellan olika tidsförlopp och temperaturer.

Hårdhetsmätningarna för koppar som hade åldrats vid 75, 125 och 175 °C hade mycket stora variationer i hårdhet, vilket gjorde det svårt att se ifall det fanns några skillnader i hårdhet mellan olika tidsförlopp och temperaturer. Den statistiska analysen visade att när jämförelser av medelhårdhet mellan olika tidsförlopp inom samma temperaturer gjordes, var det endast vissa tidsförlopp vid 75 och 175 °C som gick att särskilja från varandra vid en statistiskt signifikant nivå. Det fanns dock inget särskilt mönster för dessa hårdhetsförändringar och heller gick det inte att relatera förändringarna till ändringar i mikrostrukturen. Vidare gick det inte att dra slutsatsen att medelhårdheten för alla tidsförlopp vid 75, 125 och 175 °C gick att särskilja från varandra. Medelhårdheten för proverna åldrade vid dessa temperaturer var nära hårdheten för ett av referensproven, det kallvalsade provet, som också uppvisade stor variation i hårdhet. Sammantaget indikerade hårdhetmätningarna att ingen rekristallisation hade skett för proverna som åldrats vid 75, 125 och 175 °C, oavsett tidsförloppet. De metallografiska undersökningarna bekräftade denna misstanke, där man inte såg någon rekristallisation för någon av lågtemperaturproverna. Vissa tecken på återhämtning fanns dock.

För högtemperaturproverna var variationen i hårdhet lägre, vilket man även såg hos det glödgade referensprovet. Provet som hade åldrats vid 250 °C under 1 dag gick tydligt att urskilja från resten av högtemperaturproverna: det hade en mycket högre hårdhet. Resten av proverna hade en mycket lägre hårdhet som låg nära hårdheten hos det glödgade referensprovet. Dessa resultat från hårdhetsmätningarna stämde väl överens med de metallografiska undersökningarna, där det observerades att provet som hade åldrats vid 250 °C under 1 dag hade en begynnande rekristallisering. Efter 1 veckas åldring vid 250 °C var rekristallisationen nästan fullständig, och alla prov från längre tidsförlopp än 1 vecka vid 250 °C var helt rekristalliserade. Vid 350 och 450 °C var proven fullständigt rekristalliserade redan efter en dag.

Kornstorleken hos lågtemperaturproverna förändrades inte under åldringen, medan kornstorleken hos högtemperaturproverna ökade med ökande tidsförlopp. Det fanns även vissa signifikanta variationer i hårdhet mellan olika tidsförlopp. Vid 250 och 450 °C såg man en signifikant ökning av hårdhet efter 6 månaders åldring, en ökning som bestod vid längre tidsförlopp för samma temperaturer. Denna ökning av hårdhet kunde dock inte relateras till några ändringar i mikrostrukturen och kräver ytterligare undersökningar för att klargöra vad orsaken kan vara.

För att kunna upptäcka fosfor på kopparens brottyta, gjordes svepelektronmikroskopi på kopparbitar som hade tagits från provstavar som utsatts för krypprovning vid förhöjd temperatur. Kopparbitarna togs från den deformerade mätlängden på provstaven. Kopparbitarna bröts av strax innan mikroskopin påbörjades så att en nyskapad brottyta kunde studeras. I svepelektromikroskopet utnyttjades sedan Augerspektroskopi för att studera den kemiska sammansättningen på partiklar och dylikt som upptäcktes på ytan. Två olika labb genomförde dessa undersökningar. Hos det ena labbet fann man små partiklar på ytan som innehöll fosfor. Dessa partiklar fann man i väldefinierade strukturer på ytan som tidigare har observerats i krypprovad koppar, mer specifikt i krypprovad kommer som utsatts för stor grad av plastisk deformation. Vid det andra labbet fann man dock inte någon fosfor.

Contents

1 Background

Since phosphorus increases the ductility of copper it is the method of choice for the canister material in the KBS-3 system. This is desired because copper with high creep ductility will deform without cracking. The remaining issue is the distribution of phosphorus in the copper where the phosphorus has not been possible to observe yet. A previous study using time of flight secondary ion mass spectroscopy (TOF-SIMS) showed that the phosphorus was evenly distributed in the grains (Andersson-Östling et al. 2018). The resolution of the TOF-SIMS is however too low to detect any phosphorus at the grain boundaries if for instance a monolayer of phosphorus is present. Since grain boundaries are vital to the creep properties of a metal further research is needed.

The work presented in this report is aimed at studying phosphorus doped copper with regards to the recrystallization behaviour during ageing and the phosphorus content and grain boundaries. The recrystallization behaviour is of interest because of the extremely long timescales that are of relevance for repository of spent nuclear fuel. If the copper does not recrystallize and the grain boundaries are immobile during the repository the creep properties should remain unchanged.

In this part of the report copper specimens have been aged at different temperatures and times to if possible permit extrapolation to the temperatures of the repository.

The presence of phosphorus at the grain boundaries have been studied by Auger electron spectroscopy (AES). AES is a method which permits a close study of surfaces and the atoms present there.

2 Method and experiments – recrystallization

The copper material tested in this project comes from a copper canister lid (SKB id TX219). The test matrix is shown in Table 2-1. Rectangular (ca. 20 × 10 mm) copper specimens that had been annealed and cold-rolled were aged at temperatures ranging from 75 to 450 °C and durations ranging from one day to six or 12 months. The specimens had been annealed at 600 °C for 10 minutes and cold-rolled to a thickness reduction of 40 %. The reason for such a high reduction was to maximize the amount of cold work in the specimens in order to provoke as much recrystallization as possible. For reference, two specimens were also produced without any ageing: one that had only been annealed, and one that had been annealed and cold-rolled. This gave two well-defined states which roughly correspond to the two extremes of the ageing tests: one with large recrystallized grains and no texture corresponding to high-temperature specimens, and one heavily deformed non-recrystallized with a strong texture corresponding to low-temperature specimens.

Table 2-1 Test matrix for the ageing of copper. The reference specimens (annealed and rolled) are not included.

Duration	75 °C	125 °C	175 °C	Duration	250 °C	350 °C	450 °C
1 day	✓	✓	✓	1 day	✓	✓	✓
4 days	✓	✓	✓	1 week	✓	✓	✓
1 week	✓	✓	✓	1 month	✓	✓	✓
2 weeks	✓	✓	✓	3 months	✓	✓	✓
1 month	✓	✓	✓	6 months	✓	✓	✓
2 months	✓	✓	✓	9 months	✓	✓	✓
3 months	✓	✓	✓	12 months	✓	✓	✓
6 months	✓	✓	✓				

Some specimens in the table above were then prepared for metallographic analysis in scanning electron microscope (SEM). In the SEM, images and electron backscatter diffraction (EBSD) data were obtained to capture the behaviour most relevant for this investigation: recrystallization and grain growth. Due to the large grain sizes observed at higher temperatures, some high-temperature specimens were also selected for analysis in light optical microscope (LOM). Examinations in EBSD were made in two batches.

Hardness was investigated with a micro-indentation Vickers hardness tester, Q10A+. Hardness measurements (Vickers) were done on all of the specimens. Five indentations were made on each specimen using a 0.05 HV (50 g) indenter. Images for the hardness analysis were captured using a 100x magnification lens. The distance between two indentations was 0.8 or 0.6 mm. The 0.05 HV indenter was used because it has been used in previous copper investigations. Specimens which had been prepared for SEM were used for hardness measurements after SEM imaging had been done. These specimens had been prepared by grinding, polishing and electrolytic polishing and had a very good surface finish. This had been done by several different researchers over a long period of time.

At first, for the measurements of high-temperature specimens from one day to three months, a distance of 0.8 mm between the centre of each indentation was used. All other measurements were done with such a distance of 0.6 mm (this distance is illustrated in Figure 2-1). Later on in the project, all of the 250 °C specimens were measured again using a distance of 0.6 mm to control whether different indentation distances affected the results.

Furthermore, all of the hardness measurements were made as 5 points on a line profile. There were some issues with arranging the specimens to have them perfectly planar to the indenter, which could possibly account for some of the variation observed in the measurements. It could also be due to true variation in hardness because of the microstructure. An example of an indentation is given in Figure 2-2.

The results were further analyzed statistically in order to compare the effects of annealing.

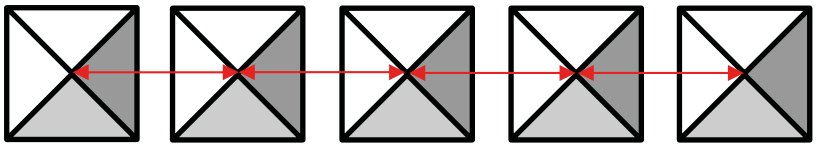

Figure 2-1. *Schematic illustration of indentations, showing that measurements were performed equidistantly in a straight line. The red arrows are not drawn to scale.*

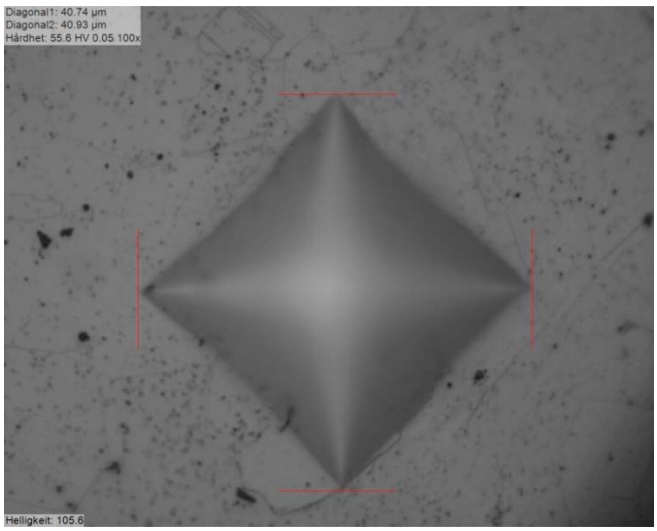

Figure 2-2. *Micro-hardness indentation made in copper examined in this study. One side of the square is ca. 30 µm in this image.*

3 Results – recrystallization

3.1 Hardness

The hardness has been measured in a factorial experiment involving annealing temperature and holding time. Table 3-1 shows the difference between the hardness of pre-annealed copper test pieces and the hardness after 40 % cold work by rolling. It also shows how the hardness measurements decrease with the most important factor temperature, and that it is rather indifferent to the second factor (holding) time. Only for high temperatures and long holding times there is an additional strengthening effect. Table 3-2 shows the previously mentioned additional measurements for 250 °C specimens.

Table 3-1. Hardness of pre-annealed, rolled, and rolled and annealed test pieces.

											N	Average
Pre-annealed			**45.1**	**49.9**	**43.5**	**44.1**	**46.4**				**5**	**45.8**
Rolled			**131**	**115**	**117**	**130**	**125**				**5**	**124**
	1 day	**4 days**	**1 week**	**2 weeks**	**1 month**	**2 mos.**	**3 mos.**	**6 mos.**	**9 mos.**	**12 mos.**		
75 °C	109	132	112	109	124	126	122	122				
	115	111	104	110	119	118	126	119				
	111	118	106	120	129	111	117	98.8				
	111	126	108	112	110	119	126	111				
	103	109	106	122	109	114	108	116				
125 °C	112	135	114	132	117	121	104	116				
	108	111	117	118	109	116	124	118				
	128	114	123	112	115	120	126	116			125	116
	119	117	105	118	115	121	123	124				
	127	112	115	110	128	113	112	109				
175 °C	119	117	112	113	108	111	123	114				
	129	116	117	112	114	105	122	118				
	124	114	118	115	119	122	122	115				
	119	106	113	117	113	124	121	113				
	114	121	122	113	118	117	124	113				
											40	51.1
250 °C	108		51.2		52.0		46.4	64.7	66.3	61.9		
	112		**68.3**		48.3		48.2	61.7	65.3	59.6		
	112		51.9		52.3		50.5	60.8	59.8	67.8		
	114		48.4		48.1		49.4	63.5	55.6	59.6		
	112		53.6		51.9		46.9	66.3	63.1	68.1		
350 °C	49.2		51.9		50.2		48.9	50.3	48.9	47.7		
	46.7		49.6		50.7		49.0	53.6	45.6	47.7		
	49.2		47.2		51.9		51.8	**70.0**	47.8	46.8	30	62.5
	51.0		50.3		52.1		50.0	52.1	46.9	45.9		
	51.6		48.8		50.9		47.7	52.3	49.0	45.7		
450 °C	45.0		48.6		48.2		44.5	64.1	54.5	58.2		
	44.8		48.0		44.0		44.2	68.6	60.8	58.9		
	45.1		48.7		43.4		45.9	61.8	**83.9**	60.7		
	47.0		45.8		48.5		41.4	62.0	59.7	56.8		
	45.4		45.6		46.2		43.3	57.8	66.0	57.4		
N			25				5				235	
Average			46.7				43.9					88

Table 3-2. Hardness measurements of the 250 °C specimens with an indentation distance of 0.6 mm.

		1	2	3	4	5	Avg.
250 °C	**1 day**	75.0	101	66.8	113	114	**94.0**
250 °C	**1 week**	45.6	50.6	54.0	48.8	58.1	**51.4**
250 °C	**1 month**	48.5	47.5	46.8	45.5	45.4	**46.7**
250 °C	**3 months**	50.1	45.4	47.0	46.9	48.6	**47.6**
250 °C	**6 months**	71.4	71.5	72.1	73.0	72.6	**72.1**
250 °C	**9 months**	62.8	75.2	57.5	60.7	70.7	**65.4**
250 °C	**12 months**	66.0	56.5	55.0	72.6	57.8	**61.6**
Mean of all durations at 250 °C (HV)							**62.7**

In order to compare the effects of annealing statistically, different populations can be defined (Blom and Holmquist 1994). Pre-annealed and rolled samples are obviously separate populations with different hardness. Since the hardness was measured five times it is at least possible to calculate an arithmetic average or a sample mean (*x-bar*). The sample mean is more precise than the individual measurements, but still not necessarily an accurate estimation of the unknown mean (*my*) of the population.

The measurements of the annealed test pieces have been grouped into populations of similar hardness according to visual examination of the values in Table 3-1. Surprisingly, the hardness after annealing at low temperature, 75–175 °C seems to be fairly constant, and if the measurements for 1 day at 250 °C are included a population made up of 25 subsets (samples) and 125 measurements can be formed. But for higher temperatures a systematic decrease in hardness is noticeable. What is the hardness for these samples before and after this systematic decrease? A first approximation would be to calculate the population means based on 125 and 40 measurements each. According to the population *means* in the Table 3-1 the hardness seems to decrease in average from 116.14 to 51.11 as the microstructure changes systematically after annealing.

When modelling random experimental sample data a normal distribution is often assumed. To check if the assumption of normality is valid, the sample data is visually examined in a probability plot. If the values plot close to a straight line in a probability plot the assumed distribution describes the data reasonably well (Montgomery and Runger 1994). To check this, the values have to be ordered from smallest to largest and the accumulated probability is calculated. Then, as in Table 3-3 the probability for each value x_j out of x_n values can be calculated according to the formula $(j–1/3)/(n + 1/3)$. The normalized score $z_j = \Phi^{-1}$ for each probability is available in tables or softwares. For example, in Excel the normalized scores equation is NORM.S.INV.

Table 3-3. The hardness of annealed copper sample after 1 week and 1 month at 250 °C.

i	1 week at 250 °C	1 month at 250 °C	Culumative probability $y_i = (i-1/3)/(n+1/3)$	Standardized normal scores $z_i = \Phi^{-1}(y_i)$
1	48.4	48.1	0.125	−1.15
2	51.2	48.3	0.31	−0.49
3	51.9	51.9	0.50	0.00
4	53.6	52	0.69	0.49
5	68.3	52.3	0.875	1.15

The plot of the standardized normal scores against the hardness in Figure 3-1 highlights an outlier of the five measurements when annealing at 250 °C at one week. On the other hand, the measurements when annealing 1 months connect closely to a normal distribution line in Figure 3-1b.

The choice of populations can also be evaluated by a formal analysis of variance, ANOVA (Montgomery and Runger 1994) in order to check the null hypothesis that there is no difference between hardness measurements of different temperatures and holding times. Consider the 40 measurements from 250 °C

and 350 °C with a sample mean of 51.11. The significance probabilities (p) 0.954 and 0.199 computed in the analysis of variance in Table 3-4 are high enough not to question the hypothesis that there are no systematic effects of temperature or from interaction of the two factors. The significance probability of a time effect at 0.057 is low enough to indicate that there is almost a significant difference in hardness.

In Figure 3-2 it can be seen that the hardness measurements before and after the change in metal structure, except for two outliers, could be fitted to straight lines in a normal probability plot and that normal distributions could be appropriate models, notwithstanding the two outliers.

Table 3-4. Analysis of variance of hardness for copper annealed at 250–350 °C, n = 40.

Source of variation	Sum of squares	Degrees of freedom	Mean squares	Ratio of mean square (F)	Significance probability (p)	Comment
Temperature	0.060	1	0.060	0.003	0.954	Not significant
Time	185.4	4	46.4	2 570	0.057	Almost significant
Interaction	61.19	2	30.6	1 697	0.199	Not significant
Error	577.1	32	18.0	-		√18.0 = 4.25
Total	**823.72**	**39**	**21.12**			**√21.12 = 4.60**

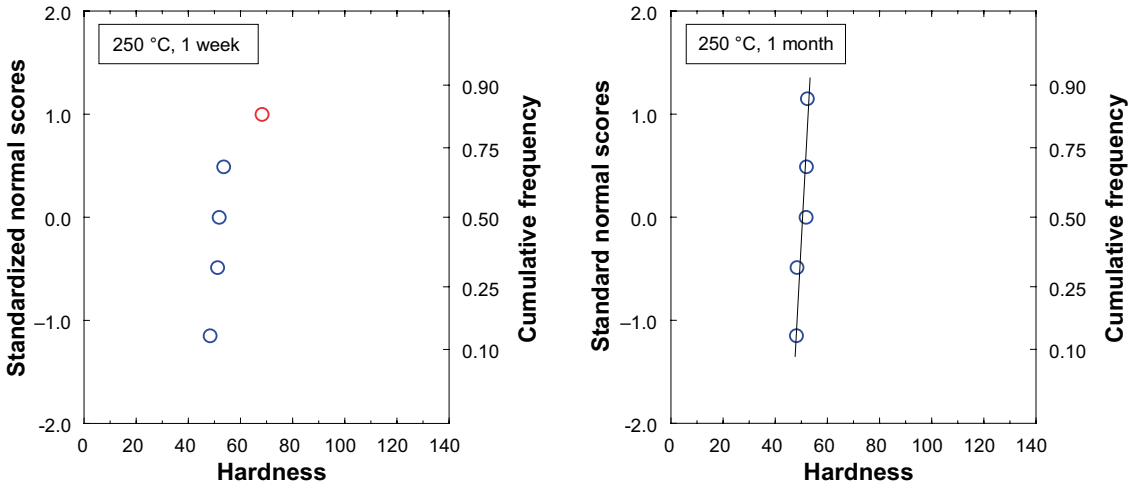

Figure 3-1. *Normal probability plots for copper hardness annealed at 250 °C for a) 1 week and b) for 1 month.*

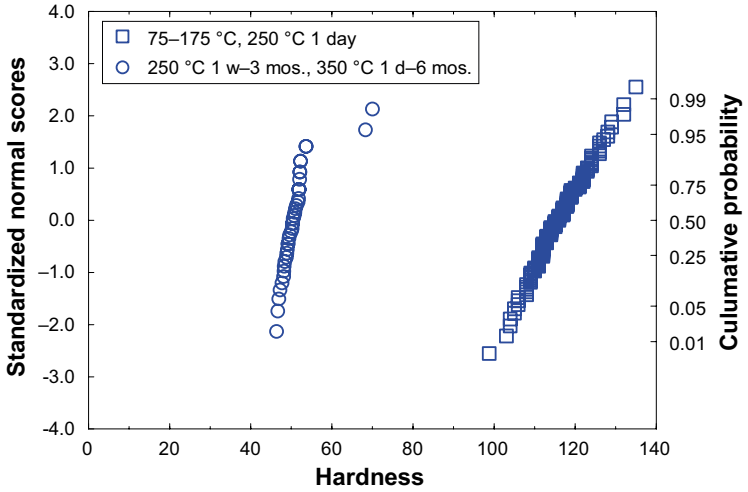

Figure 3-2. *Normal probability plot of rolled and annealed copper samples.*

Figure 3-3 and Figure 3-4 show all of the measured hardness values as points, and lines connecting the average for each group of measurements (one group being, e.g., 350 °C one day) with straight vertical lines between data points within a group indicate the range . The straight black horizontal lines corresponds to the average hardness for the rolled (Figure 3-3) and annealed state (Figure 3-4) and the actual data points, 5 for each specimen, are plotted at the left extreme of the graph.

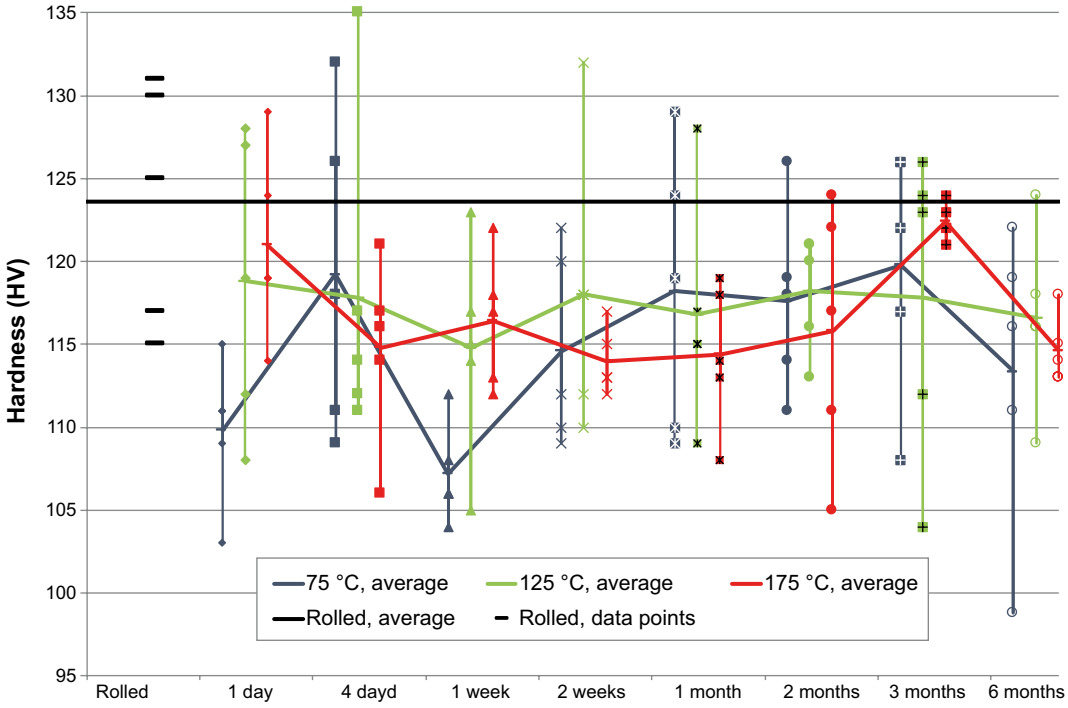

Figure 3-3. *Micro-hardness (Vickers) measurements of 75, 125 and 175 °C at aging durations ranging from 1 day to 6 months. All groups have 5 measurements, but some values were identical which is why some groups seem to have only 4 data points.*

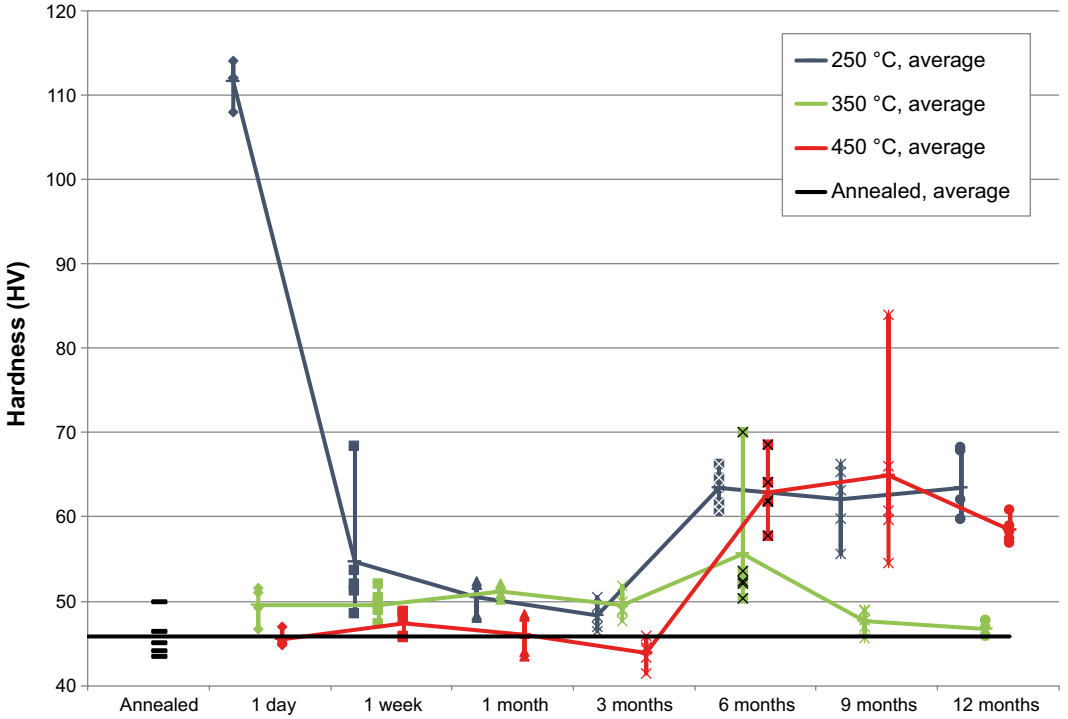

Figure 3-4. *Micro-hardness (Vickers) measurements of 250, 350, 450 °C at aging durations ranging from 1 day to 12 months.*

From Figure 3-3 and Figure 3-4, it is evident that there is large variation in the hardness measurements. For the low-temperature specimens, there is large variation within each group (a certain temperature and ageing duration). For the specimens aged at high temperatures, the variation within each group is, for the most part, smaller than for the specimens aged at low temperatures, though with some outlier values.

A one-way analysis of variance (ANOVA) of the hardness for samples aged at different temperatures was conducted (see Appendix) with the objective of understanding if there is a statistically significant difference (at a level of 0.05) in the mean hardness.

It was concluded that the mean hardness from the 75, 125 and 175 °C samples were different from 250, 350 and 450 °C samples. It could not be concluded that mean hardness values of 75, 125 and 175 °C were different from each other. The mean hardness values of 350 and 450 °C were not different from each other, but they were different from that of 250 °C. Based on this analysis, two groups of samples with comparable hardness could be identified: one group with samples aged at a lower temperature (75, 125 and 175 °C) and one with samples aged at a higher temperature (350 and 450 °C). The sample aged at 250 °C had a larger variability than the other samples and cannot be grouped with any of the other samples.

When considering variation within temperature groups, the following variation was statistically significant at a level of 0.05:

At 75 °C, the only mean hardness values that differed were those for an aging time of 1 week and an aging time of 3 months. At 125 °C, there were no differences among the means. At 175 °C, the only mean hardness values that differed were that for an aging time of 3 months which differed from 2 weeks and 6 months.

At 250 °C, an aging time of 1 day differed from all other aging times. 1 week, which had a large variation, differed only from 1 day. 1 month and 3 months did not differ from each other but differed from 1 day, 6 months, 9 months, 12 months. At 350 °C, 1 month differed from 9 months and 12 months. 6 months did not differ from any else, but it had a large variation. At 450 °C, 12 and 6 months differed from 1 day, 1 week, 1 month and 3 months. 9 months did not differ from any else, but it had a large variation.

3.2 Grain structure

Scanning electron microscopy (SEM) images of the annealed and cold-rolled specimens are shown in Figure 3-5 and Figure 3-6. These are shown coloured according to an inverse pole figure (IPF) colour key, using data obtained by electron backscatter diffraction (EBSD). Different colours thus indicate different crystal orientations, and grain boundaries are shown in black based on a specified misorientation criteria of 10 degrees. Low angle boundaries are shown based on a criteria of 1 or 2 degrees.

It is expected that the low-temperature specimens are similar to the non-recrystallized microstructure in Figure 3-6, while the high-temperature specimens are similar to the microstructure in Figure 3-5. The deformation direction in the images is random.

Metallographic investigation showed no evidence of recrystallization in any of the low-temperature specimens. A deformed substructure, in the images seen as thin black low angle boundaries which cover virtually the whole surface captured in the images, is present in all of the low-temperature specimens, indicating that no recrystallization has occurred. Recrystallized areas would instead show up as areas where this deformed substructure has been consumed and new grains are forming. A select number of low-temperature specimens have been shown in Figure 3-8 to Figure 3-12 to show that the microstructure is not recrystallized.

Recrystallization was observed starting from 250 °C one day and it was fully developed after more than one week. 350 °C and 450 °C were fully recrystallized already starting from one day.

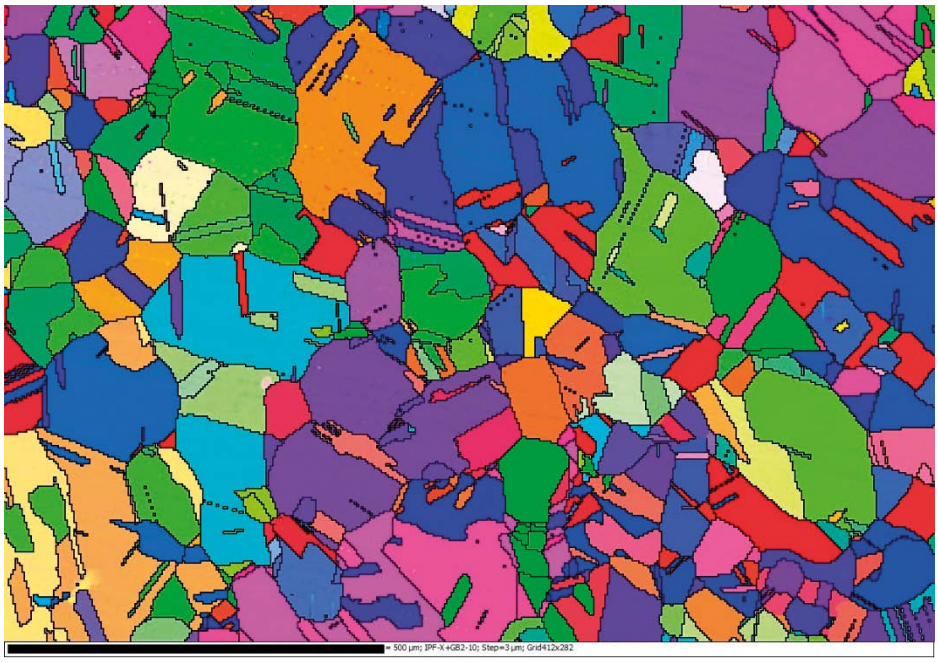

Figure 3-5. *Annealed specimen. Fully recrystallized with an average grain size of 116 µm. 500 µm scale bar.*

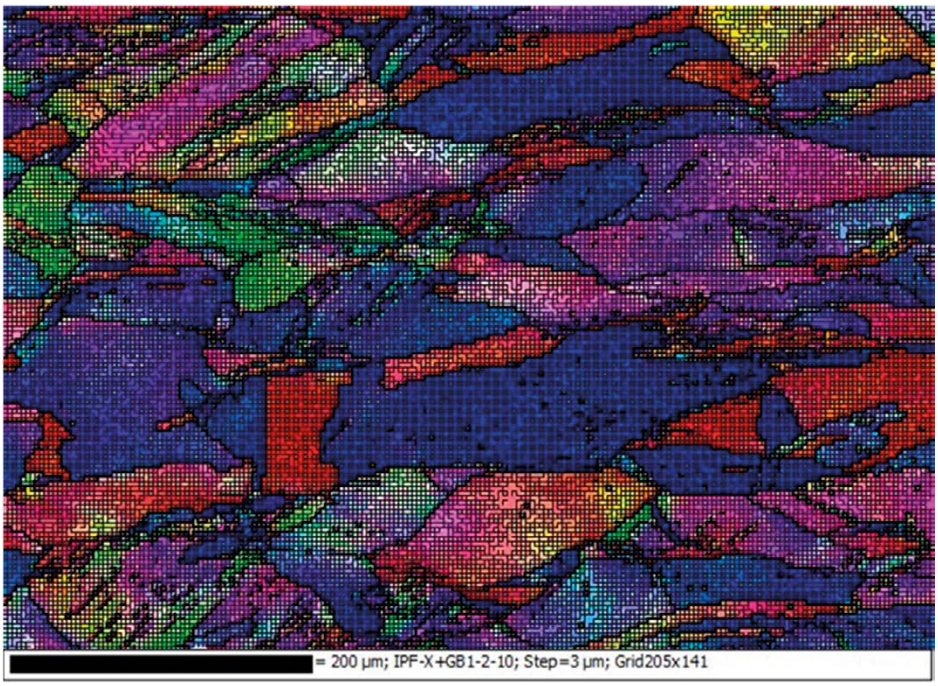

Figure 3-6. *Cold-rolled specimen. The microstructure is dominated by low angle boundaries, seen as black pixels covering the whole surface. This is the deformed substructure. 200 µm scale bar.*

The average grain size (as evaluated by software using EBSD data) increased as the duration increased for all of the higher temperatures (Figure 3-7), but especially so for 350 °C and even more so for 450 °C. Starting from duration of six months, the 450 °C specimens had grains so large that the grain size analysis had to be done manually using LOM images.

The grain sizes for the low-temperature specimens were virtually constant: this can be seen from the images in 3.2.1. This is expected since they had not recrystallized.

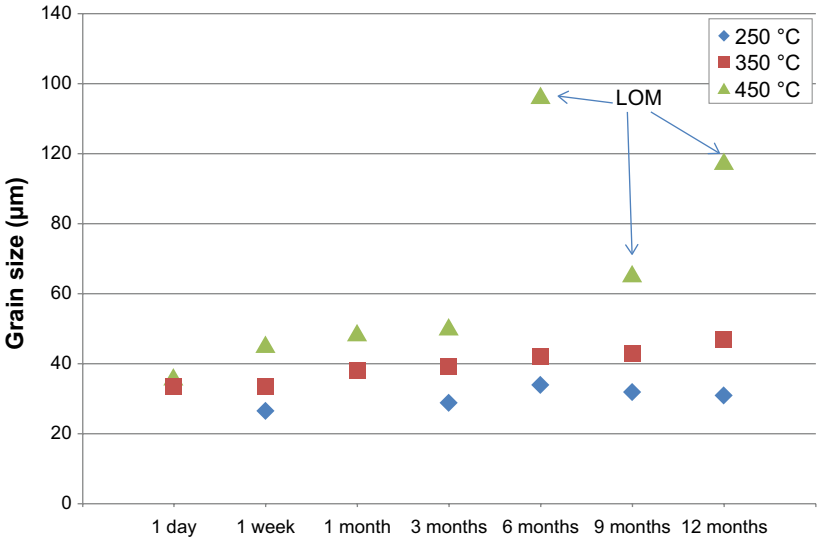

Figure 3-7. *Average grain size (µm) for 250, 350 and 450 °C for ageing durations ranging from 1 day to 12 months. For 250 °C, the 1 day specimen had only recrystallized partially so the grain size was not measured. Data for 250 °C 1 month was not available. For 450 °C, the three last durations (6, 9 and 12 months) were measured manually using LOM images as opposed to a software evaluation using EBSD data which is how the remaining measurements were done.*

3.2.1 Low-temperature specimens

None of the low-temperature specimens showed any signs of recrystallization at any duration (Figure 3-8, Figure 3-9, Figure 3-10, Figure 3-11, Figure 3-12). In some images there are areas that are completely white (Figure 3-8, Figure 3-9, Figure 3-12): these are pixels that have not been indexed. If trends of increasing hit-rate are seen, i.e., if non-indexed white areas progressively disappear as ageing progresses, it could be a sign of recovery.

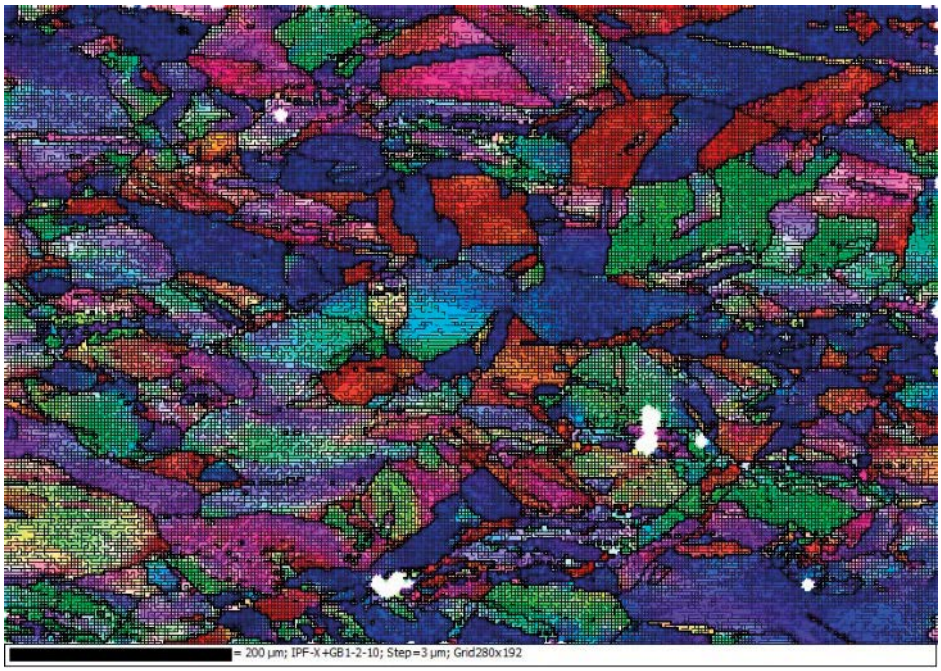

Figure 3-8. *75 °C, 1 week, step length 3 µm. A heavily deformed non-recrystallized microstructure is seen. White areas are pixels that have not been indexed, which can be due to e.g. the heavy deformation or specimen preparation. 200 µm scale bar.*

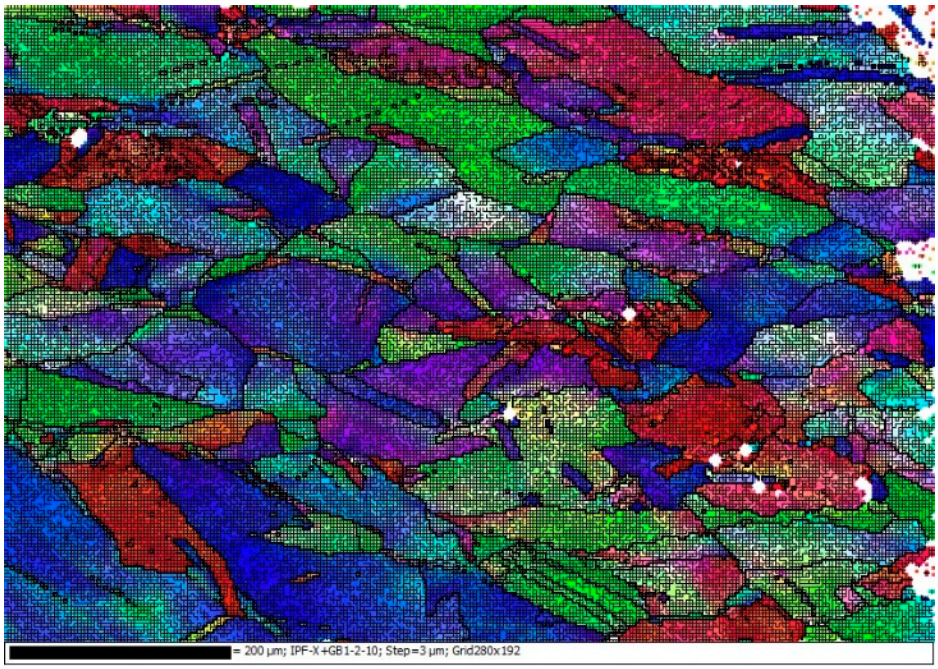

Figure 3-9. *75 °C, 3 months, step length 3 µm. This microstructure is also deformed and has not recrystallized. White areas are pixels that have not been indexed. 200 µm scale bar.*

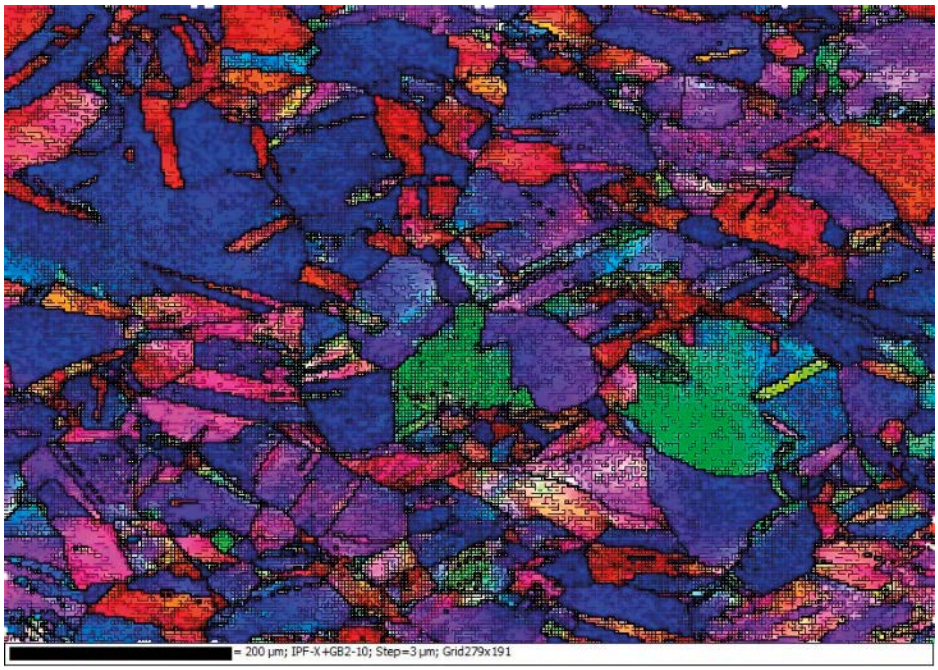

Figure 3-10. *175 °C, 2 weeks, 3 µm step length. The deformed substructure previously seen still persists and no recrystallization has occurred. The previously seen white areas have now disappeared, a possible indication that recovery has occurred. 200 µm scale bar.*

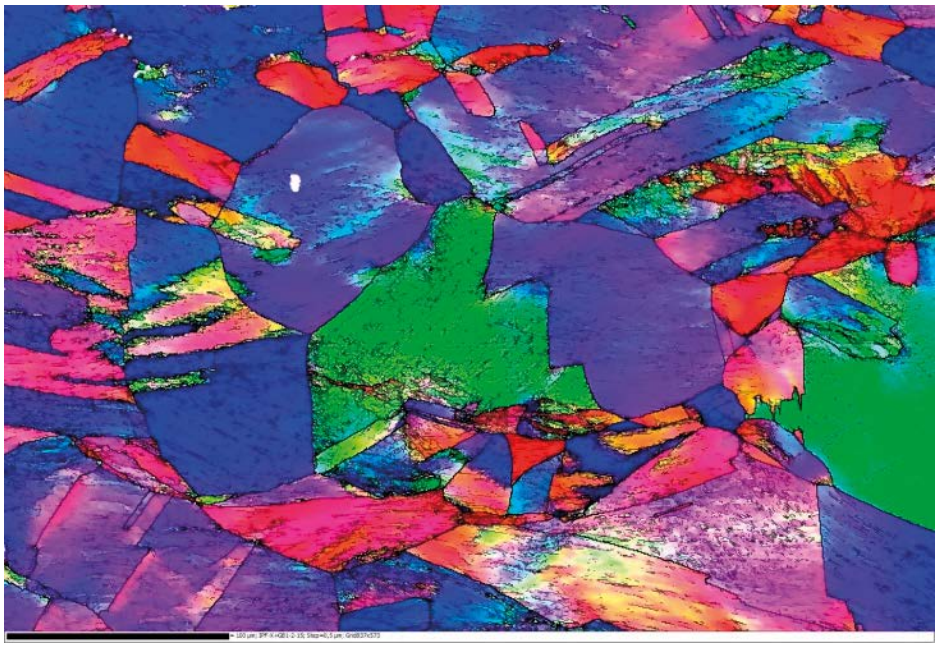

Figure 3-11. *175 °C, 2 weeks, 0.5 µm step length. 100 µm scale bar.*

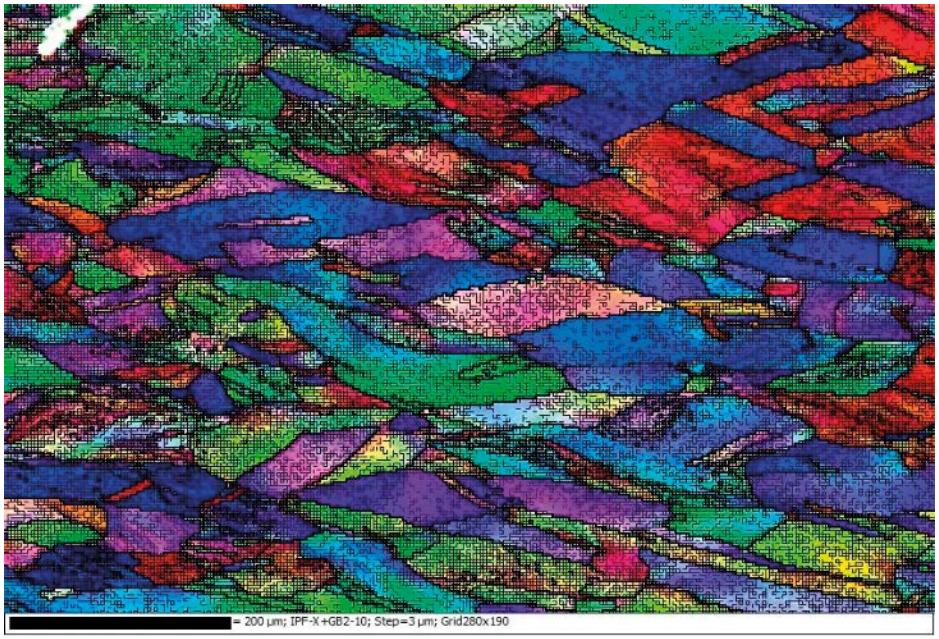

Figure 3-12. *175 °C, 6 months, 3 µm step length. The deformed substructure is very clearly still present, despite the long ageing duration at 175 °C. 200 µm scale bar.*

3.2.2 250 °C

Recrystallization was observed in the high-temperature specimens starting from the lowest temperature and time: 250 °C one day (Figure 3-13, Figure 3-14, Figure 3-15). Recrystallization is well developed by one week (Figure 3-17) and for all durations beyond that microstructure is fully recrystallized (Figure 3-19, Figure 3-21, Figure 3-22), as indicated by the absence of a deformed substructure (white areas in Figure 3-15) and the abundance of twins (Figure 3-15, Figure 3-16, Figure 3-18, Figure 3-20). Grain growth also occurred in the material (Figure 3-7).

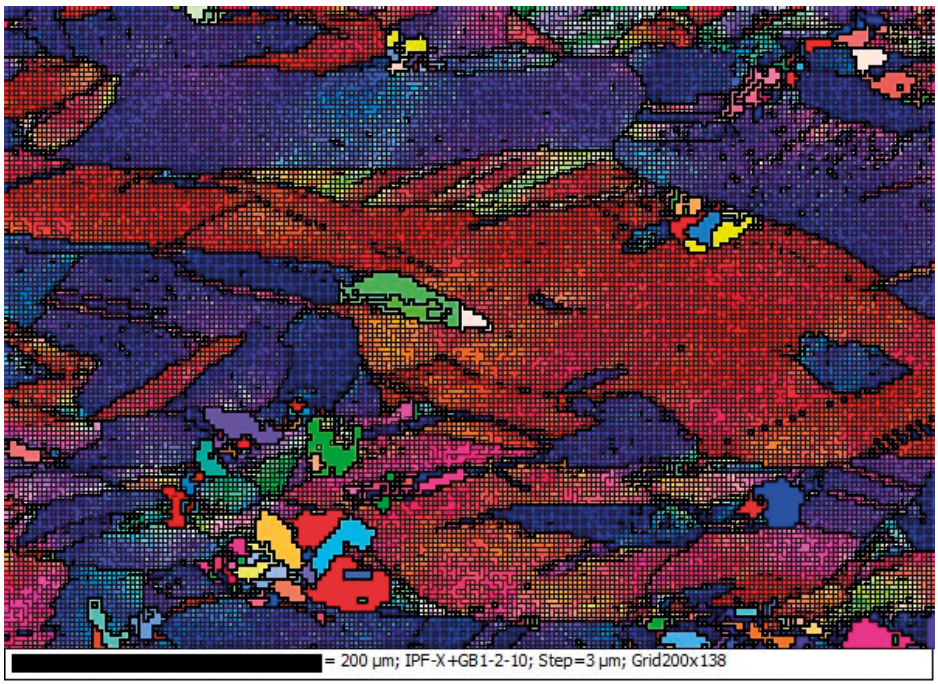

Figure 3-13. *250 °C, 1 day specimen. It is very clear that recrystallization has started at several locations in the microstructure, here seen as light areas free of the deformed substructure. These are new grains forming. 200 µm scale bar.*

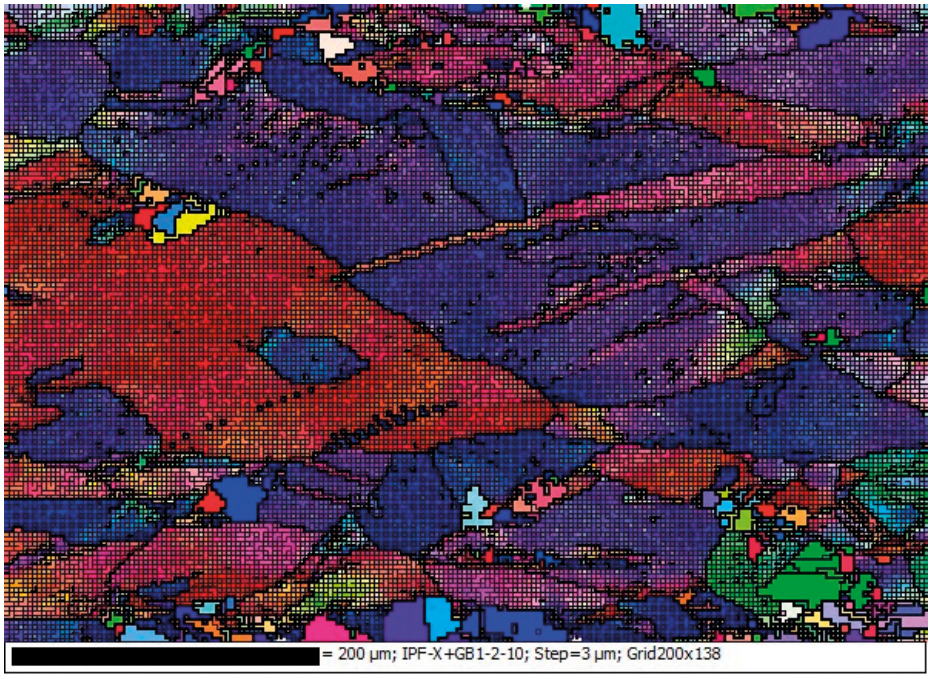

Figure 3-14. *250 °C, 1 day, showing additional spots of recrystallization. 200 µm scale bar.*

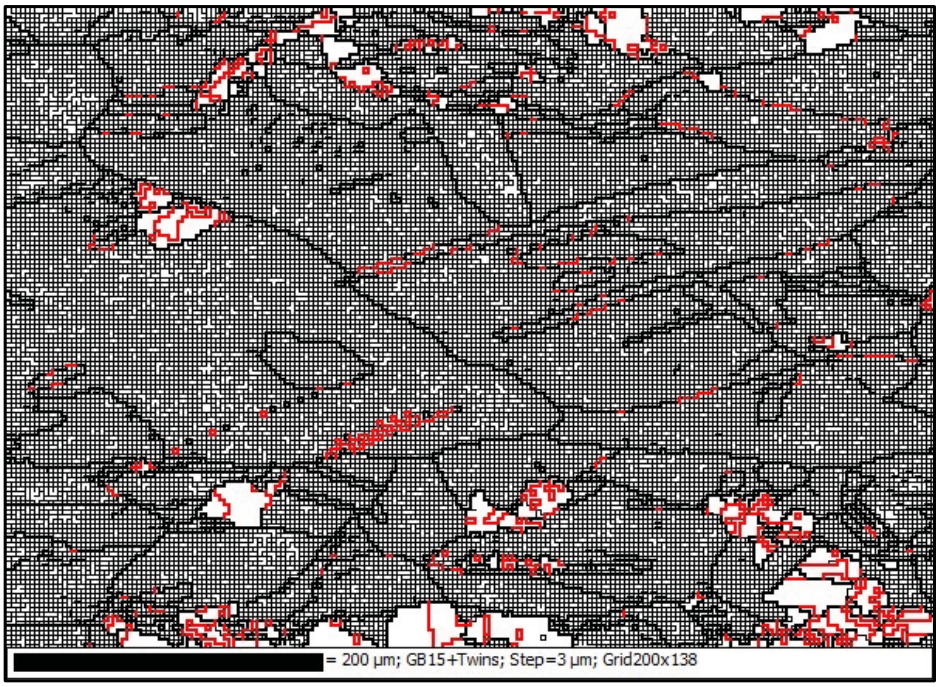

Figure 3-15. *250 °C, 1 day, same area as in Figure 3-14, showing grain boundaries (thick black), low angle boundaries (thin black) as well as twin boundaries (red). Twinning is observed to be an important mechanism associated with recrystallization. 200 µm scale bar.*

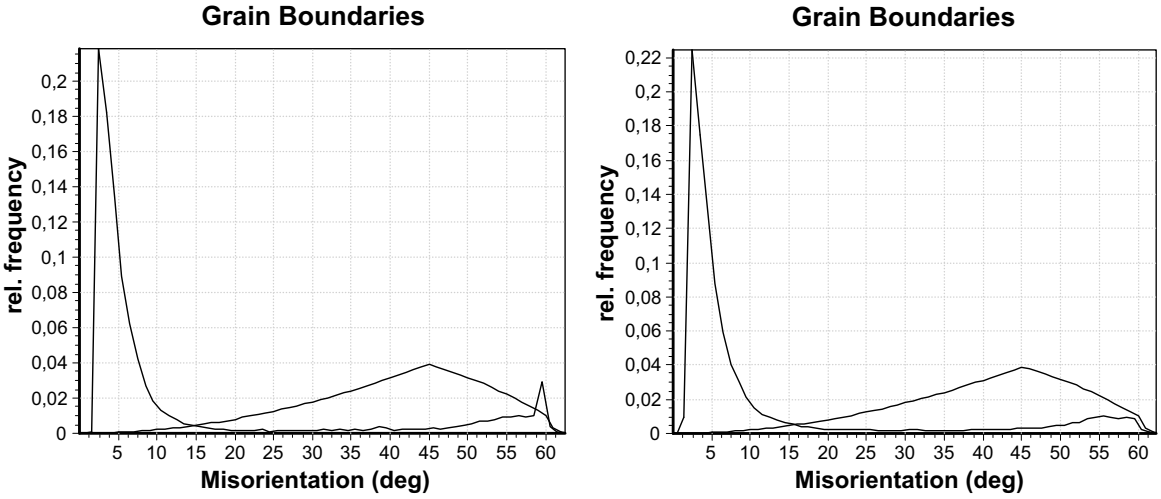

Figure 3-16. *Misorientation distribution for 250 °C 1 day (left) seen in Figure 3-13 and as cold-rolled (right) seen in Figure 3-6. Twinning can be seen as a sharp spike at the 60 degree position, indicating an increased presence of 60° <111> twins as recrystallization begins. The deformed substructure, visible as a high frequency of low angle boundaries in this figure, is present in both of the distributions since recrystallization has just started in the 250 °C 1 day specimen and only a small fraction of the sub-structure has yet been consumed.*

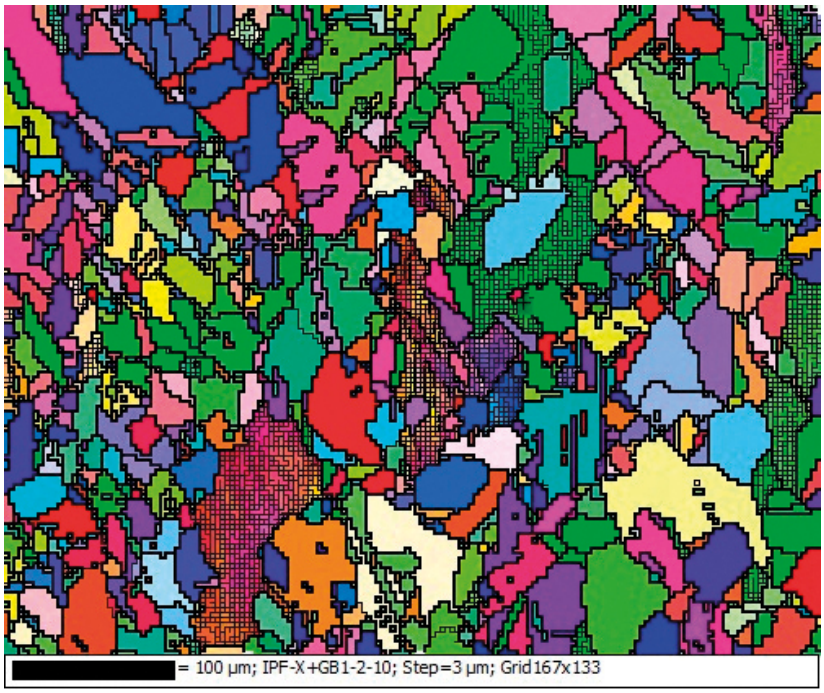

Figure 3-17. *250 °C, 1 week. After 1 week of annealing at 250 °C, most of the deformed substructure has been consumed in the recrystallization process. 100 µm scale bar.*

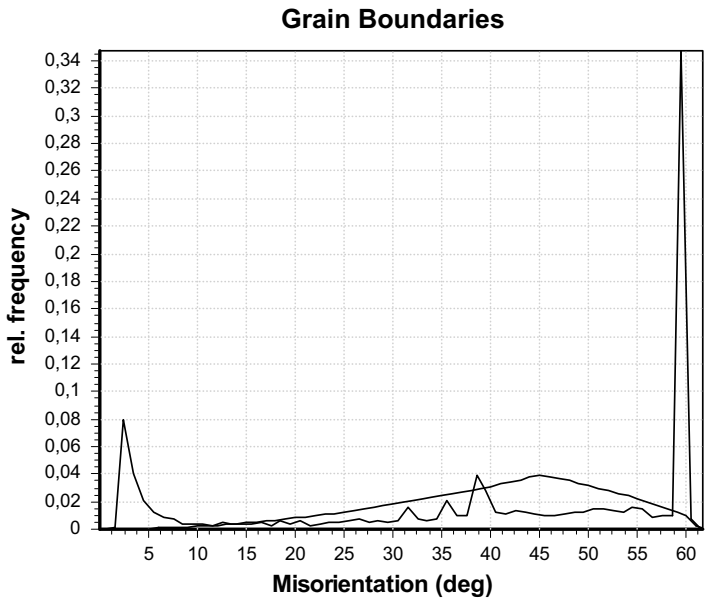

Figure 3-18. *Misorientation profile for 250 °C, 1 week. Twins are much more frequent and low angle boundaries have been dramatically reduced in frequency compared to Figure 3-16.*

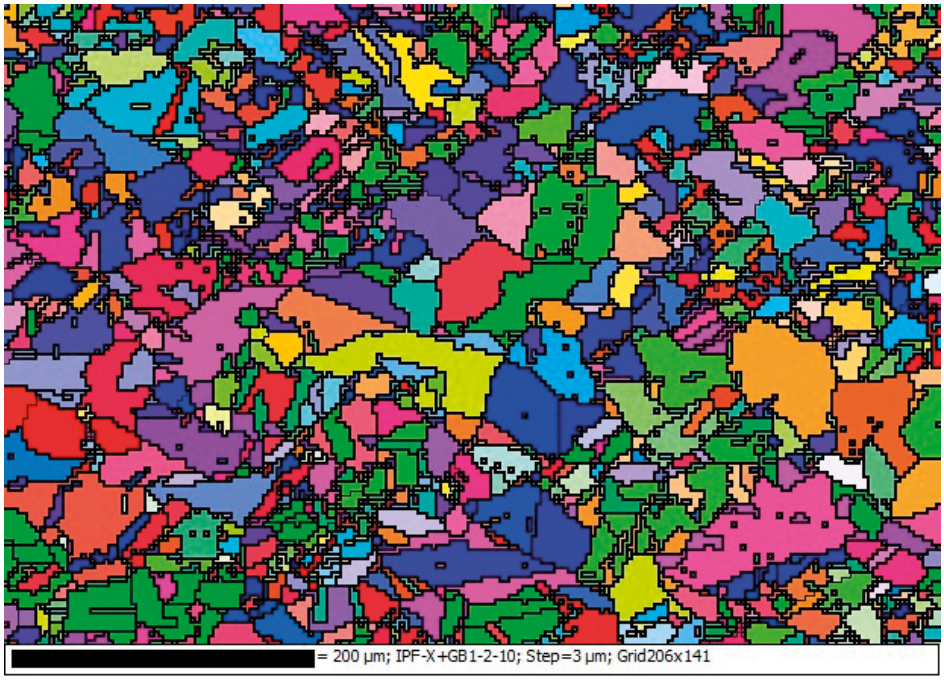

Figure 3-19. *250 °C, 3 months. All deformed substructure has been consumed and the recrystallization is fully developed. The grain size distribution has large variation: the average size was 28 µm, but some grains were in excess of 150 µm in diameter. 200 µm scale bar.*

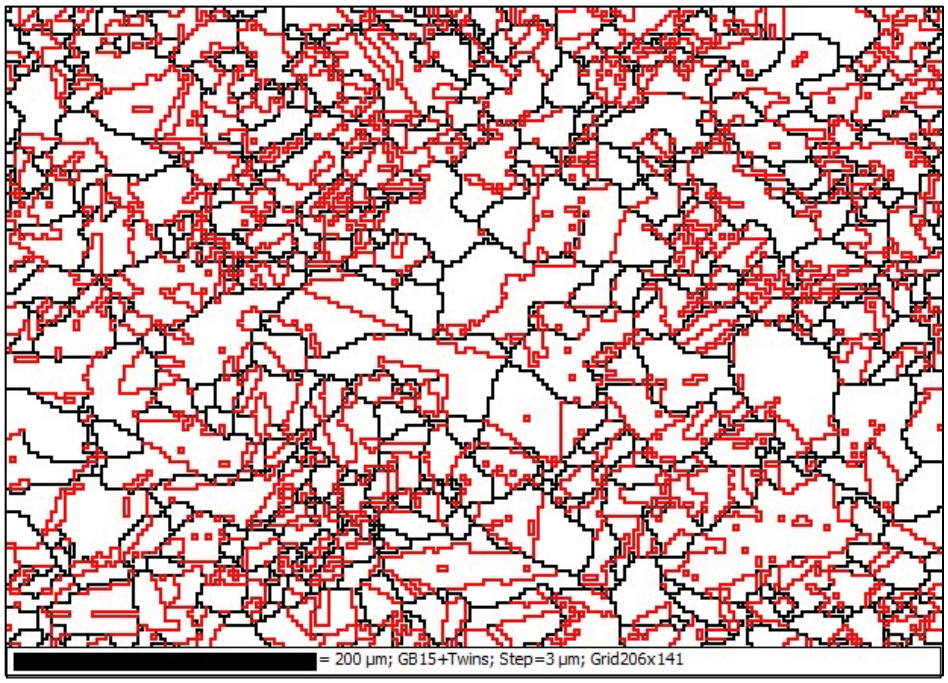

Figure 3-20. *250 °C, 3 month. Twins (red) are abundant. 200 µm scale bar.*

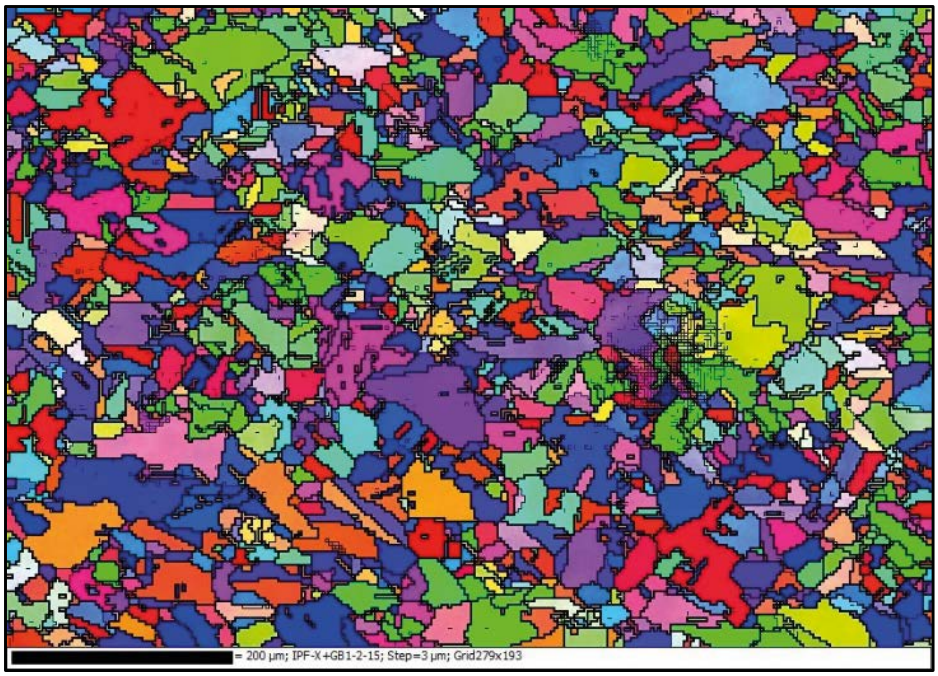

Figure 3-21. *250 °C, 6 months. The microstructure is completely recrystallized. Some deformation remained from specimen preparation. 200 µm scale bar.*

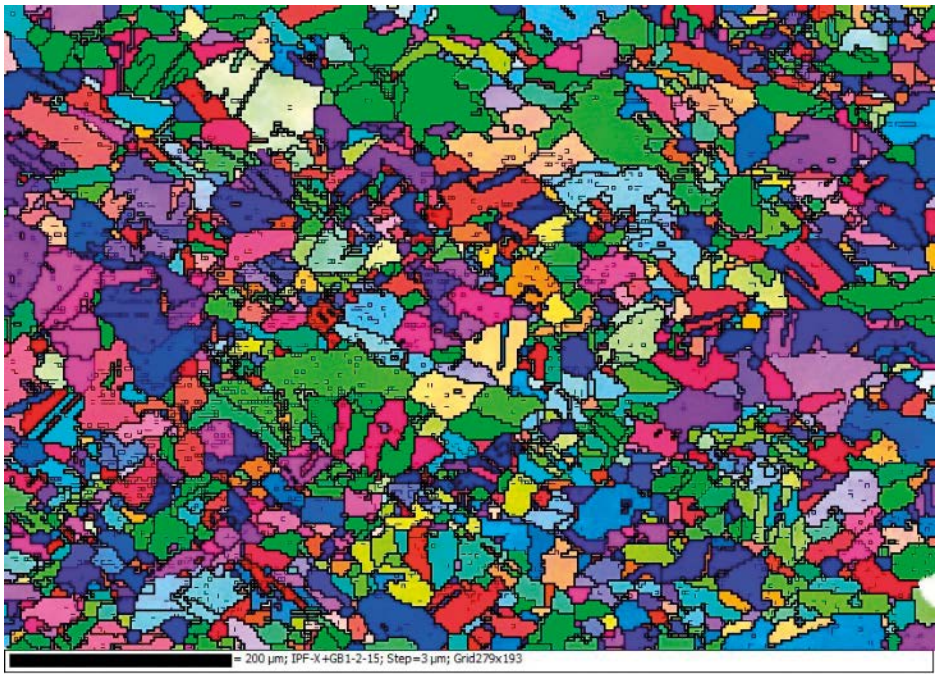

Figure 3-22. *250 °C, 12 months. Some deformation remained from specimen preparation. However, the specimen is completely recrystallized. 200 µm scale bar.*

3.2.3 350 °C

The overarching trend in the 350 °C series is that of an increasing grain size as the duration increases. The microstructure is completely recrystallized starting from the first duration of one day (Figure 3-23). Abnormal grain growth is observed (Figure 3-24, Figure 3-25, Figure 3-26, Figure 3-27).

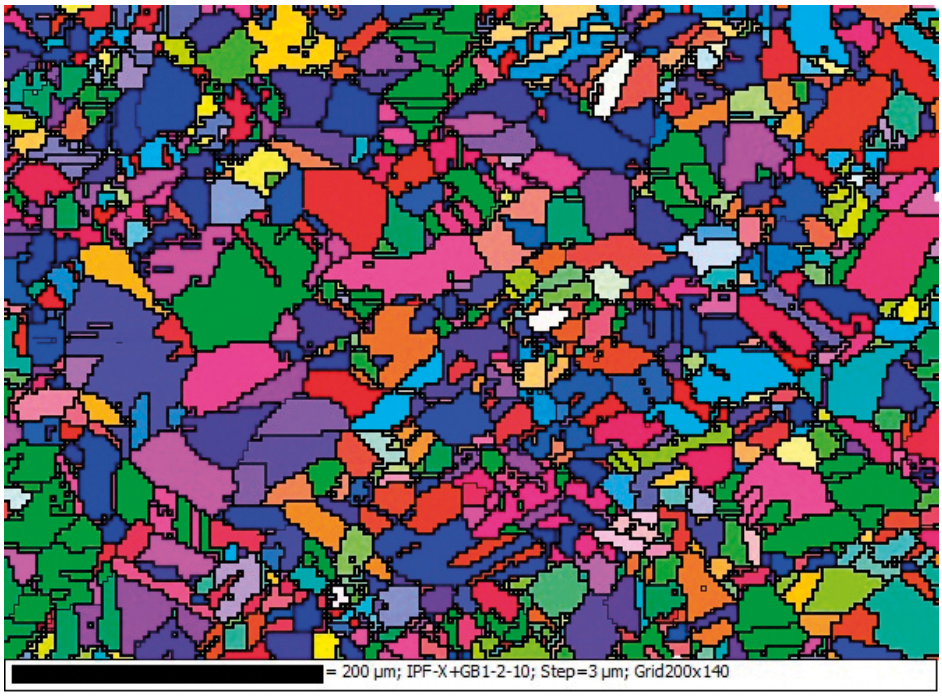

Figure 3-23. *350 °C, 1 day. Fully recrystallized. 200 µm scale bar.*

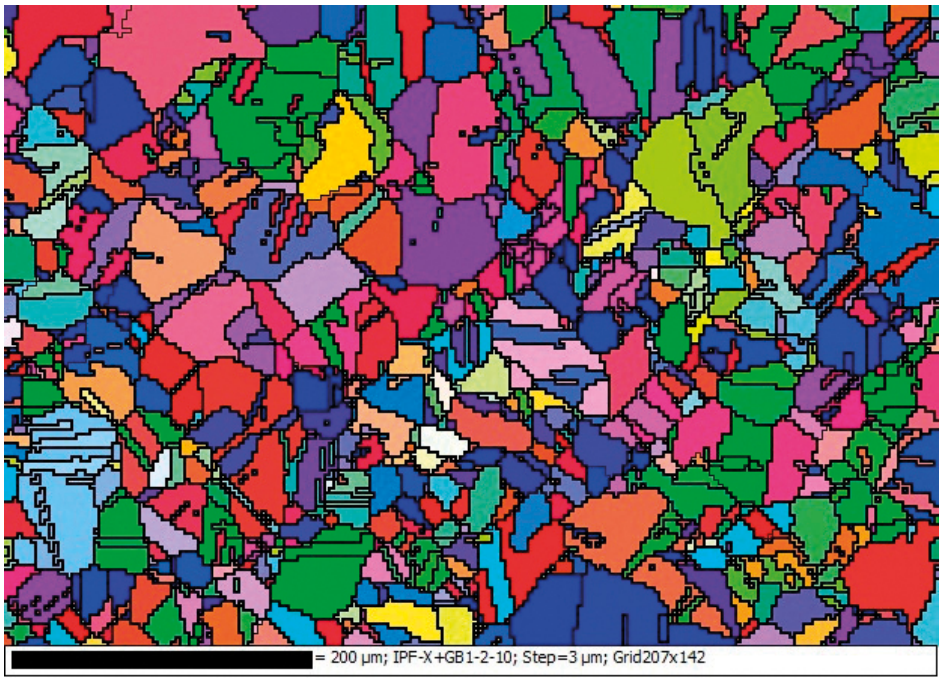

Figure 3-24. *350 °C, 1 month. 200 µm scale bar.*

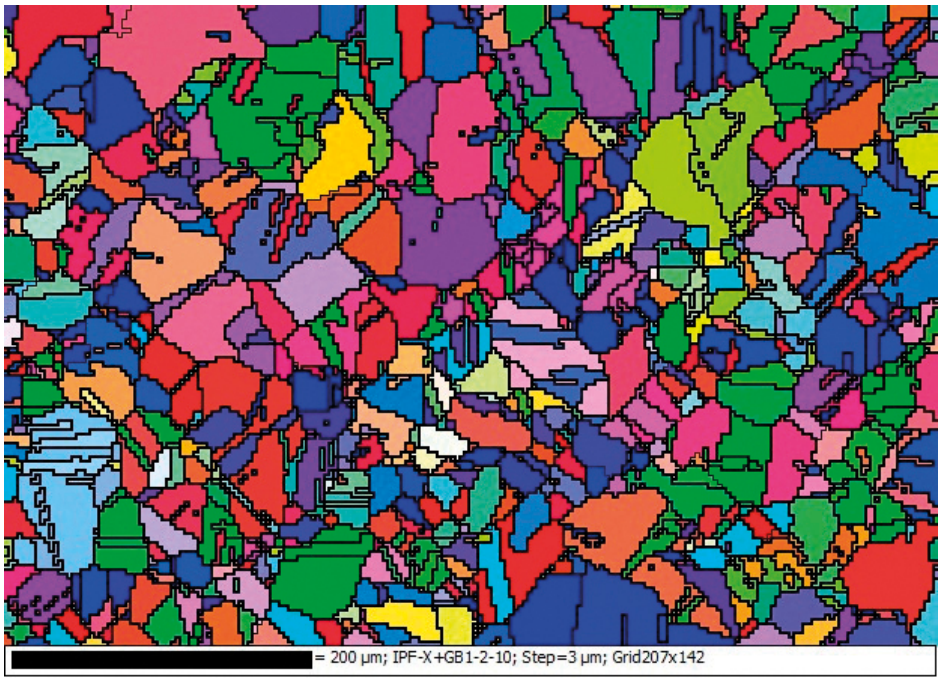

Figure 3-25. *350 °C, 3 months. 200 µm scale bar.*

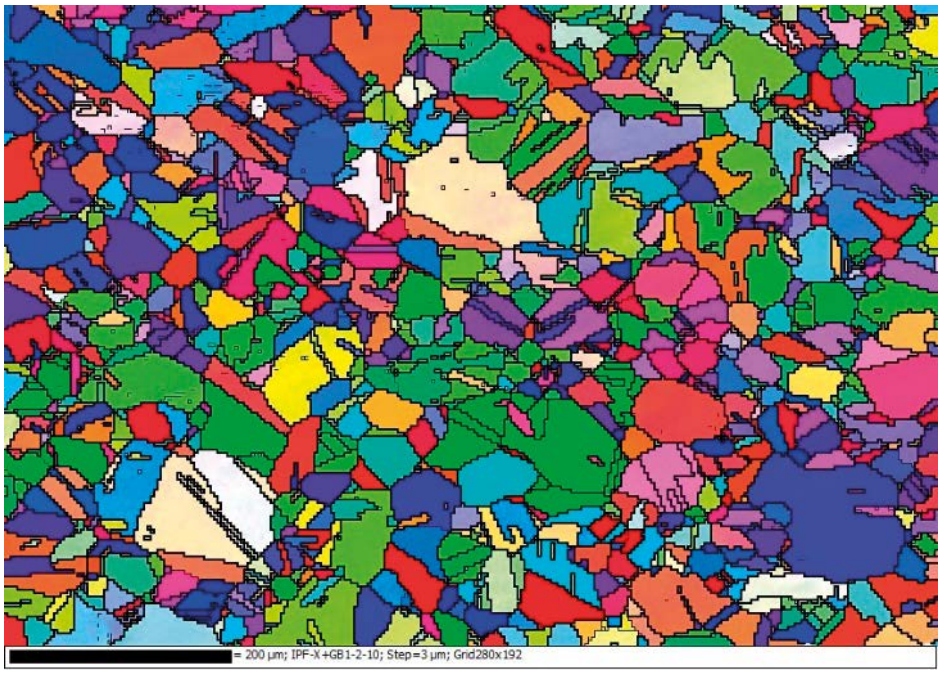

Figure 3-26. *350 °C, 6 months. Average grain size: 42 µm. 200 µm scale bar.*

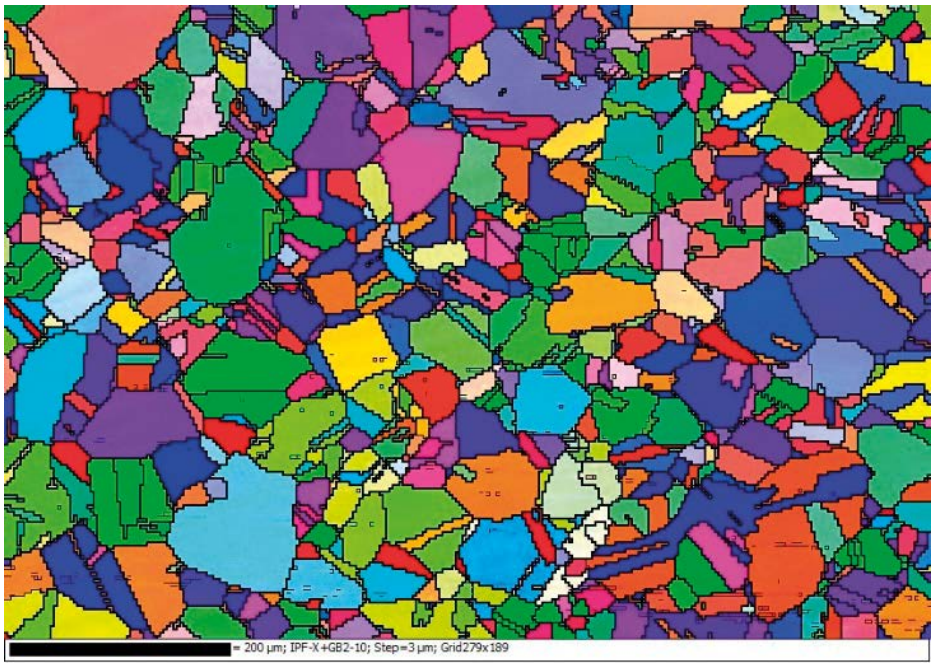

Figure 3-27. *350 °C, 12 months. 200 µm scale bar.*

3.2.4 450 °C

Similarly to 350 °C, the microstructure is completely recrystallized from one day (Figure 3-28) and the grain size increases as the duration does (Figure 3-29, Figure 3-30, Figure 3-31). In fact, the grain size beyond three months is so large that grain size measurements required light optical microscopy to capture a sufficient number of grains to make measurements on (Figure 3-32, Figure 3-33).

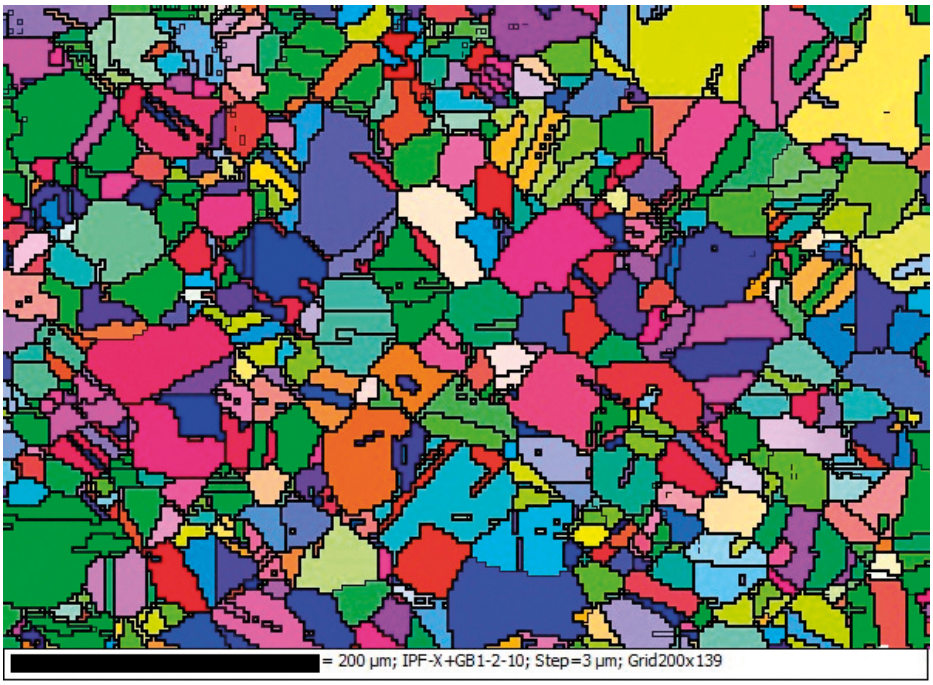

Figure 3-28. *450 °C, 1 day. 200 µm scale bar.*

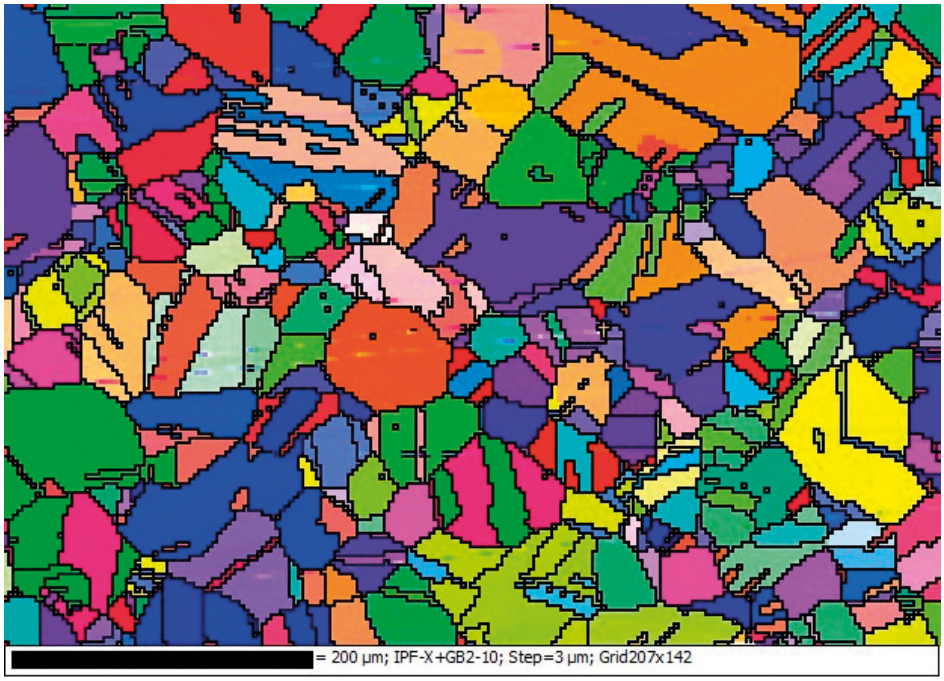

Figure 3-29. *450 °C, 1 week. 200 µm scale bar.*

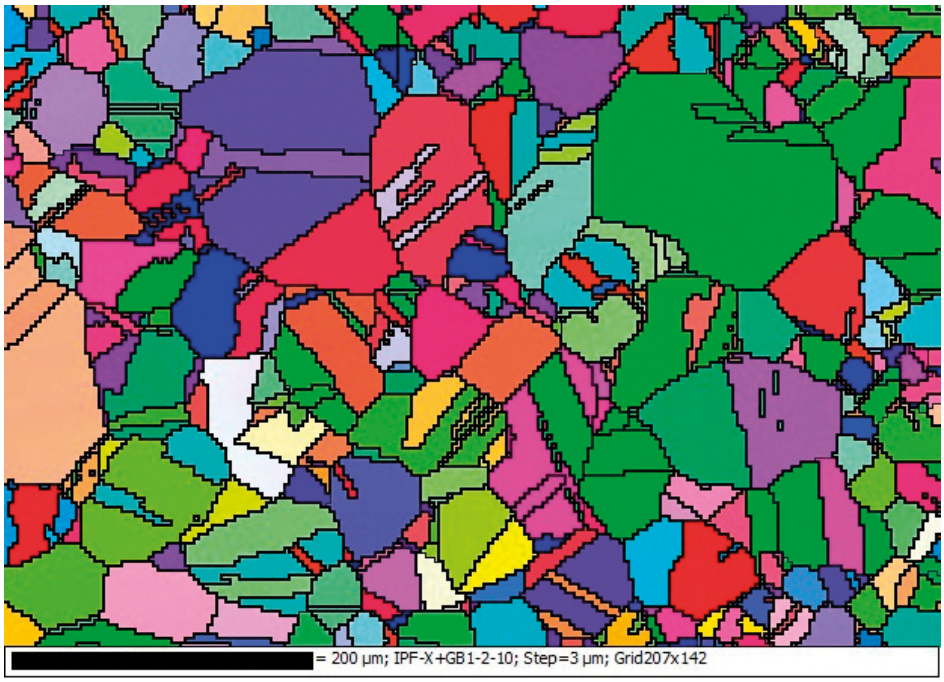

Figure 3-30. *450 °C, 1 month. 200 µm scale bar.*

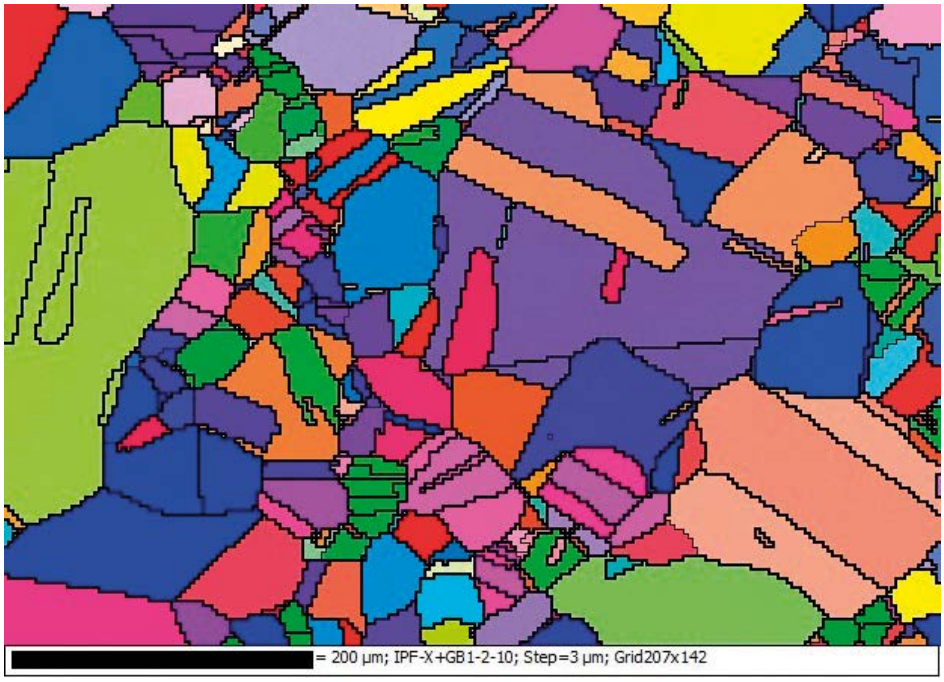

Figure 3-31. *450 °C, 3 months. 200 µm scale bar.*

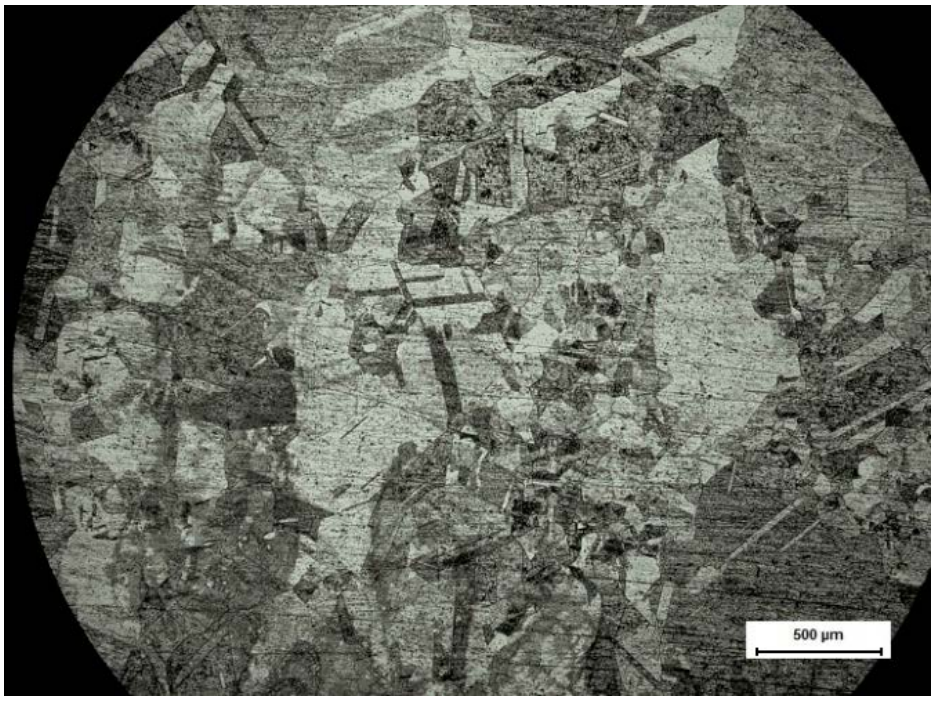

Figure 3-32. *450 °C, 6 months. 500 µm scale bar.*

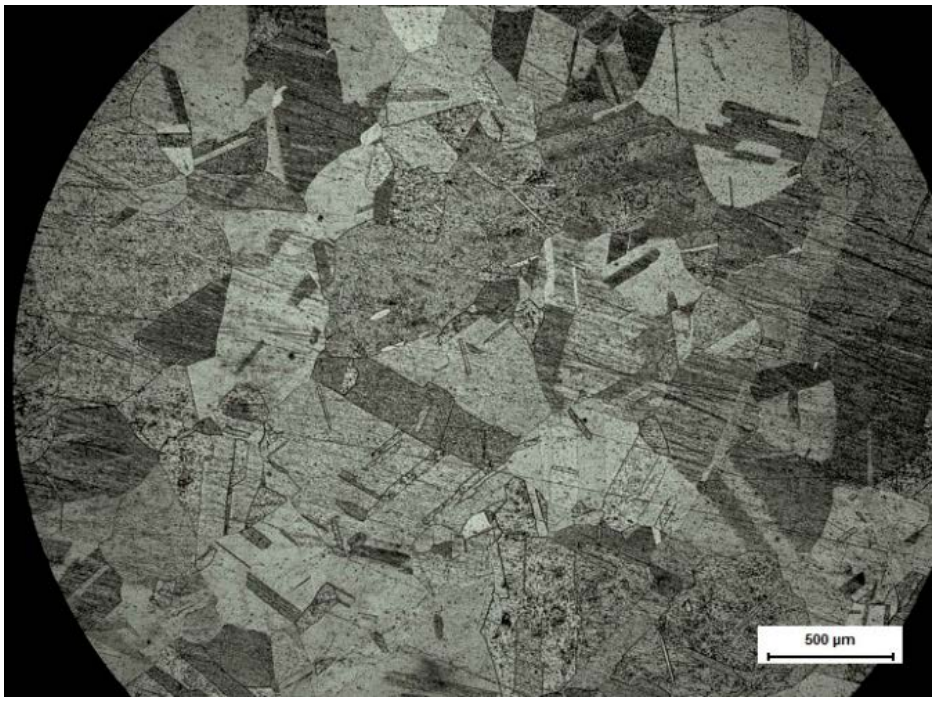

Figure 3-33. *450 °C, 12 months. 500 µm scale bar.*

4 Method and experiments – Auger spectroscopy

An Auger electron spectroscopy (AES) equipment is especially attuned to the study of surfaces using Auger electrons. An object is bombarded with either X-rays or electrons and the amount of Auger electrons emitted is then measured. The difference between normal scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDS) on one hand and AES on the other hand is that AES only studies the outmost surface, 1–3 nm, and that the energy bands studied are other than those in EDS.

Simply put, AES studies the surface of the specimen and is able to distinguish between elements that might be difficult to study using EDS if the energy peaks in EDS overlap. AES can also detect lighter elements than EDS can.

In this study, two different AES instruments have been used. One at Dalarna University in Borlänge and one at Chalmers University of Technology in Gothenburg. They use the same principle but differ in capabilities. The equipment in Borlänge has an extra chamber where a specimen can be broken in ultra-high vacuum whereas the one in Gothenburg is newer and has a lower detection limit. In both cases personnel from the respective lab operated the equipment.

The specimens used in the studies were taken from previously creep tested specimens (Mannesson and Andersson-Östling 2014). The material came from a tube with the SKB identity T58. However, no individual Auger specimen in the current project can be related to a specific creep specimen in the previous project where the actual creep testing was conducted. Copper does not exhibit a ductile to brittle transformation when cooled as do steels but remains ductile throughout. This means that it is difficult in copper to obtain by shear a fracture surface 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 fairly brittle looking surface can be achieved, a surface that should contain weakened grain boundaries. In this manner it should be possible to study the grain boundaries and find out if they are decorated by phosphorus. The tests had been interrupted just before final fracture, perhaps 20 minutes before, and exhibited a distinct necking region, Figure 4-1.

Into the necking region of the creep specimens, square specimens $3 \times 3 \times 30$ mm were machined. For most specimens this meant that remnants of the necking area were visible on the surface of the specimens. Into the necking region a 0.3 mm wide notch was spark eroded to further weaken the specimens, Figure 4-2. Finally the specimens were broken by the application of sideways force to the upper part of the specimen and the fracture surface observed in AES, Figure 4-2. The fracturing was performed in high vacuum in Borlänge and in laboratory air in Gothenburg. In Table 4-1, the chemical composition and grain size of the tube from which specimens came, is shown.

Table 4-1. Chemical composition and grain size of the tube T58. The AES specimens came from material from this tube.

	T58 (wt.ppm)	Method
O	3.2	Melt extraction, Leco TC 436 DR
P	54	Spectroscope, ARL 3460
S	< 5	Melt extraction, Leco CS 225
Grain size	198 µm	

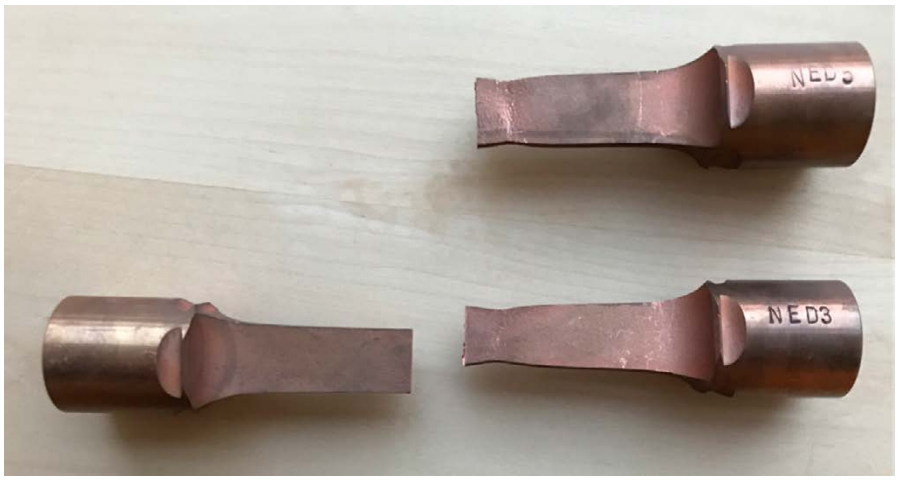

Figure 4-1. *The type of creep test specimens the specimens for the Auger studies were taken from. These pieces were used for other purposes, but the necking region is clearly visible on the right hand parts. (Mannesson and Andersson-Östling 2014)*

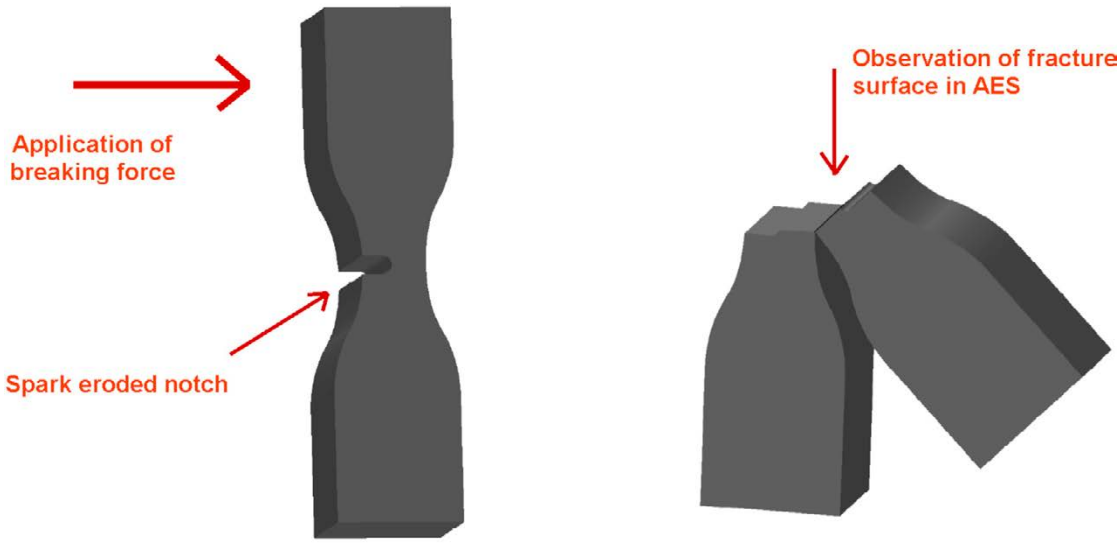

Figure 4-2. *Before study the specimens were broken by the application of force to the upper part of the specimen. The fracture surface was then studies in the AES equipment.*

5 Results – Auger spectroscopy

5.1 Dalarna University in Borlänge

The specimens were broken in vacuum and were immediately studied in AES without being subjected to oxygen, Figure 5-1. The vacuum in the system allows for approximately 20–30 minutes of study before the residual carbon and oxygen in the vacuum chamber contaminates the surface. An example of the fracture surface studied is given in Figure 5-2, where a SEM-AES image of the fracture surface is shown, with a close-up in Figure 5-3. In Figure 5-4 the results from this study are given. If phosphorus had been present on the surface there would have been a peak at around 160 eV. No phosphorus was present at any of the surfaces studied in Borlänge. This suggests that there is no monolayer of phosphorus at the grain boundaries and likely no great accumulation of smaller particles containing phosphorus either. There is no information about detection limit for phosphorus at grain boundaries in Auger spectroscopy, but the operator of the equipment stated that he should be able to see the phosphorus had it been there.

Figure 5-1. *An Auger specimen in its holder after AES.*

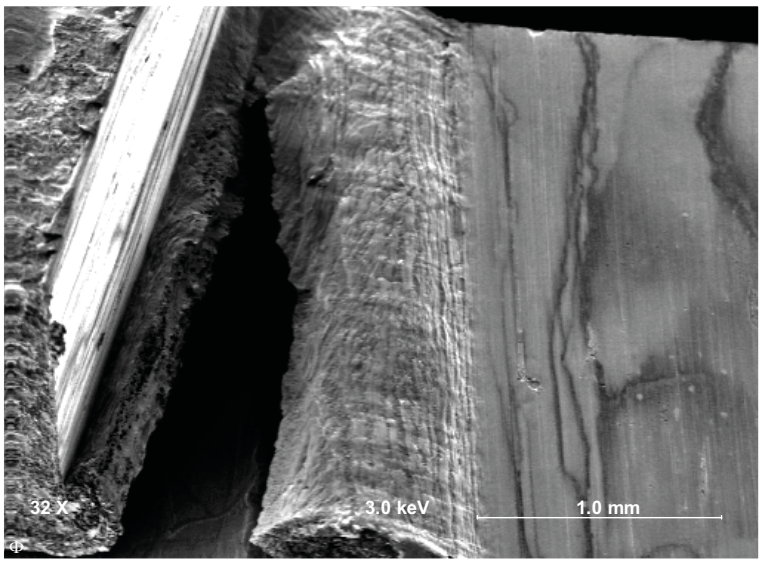

Figure 5-2. *The fracture surface studied in Borlänge. The flat surface on the right hand side is the remains of the spark eroded notch and the ridge structure in the middle the fractured surface.*

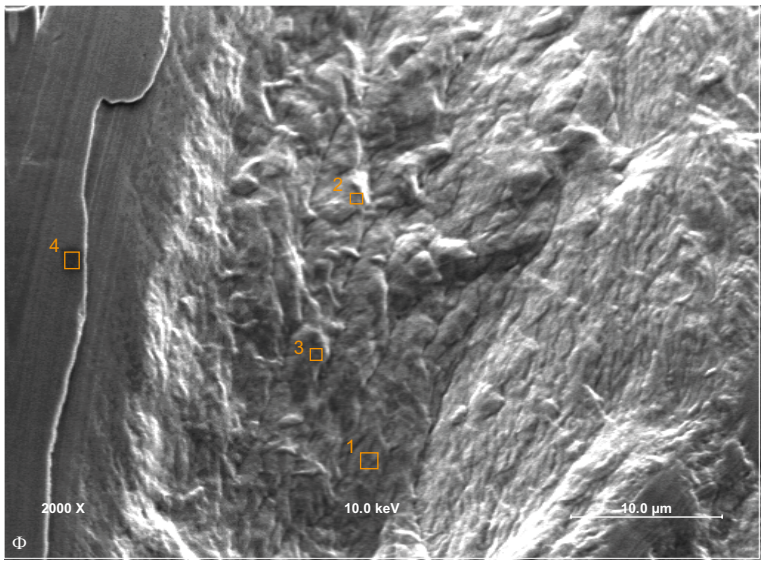

Figure 5-3. *A close-up of the fracture surface with spots for analysis marked.*

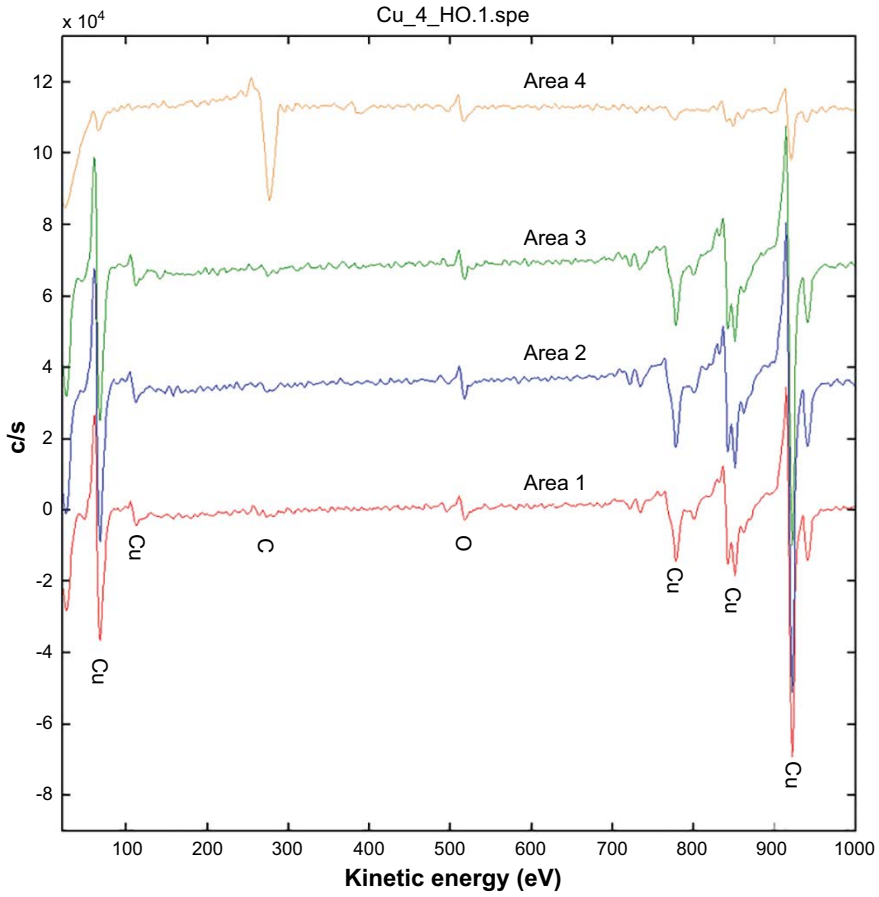

Figure 5-4. *The result from the analysis shown in Figure 5-3. If phosphorus had been present in the analysis it would have shown up as a peak around 160 eV.*

5.2 Chalmers University of Technology in Göteborg

The same type of specimens as in Borlänge was used in Göteborg, but the breaking of the specimens was performed in laboratory air immediately before insertion into the AES equipment. After breaking several areas of interest was studied in the AES equipment.

The first was the flat surface immediately adjacent to the spark eroded notch: a SEM-AES image of this is shown in Figure 5-5. In this region several particles could be found, Figure 5-6 and Figure 5-7. The AES analysis showed one very distinct particle (position 1) to consist of zinc, chlorine and sulphur. Another, more faintly visible particle (position 3) consisted of calcium, chlorine, nitrogen and antimony. The final position studied was without particles and consisted of copper and oxygen, what would be expected if the copper surface was broken in air before study in the AES. Both zinc and antimony occurs in the copper at very low levels, usually under 1 ppm, and sulphur has in the case of this material been analyzed as below 5 ppm, Table 4-1. It is impossible to say if the particles originated from the material or from contamination from the air when the specimen was broken.

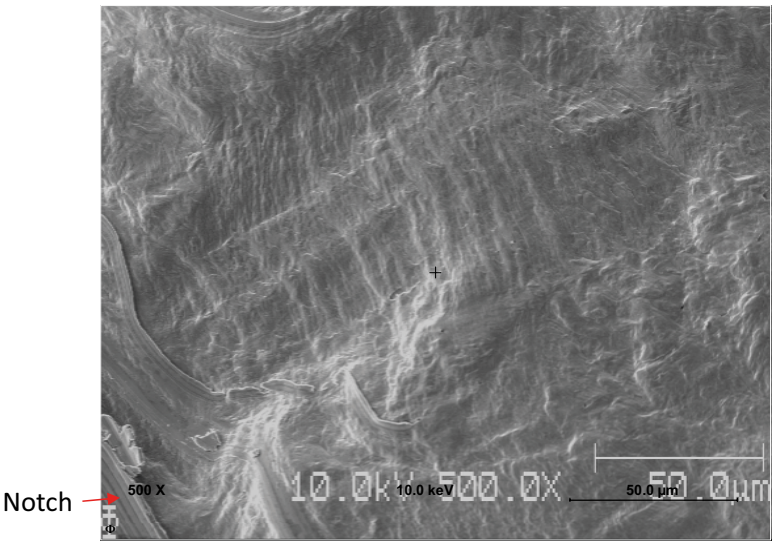

Figure 5-5. *Overview AES/SEM image of the area closest to the notch.*

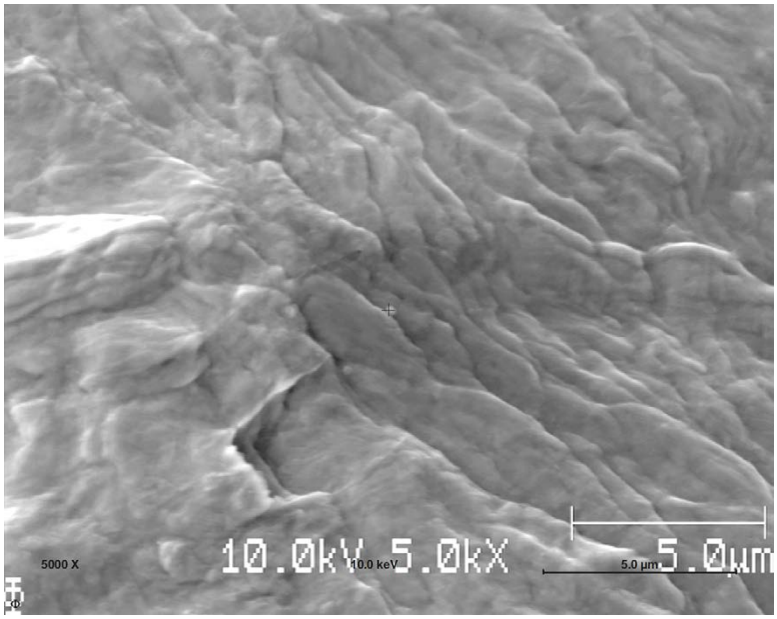

Figure 5-6. *Closeup from Figure 5-5 where a particle can be seen right in the middle of the image overlaid by a black marker.*

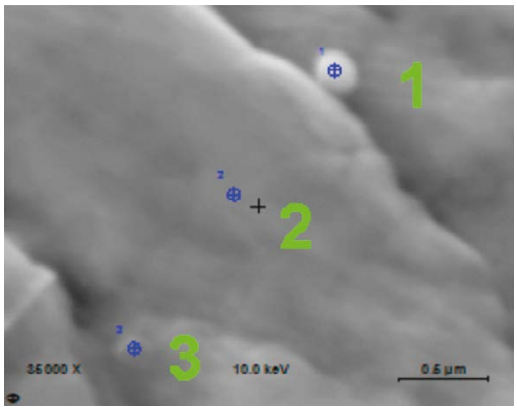

Figure 5-7. *Larger resolution of Figure 5-6 with the three analysis positions marked 1, 2 and 3.*

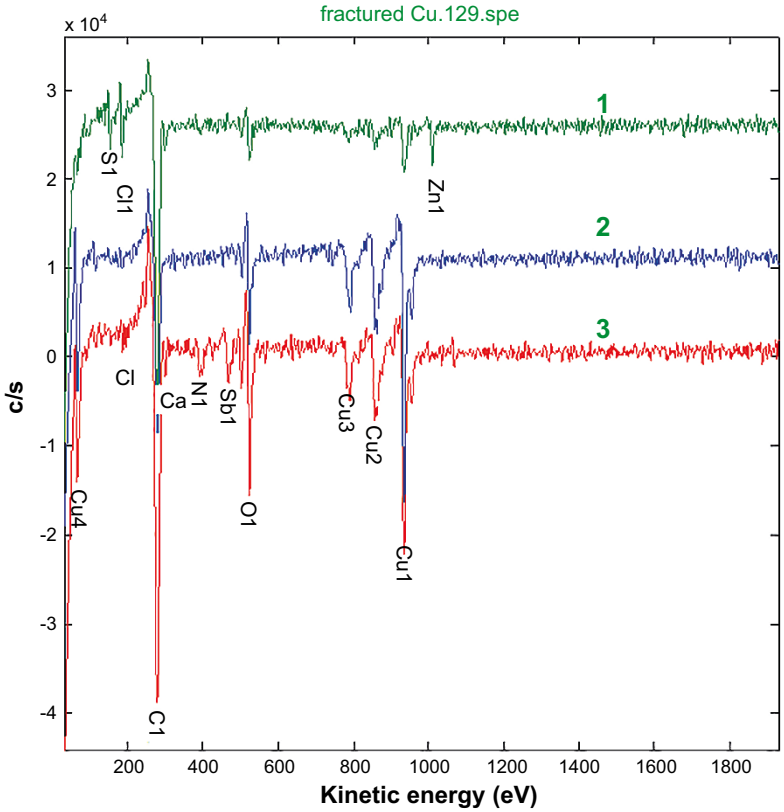

Figure 5-8. *The AES analysis from Figure 5-7 with the positions marked 1, 2 and 3. The particle at position 1 contains zinc, chlorine and sulphur. Position 3 contains calcium, chlorine, nitrogen and antimony. At position 2 signal is just copper and oxygen. The y-axis (c/s) indicates counts per second.*

A small distance further in from the notch a distinctive type of structure appeared, Figure 5-9. These wake-like structures, so named after their resemblance to the wake after a boat on water, has been observed earlier in creep crack growth specimens (Björkblad and Faleskog 2018). In that work they were attributed to large plastic deformation. In fact in uniaxial specimens, which had showed high ductility in the necking region of the gauge length, similar structures could be observed on the final fracture surface. The structures are thus associated with large creep deformation.

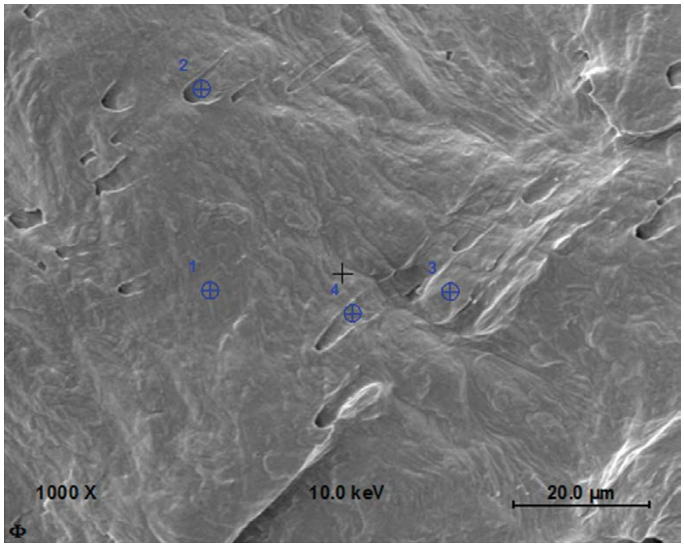

Figure 5-9. *Another overview of the shape of the fracture surface close to the notch. Note the distinctive wake-like structures on the flat surfaces.*

Inside the root of many of these structures, particles could be observed (Figure 5-10). These were analyzed by AES as depicted in Figure 5-11 through Figure 5-13, with the results summarized in Table 4.2. The results show that the particles contain significant amounts of phosphorus along with oxygen and small amounts of sulphur. One particle contained lead as well. The particles with phosphorus could only be found in the roots of the wake-like structures. Some of the particles also showed traces of iron. Sputtering to clean the surface up to 13 nm removed the phosphorus, and also the sulphur, and no new particles were revealed. Analysis of the surrounding surface showed only copper and oxygen. The phosphorus was found to be restricted only to the particles in the roots of the wake-like structures. Contaminants, even if in particle form, should be randomly distributed on the surface. However, the phosphorus containing particles are only found in the roots of these wake-like structures and the conclusion must be that they were in the material before fracture.

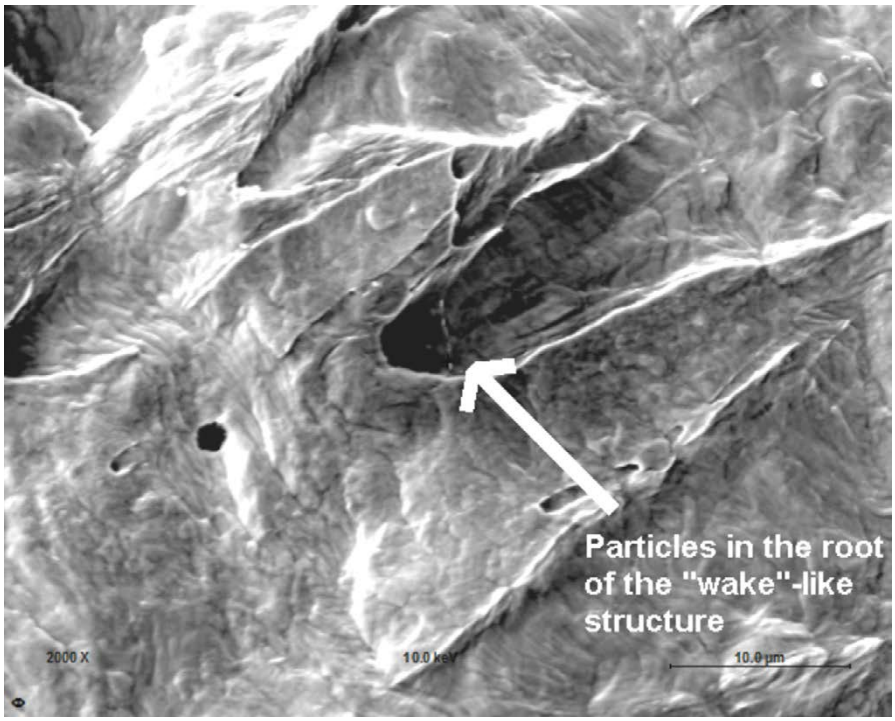

Figure 5-10. *Particles at the root of the wake-like structures on the fracture surface.*

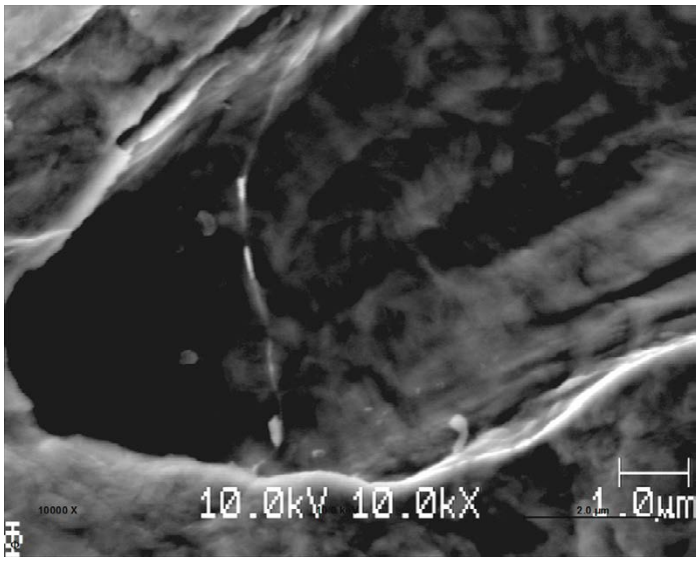

Figure 5-11. *Further close-up of the same area as in Figure 5-10.*

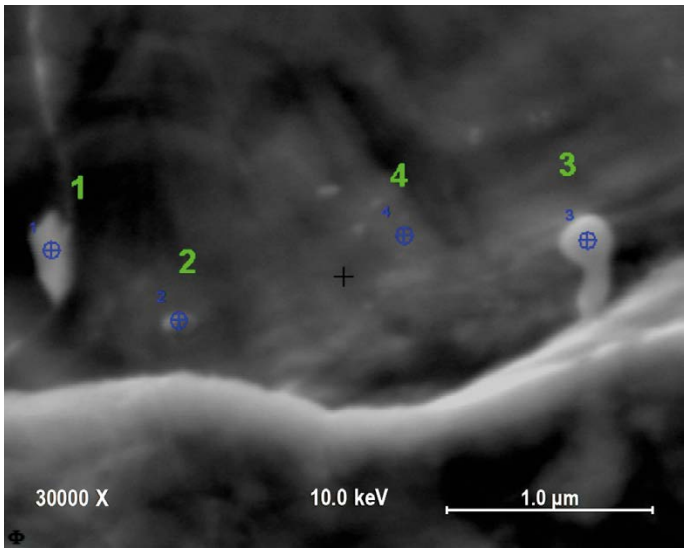

Figure 5-12. *Positions for AES analysis on the particles in Figure 5-10.*

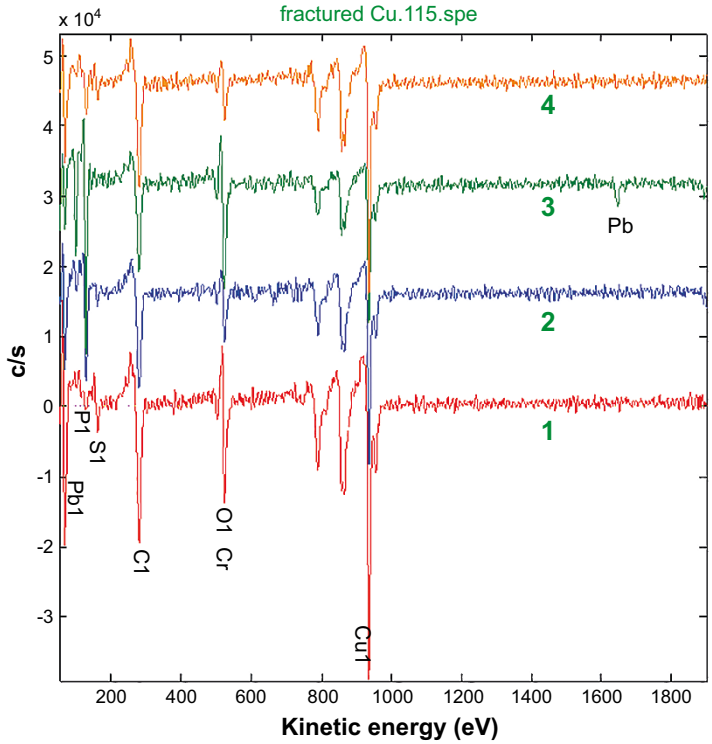

Figure 5-13. *The AES evaluation of the positions in Figure 5-12. Note the presence of phosphorus and sulphur in the analysis.*

Table 4.2. AES analysis of the positions in Figure 5-12 and Figure 5-13.

Element	Position 1 at.%	Position 2 at.%	Position 3 at.%	Position 4 at.%
Cu	56.3	51.2	25.4	64.6
O	34.5	23.1	31.0	20.2
P	4.9	23.4	27.4	11.3
S	4.2	2.4	1.2	3.9
Pb			14.9	

Towards the back of the specimen the fracture surface is more heavily deformed and the wake-like structures disappear. In their place a great number of plastic deformation dimples can be seen, Figure 5-14. Particles found in the dimples and the dimple walls were analysed, Figure 5-15 and Figure 5-16, and were found to contain sulphur but no phosphorus. The dimple walls were made up from only copper and oxygen.

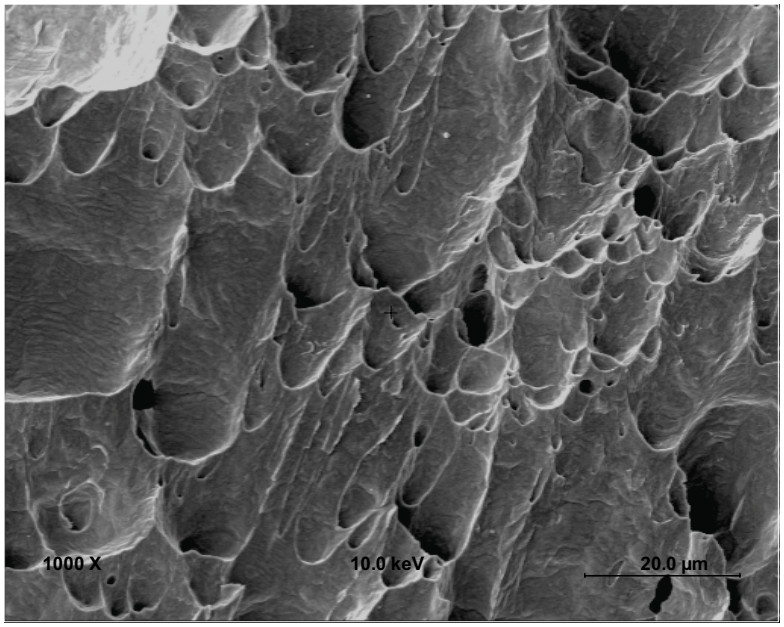

Figure 5-14. *The back end of the specimen fracture surface. The surface here is plastically deformed with a great amount of dimples.*

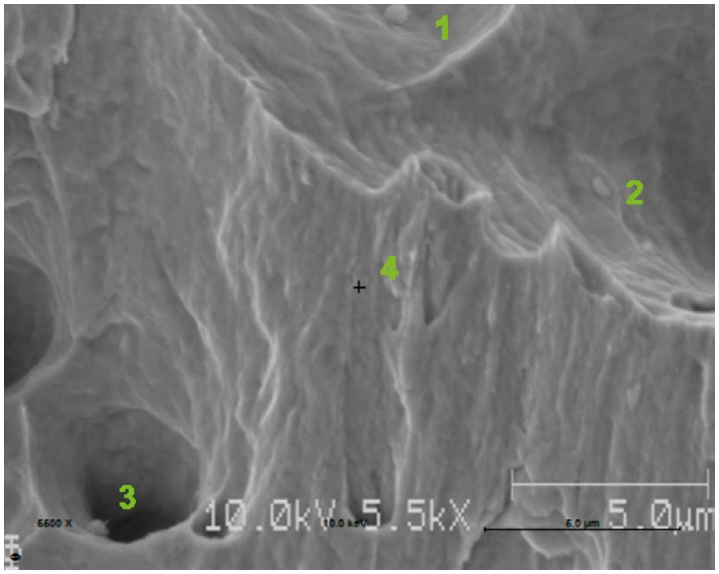

Figure 5-15. *Inside some of the dimples particles could be seen. These were analyzed (positions 1, 2 and 3) along with a part of the surrounding matrix (position 4)*

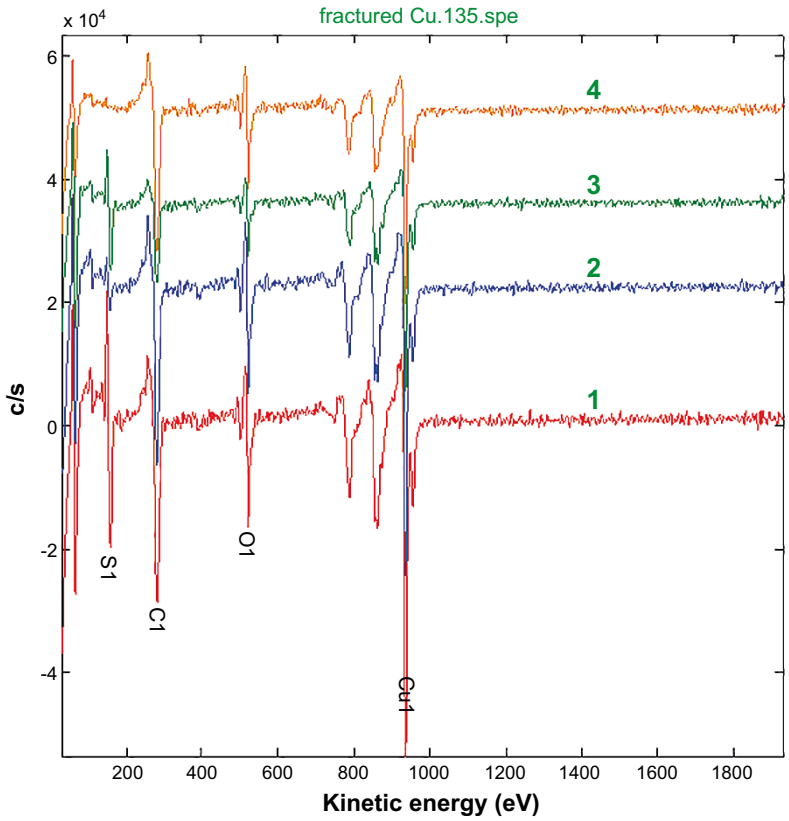

Figure 5-16. *The Analysis of the positions in Figure 5-15. The particles contained sulphur along with copper and oxygen. No phosphorus could be detected. In position 4 only copper and oxygen was detected.*

6 Discussion

6.1 Hardness and recrystallization

From the hardness measurements it is evident that there is large variation in the measurements. For the low-temperature specimens, there is large variation within groups (a certain temperature and ageing duration). For the high-temperature specimens, the variation within groups is for the most part quite small compared to the low-temperature specimens, though with some outlier values.

Based on a one-way analysis of variance (ANOVA) of the hardness for samples aged at different temperatures (see Appendix) it was concluded that the mean hardness from the 75, 125 and 175 °C samples were different from 250, 350 and 450 °C samples. It could not be concluded that mean hardness values of 75, 125 and 175 °C were different from each other. The mean hardness values of 350 and 450 °C were not different from each other, but they were different from that of 250 °C which also had a higher variance. This difference in mean hardness and the higher variance is explained by observations in EBSD images (see subsection 3.2.2), where it is seen that recrystallization had just begun after 1 day of ageing at 250 °C, so it had a higher hardness than specimens from longer ageing times and higher temperatures where recrystallization had proceeded further, in many cases fully.

For specimens at 75 and 175 °C, there were some statistically significant differences between different durations. No such differences were however present at 125 °C. There was also no clear pattern to the differences, and they could be related to any developments in microstructure, see subsection 3.2.1.

One interesting observation is what appears to be an increase in hardness at 6 months for some of the high-temperature specimens. At 250 °C, the mean hardness values of 6, 9 and 12 months are higher and statistically different from specimens aged at 1 months and 3 months. The 1 week specimen had an outlier value which makes it impossible to claim statistically significant differences between 1 week and all other ageing durations except for 1 day. The specimen from 1 day had a higher hardness than all the others because of the small amount of recrystallization that had occurred. At 350 °C, the only statistically significant difference in mean hardness is between 1 month and 12 and 9 months; the latter have a lower hardness than the former. At 6 months there is an outlier value which makes the mean statistically indistinguishable from all other durations at this temperature. At 450 °C, the trend is similar to that seen in 250 °C. The mean hardness values for 12 and 6 months are higher than, and statistically different from 1 day, 1 week, 1 month and 3 months. At 9 months, there is once again an outlier value which makes the mean statistically indistinguishable from all other durations at this temperature.

In other words, what is captured here is that for 250 °C and 450 °C there is a statistically significant increase in hardness at 6 months which, notwithstanding large variance in some measurements, persists for the remaining ageing durations. For 350 °C there appears to be a slight increase in the mean hardness value, but an outlier value at 6 months makes it hard to claim that it is statistically significant. Exactly why the hardness would increase at 6 months and remain at that level for 250 °C and 450 °C but not for 350 °C is not known, and it does not appear to be reflected in any developments in the microstructure, see subsection 3.2.2 to 3.2.4.

Conceivable reasons for variation in these measurements could be microstructural variation and that specimens were not sufficiently planar to the indenter. The fact that there is a difference in variation between the low-temperature and high-temperature specimens, and that the variation in the rolled specimen is similar to the variation in low-temperature specimens and the variation in the annealed specimen is similar to the variation in high-temperature specimens, suggests that microstructure is one explanation for this difference in variation.

Combining the observations from hardness measurements and metallographic investigations, it is evident that:

- The low-temperature specimen hardness correspond well to the observed microstructure in the respect that there is not much change, at least not recrystallization, between different durations and temperatures, although the hardness variation within groups is very large.
- The cause of hardness increasing at the three month to six month transition for 250 and 450 °C is not clear based on this study and should be studied further.

- The change in microstructure (the recrystallization that occurs) at 250 °C from one day to one week is reflected in the hardness measurement: it decreases dramatically.
- Recrystallization is fully developed (i.e., all deformed substructure has disappeared) in 350 °C and 450 °C starting from ageing durations of one day. In 250 °C, this is achieved shortly after one week. Grain growth also occurs.
- There are indications from the metallographic investigation that recovery has occurred in some of the low-temperature specimens. However, it should be stated that the EBSD data that was collected related to recrystallization (e.g., misorientation distributions), not recovery. Recovery should be more easily seen in hardness measurements, but the large scatter in those measurements does not allow for any conclusions about recovery. Furthermore, it has been suggested by Lin (2013) that recovery in rolled and annealed OFHC copper is limited.

The goal was to evaluate the recrystallization properties of Cu-OFP and if possible make predictions for whether the initial structure will persist over the very long timescales relevant for disposal of spent fuel. The results from the experiments do not clearly show this even if there is an indication that not much is happening at 175 °C or below. The maximum temperature of the copper in the repository is estimated to 100 °C for the first couple of thousands of years, and then it will slowly drop to the temperature of the surrounding bedrock and remain there for the remainder of the repository. More detailed studies on the ageing properties between 175 and 250 °C will be needed to permit extrapolation of recrystallization behaviour since the threshold temperature at long ageing times (6 months in this experiment) is somewhere in that temperature range. Such a study is currently being conducted and will be reported separately in the future.

Some comparison can be made with hardness measurements on OFHC copper seen in literature. Lin (2013) showed that the hardness in cold-rolled (90%) OFHC copper started to decrease markedly after a few hours of annealing at 150 °C and that recrystallization was complete after about one week. Benchabane et al. (2008) showed hardness measurements on 70% cold-rolled pure copper (.999 % purity) where recrystallization began after only a few minutes at 250 °C and was complete after a few hours.

6.2 Auger spectroscopy

Auger spectroscopy analysis was performed to evaluate if phosphorus was present at the grain boundaries. To this end creep tested material was used for specimens and broken open just before analysis to reveal fresh fracture surfaces.

Analyses were performed at two different laboratories and with slightly dissimilar specimen preparation methods. In the first laboratory the main focus was the flat surfaces that were most probably grain boundaries weakened by creep testing. No trace of phosphorus was found at this laboratory. The other laboratory focused on particles found at the root of distinctive structures on the fracture surface. The particles were found to contain phosphorus, copper, oxygen and often additional sulphur, iron or lead. The surface surrounding the particles was found to be devoid of any elements except copper and oxygen. The oxygen in the analysis is most probably due to the fact that the specimen was broken in air before the analysis and should thus be neglected, which most likely makes the particles copper phosphides. The other elements found can come from two sources, either they were present in the copper before fracture or they are contaminants from the laboratory air. Contaminants, even if in particle form, should be randomly distributed on the surface. These phosphorus containing particles are only found in the roots of these wake-like structures and the conclusion must be that they were in the material before fracture. The slow diffusion of these materials at the temperature at which they were creep tested (75 °C) also suggests that they formed during the manufacturing of the materials, not during creep testing. The phosphides might then have been co-nucleated with the other elements during the manufacturing step.

The discoveries of these particles pose an intriguing question. Phosphorus has been detected in bulk analysis previously in Cu-OFP (e.g. Andersson-Östling et al. 2018), but to the authors knowledge no particulate phosphides has been identified before in this grade of copper material. Thermodynamic calculations predict that copper phosphides form during manufacturing (Magnusson 2017). If they are formed, the fact that they have not been observed previously is surprising, but the reason that they were observed in the current study may be because the experimental methods used are different from those used before.

In the present investigation the material was creep tested almost to failure and it could be assumed that the surfaces studied are grain boundaries as grain boundaries are more likely to accumulate the creep cavities associated with third stage creep development. And cavitated grain boundaries are more likely to rupture when an external force perpendicular to the grain boundary is applied. But the studies performed here do only indicate the surfaces are former grain boundaries, not conclusively prove the same. Further research is needed on these particles.

The wake-like structures are also puzzling, but permit some speculation. They have been observed before and are in those cases always associated with large plastic strains locally. It is not known if all such structures have a particle containing phosphorus in the root or if all particles create a wake-like structure when the surrounding materials strains under load. It is also unknown if this is associated with previous creep deformation of the structure. It is possible that the creep deformation dissociates the phosphides from the surrounding matrix and that it is this that accounts for the formation of the wake-like structures. It could also be that the phosphides accumulate dislocations in a cloud around the phosphide, which hardens the material locally. After more studies in AES and using other metallographical methods, some modelling of the creep stresses and strains around the phosphide might shed light on the process.

A rough estimation of the mean free distance between the structures can be made from Figure 5-9 and ends up somewhere between 10 and 30 µm. This distance is too great to account for the increase in creep strength compared to Cu-OF (Andersson-Östling and Sandström 2009) if particle hardening is the strengthening factor (e.g. Magnusson 2007). But it is not known if all particles create a wake-like structure. The distance for effective particle hardening in steels is in the region of a few µm or less, and the difference to what it would need to be in copper is similar. The TEM studies performed on copper should have seen particles if they were as prevalent as this but none were observed in a study preformed on this material (Magnusson and Bergqvist 2018).

The presence of copper phosphides needs to be further studied to elucidate where they are in the structure, their size and the density. AES on ion milled slices of Cu-OFP might be the most fruitful way forward with the studies.

7 Conclusions

Some conclusions that can be made from the present study:

- The threshold temperature for recrystallization at times up to 6 months is between 175 and 250 °C.
- It is not known why the hardness increased in the 250 and 450 °C specimens at 6 months ageing.
- Copper phosphides were found during Auger spectroscopy studies of creep tested Cu-OFP.
- The exact size distribution and density of the phosphides is not known at this time.

Acknowledgement

The statistical analysis of hardness data was performed by Jan Sarnet and Mikael Jansson, both employed at Svensk Kärnbränslehantering AB. Their help is gratefully acknowledged.

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Appendix A

Statistical analysis (analysis of variance, one-way) of hardness of 75, 125, 175, 250, 350 och 450 °C, with respect to average values

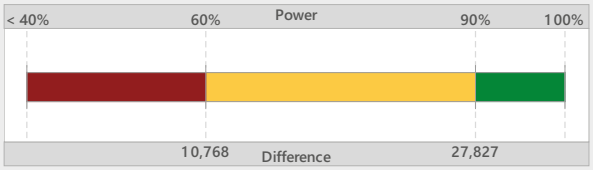
A1 75 °C, with respect to mean values of durations

One-Way ANOVA for 1w 75c; 2w 75c; 1m 75c; 2m 75c; 3m 75c; 6m 75 c
Report Card

Check	Status	Description
Unusual Data	✓	There are no unusual data points. Unusual data can have a strong influence on the results.
Sample Size	✓	The sample is sufficient to detect differences among the means.
Normality	!	Because some sample sizes are less than 15, normality can be an issue. If the data are not normally distributed, the p-value may be inaccurate with small samples. Because normality cannot be reliably checked with small samples, you should use caution when interpreting the test results.
Equal Variance	i	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 1w 75c; 2w 75c; 1m 75c; 2m 75c; 3m 75c; 6m 75 c
Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 27,827, and at most a 60% chance of detecting a difference of 10,768.

What difference can you detect with your sample sizes?

Difference	Power
10,768	16,2 - 60,0%
20,051	60,0 - 100,0%
22,162	70,0 - 100,0%
24,615	80,0 - 100,0%
27,827	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 24,615, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
1w 75c	5	107,2	3,0332	(103,43; 110,97)
2w 75c	5	114,6	5,9833	(107,17; 122,03)
1m 75c	5	118,2	8,7006	(107,40; 129,00)
2m 75c	5	117,6	5,6833	(110,54; 124,66)
3m 75c	5	119,8	7,5631	(110,41; 129,19)
6m 75 c	5	113,36	9,0966	(102,07; 124,65)

One-Way ANOVA for 1w 75c; 2w 75c; 1m 75c; 2m 75c; 3m 75c; 6m 75 c
Summary Report

Do the means differ?

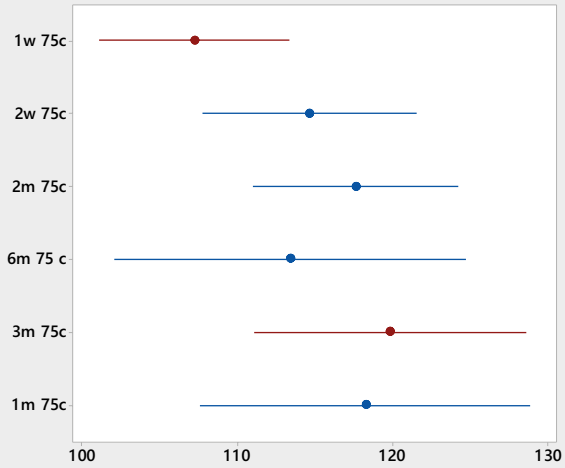
Differences among the means are significant (p < 0,05).

Which means differ?

#	Sample	Differs from
1	1w 75c	5
2	2w 75c	
3	2m 75c	
4	6m 75 c	
5	3m 75c	1
6	1m 75c	

Means Comparison Chart

The red intervals are the most likely to differ.



Comments

- Test: You can conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: The intervals with the least amount of overlap are red, and indicate the means that are the most likely to differ. Consider the size of the difference to determine if it has practical implications.

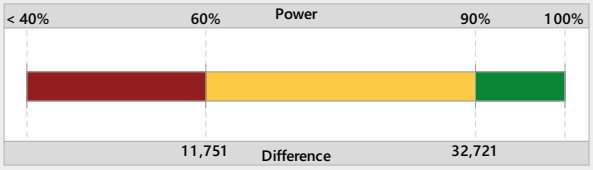
A2 125 °C, with respect to mean values of durations

One-Way ANOVA for 1d 125c; 4d 125c; 1w 125c; 2w 125c; 1m 125c;...
Report Card

Check	Status	Description
Unusual Data	✓	There are no unusual data points. Unusual data can have a strong influence on the results.
Sample Size	i	Your data does not provide sufficient evidence to conclude that there are differences among the means. This may result from having sample sizes that are too small. The Power Report shows that, based on your sample sizes and α, you would have at least a 90% chance of detecting a difference of 32,7 between any two means. Some practitioners feel that an 80% chance of detection is sufficient. If this is your case, you can conclude that it is unlikely that there are any differences of 32,7 or larger. To determine how large your samples need to be to detect a difference that has practical implications, repeat the analysis and enter a value for the difference.
Normality	!	Because some sample sizes are less than 15, normality can be an issue. If the data are not normally distributed, the p-value may be inaccurate with small samples. Because normality cannot be reliably checked with small samples, you should use caution when interpreting the test results.
Equal Variance	i	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 1d 125c; 4d 125c; 1w 125c; 2w 125c; 1m 125c;...
Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 32,721, and at most a 60% chance of detecting a difference of 11,751.

What difference can you detect with your sample sizes?

Difference	Power
11,751	12,2 - 60,0%
23,959	60,0 - 100,0%
26,363	70,0 - 100,0%
29,135	80,0 - 100,0%
32,721	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 29,135, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
1d 125c	5	118,8	8,8713	(107,78; 129,82)
4d 125c	5	117,8	9,8843	(105,53; 130,07)
1w 125c	5	114,8	6,4962	(106,73; 122,87)
2w 125c	5	118	8,6023	(107,32; 128,68)
1m 125c	5	116,8	6,9426	(108,18; 125,42)
2m 125c	5	118,2	3,5637	(113,78; 122,62)
3m 125c	5	117,8	9,4446	(106,07; 129,53)
6m 125c	5	116,6	5,3666	(109,94; 123,26)
---3m	5	114,2	7,0498	(105,45; 122,95)

One-Way ANOVA for 1d 125c; 4d 125c; 1w 125c; 2w 125c; 1m 125c;...
Summary Report

Do the means differ?

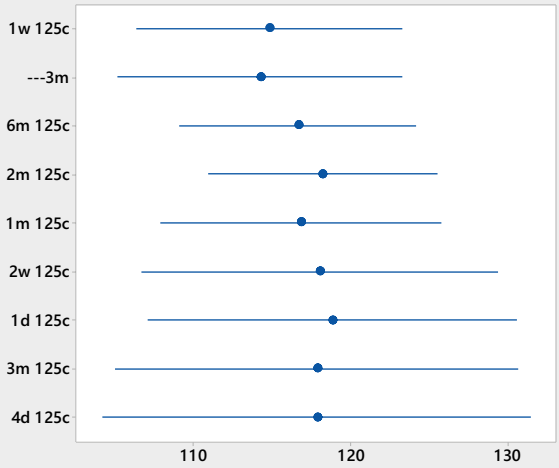
Differences among the means are not significant (p > 0,05).

Which means differ?

#	Sample	Differs from
1	1w 125c	
2	---3m	
3	6m 125c	
4	2m 125c	
5	1m 125c	None Identified
6	2w 125c	
7	1d 125c	
8	3m 125c	
9	4d 125c	

Means Comparison Chart

Blue indicates there are no significant differences.



Comments

- Test: There is not enough evidence to conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: Blue intervals indicate that the means do not differ significantly.

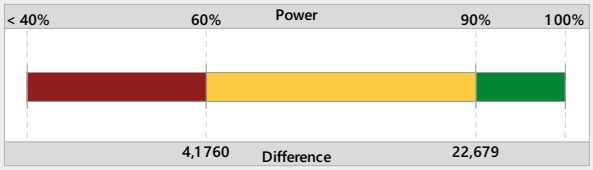
A3 175 °C, with respect to mean values of durations

One-Way ANOVA for 1d 175c; 4d 175c; 1v 175c; 2v 175c; 1m 175c;...
Report Card

Check	Status	Description
Unusual Data	✓	There are no unusual data points. Unusual data can have a strong influence on the results.
Sample Size	✓	The sample is sufficient to detect differences among the means.
Normality	!	Because some sample sizes are less than 15, normality can be an issue. If the data are not normally distributed, the p-value may be inaccurate with small samples. Because normality cannot be reliably checked with small samples, you should use caution when interpreting the test results.
Equal Variance	i	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 1d 175c; 4d 175c; 1v 175c; 2v 175c; 1m 175c;...
Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 22,679, and at most a 60% chance of detecting a difference of 4,1760.

What difference can you detect with your sample sizes?

Difference	Power
4,1760	4,0 - 60,0%
16,627	60,0 - 100,0%
18,320	70,0 - 100,0%
20,250	80,0 - 100,0%
22,679	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 20,250, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
1d 175c	5	121	5,7009	(113,92; 128,08)
4d 175c	5	114,8	5,5408	(107,92; 121,68)
1v 175c	5	116,4	4,0373	(111,39; 121,41)
2v 175c	5	114	2	(111,52; 116,48)
1m 175c	5	114,4	4,3932	(108,95; 119,85)
2m 175c	5	115,8	7,8549	(106,05; 125,55)
3m 175c	5	122,4	1,1402	(120,98; 123,82)
6m 175c	5	114,6	2,0736	(112,03; 117,17)

One-Way ANOVA for 1d 175c; 4d 175c; 1v 175c; 2v 175c; 1m 175c;...
Summary Report

Do the means differ?

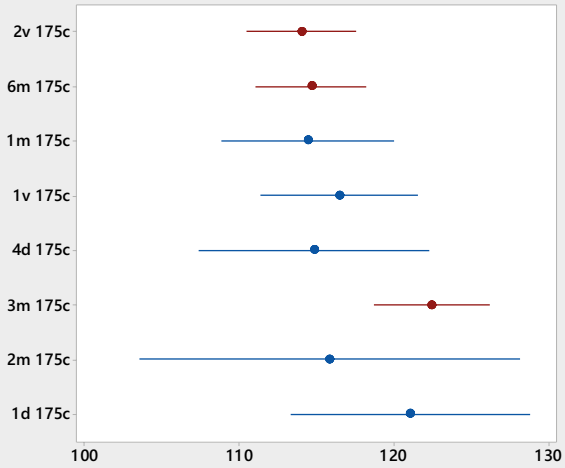
Differences among the means are significant (p < 0,05).

Which means differ?

#	Sample	Differs from
1	2v 175c	6
2	6m 175c	6
3	1m 175c	
4	1v 175c	
5	4d 175c	
6	3m 175c	1 2
7	2m 175c	
8	1d 175c	

Means Comparison Chart

Red intervals that do not overlap differ.



Comments

- Test: You can conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: Look for red comparison intervals that do not overlap to identify means that differ from each other. Consider the size of the differences to determine if they have practical implications.

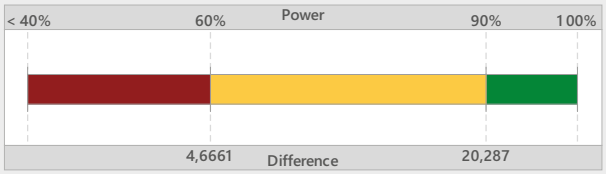
A4 250 °C, with respect to mean values of durations

One-Way ANOVA for 1d 250c; 1w 250; 1m 250; 3m 250; 6m 250c; 9m 250c;...
Report Card

Check	Status	Description
Unusual Data	✓	There are no unusual data points. Unusual data can have a strong influence on the results.
Sample Size	✓	The sample is sufficient to detect differences among the means.
Normality	!	Because some sample sizes are less than 15, normality can be an issue. If the data are not normally distributed, the p-value may be inaccurate with small samples. Because normality cannot be reliably checked with small samples, you should use caution when interpreting the test results.
Equal Variance	i	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 1d 250c; 1w 250; 1m 250; 3m 250; 6m 250c; 9m 250c;...
Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 20,287, and at most a 60% chance of detecting a difference of 4,6661.

What difference can you detect with your sample sizes?

Difference	Power
4,6661	5,8 - 60,0%
14,902	60,0 - 100,0%
16,465	70,0 - 100,0%
18,207	80,0 - 100,0%
20,287	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 18,207, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
1d 250c	5	111,6	2,1909	(108,88; 114,32)
1w 250	5	54,68	7,8414	(44,944; 64,416)
1m 250	5	50,52	2,1241	(47,883; 53,157)
3m 250	5	48,28	1,7050	(46,163; 50,397)
6m 250c	5	63,4	2,2226	(60,640; 66,160)
9m 250c	5	62,02	4,3700	(56,594; 67,446)
12m 250c	5	63,4	4,2597	(58,111; 68,689)

One-Way ANOVA for 1d 250c; 1w 250; 1m 250; 3m 250; 6m 250c; 9m 250c;...
Summary Report

Do the means differ?

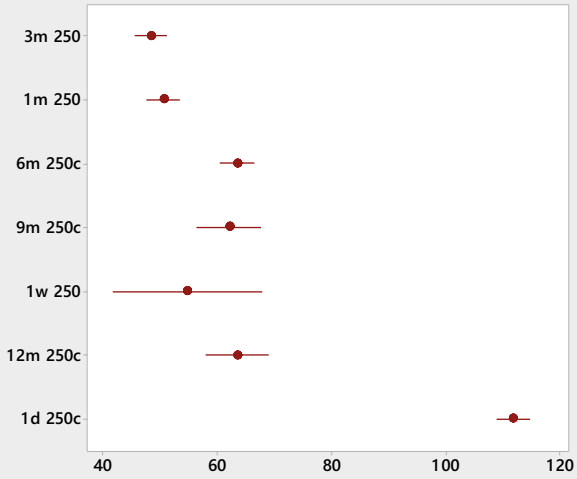
Differences among the means are significant (p < 0,05).

Which means differ?

#	Sample	Differs from
1	3m 250	3 4 6 7
2	1m 250	3 4 6 7
3	6m 250c	1 2 7
4	9m 250c	1 2 7
5	1w 250	7
6	12m 250c	1 2 7
7	1d 250c	1 2 3 4 5 6

Means Comparison Chart

Red intervals that do not overlap differ.



Comments

- Test: You can conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: Look for red comparison intervals that do not overlap to identify means that differ from each other. Consider the size of the differences to determine if they have practical implications.

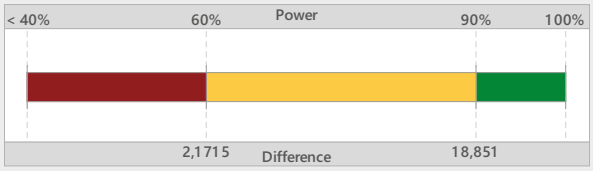
A5 350 °C, with respect to mean values of durations

One-Way ANOVA for 1d 350c; 1w 350c; 1m 350c; 3m 350c; 6m 350c;... Report Card

Check	Status	Description
Unusual Data	✓	There are no unusual data points. Unusual data can have a strong influence on the results.
Sample Size	✓	The sample is sufficient to detect differences among the means.
Normality	!	Because some sample sizes are less than 15, normality can be an issue. If the data are not normally distributed, the p-value may be inaccurate with small samples. Because normality cannot be reliably checked with small samples, you should use caution when interpreting the test results.
Equal Variance	i	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 1d 350c; 1w 350c; 1m 350c; 3m 350c; 6m 350c;... Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 18,851, and at most a 60% chance of detecting a difference of 2,1715.

What difference can you detect with your sample sizes?

Difference	Power
2,1715	3,0 - 60,0%
14,104	60,0 - 100,0%
15,606	70,0 - 100,0%
17,182	80,0 - 100,0%
18,851	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 17,182, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
1d 350c	5	49,54	1,9152	(47,162; 51,918)
1w 350c	5	49,56	1,7444	(47,394; 51,726)
1m 350c	5	51,16	0,81117	(50,153; 52,167)
3m 350c	5	49,48	1,5320	(47,578; 51,382)
6m 350c	5	55,66	8,1020	(45,600; 65,720)
9m 350c	5	47,64	1,4293	(45,865; 49,415)
12m 350c	5	46,76	0,95289	(45,577; 47,943)

One-Way ANOVA for 1d 350c; 1w 350c; 1m 350c; 3m 350c; 6m 350c;...
Summary Report

Do the means differ?

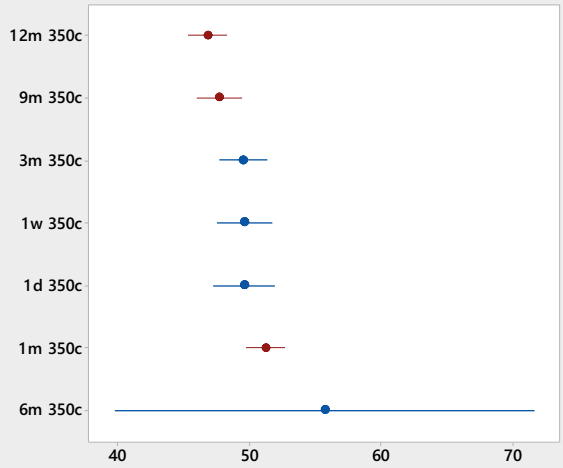
Differences among the means are significant (p < 0,05).

Which means differ?

#	Sample	Differs from
1	12m 350c	6
2	9m 350c	6
3	3m 350c	
4	1w 350c	
5	1d 350c	
6	1m 350c	1 2
7	6m 350c	

Means Comparison Chart

Red intervals that do not overlap differ.



Comments

- Test: You can conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: Look for red comparison intervals that do not overlap to identify means that differ from each other. Consider the size of the differences to determine if they have practical implications.

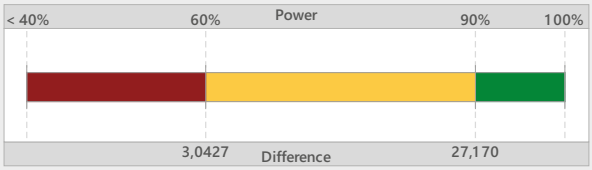
A6 450 °C, with respect to mean values of durations

One-Way ANOVA for 1d 450c; 1w 450c; 1m 450c; 3m 450c; 6m 450c;...
Report Card

Check	Status	Description
Unusual Data	✓	There are no unusual data points. Unusual data can have a strong influence on the results.
Sample Size	✓	The sample is sufficient to detect differences among the means.
Normality	!	Because some sample sizes are less than 15, normality can be an issue. If the data are not normally distributed, the p-value may be inaccurate with small samples. Because normality cannot be reliably checked with small samples, you should use caution when interpreting the test results.
Equal Variance	i	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 1d 450c; 1w 450c; 1m 450c; 3m 450c; 6m 450c;...
Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 27,170, and at most a 60% chance of detecting a difference of 3,0427.

What difference can you detect with your sample sizes?

Difference	Power
3,0427	2,9 - 60,0%
20,231	60,0 - 100,0%
22,369	70,0 - 100,0%
24,658	80,0 - 100,0%
27,170	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 24,658, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
1d 450c	5	45,46	0,88769	(44,358; 46,562)
1w 450c	5	47,34	1,5225	(45,450; 49,230)
1m 450c	5	46,06	2,3384	(43,157; 48,963)
3m 450c	5	43,86	1,6622	(41,796; 45,924)
6m 450c	5	62,86	3,9355	(57,973; 67,747)
9m 450c	5	64,98	11,338	(50,902; 79,058)
12m 450c	5	58,4	1,5116	(56,523; 60,277)

One-Way ANOVA for 1d 450c; 1w 450c; 1m 450c; 3m 450c; 6m 450c;...
Summary Report

Do the means differ?

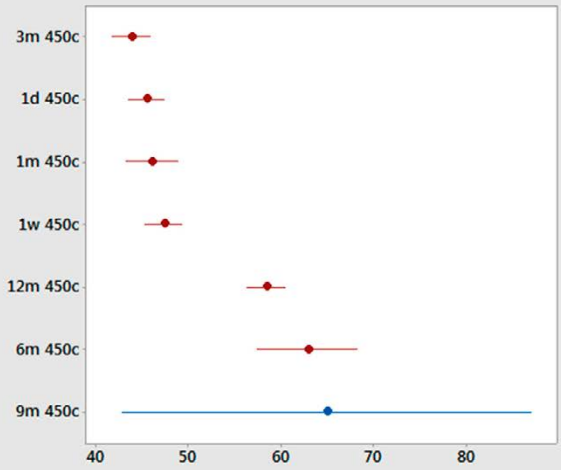
Differences among the means are significant (p < 0,05).

Which means differ?

#	Sample	Differs from
1	3m 450c	5 6
2	1d 450c	5 6
3	1m 450c	5 6
4	1w 450c	5 6
5	12m 450c	1 2 3 4
6	6m 450c	1 2 3 4
7	9m 450c	

Means Comparison Chart

Red intervals that do not overlap differ.



Comments

- Test: You can conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: Look for red comparison intervals that do not overlap to identify means that differ from each other. Consider the size of the differences to determine if they have practical implications.

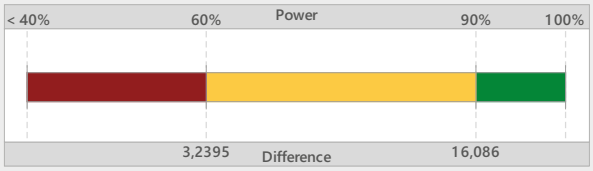
A7 75, 125, 175, 250, 350 and 450 °C, with respect to mean values of whole series

One-Way ANOVA for 450; 75; 125; 175; 350; 250
Report Card

Check	Status	Description
Unusual Data	⚠	Some of the data points are unusual compared to the others in the same sample. Because unusual data can have a strong influence on the results, you should try to identify the cause of their unusual nature. These points are marked in red on the Diagnostic Report. You can hover over a point or use Minitab's brushing feature to identify the worksheet row. Correct any data entry or measurement errors. Consider removing data that are associated with special causes and repeating the analysis.
Sample Size	✓	The sample is sufficient to detect differences among the means.
Normality	✓	Because all your sample sizes are at least 15, normality is not an issue. The test is accurate with nonnormal data when the sample sizes are large enough.
Equal Variance	ℹ	Minitab's Assistant uses Welch's method, which does not assume or require that the samples have equal variances. Research shows that the test performs well with unequal variances, even when the sample sizes are not equal.

One-Way ANOVA for 450; 75; 125; 175; 350; 250
Power Report

What is the chance of detecting a difference?



Based on your samples and α level (0,05), you have at least a 90% chance of detecting a difference of 16,086, and at most a 60% chance of detecting a difference of 3,2395.

What difference can you detect with your sample sizes?

Difference	Power
3,2395	8,2 - 60,0%
11,580	60,0 - 100,0%
12,795	70,0 - 100,0%
14,193	80,0 - 100,0%
16,086	90,0 - 100,0%

Power is a function of the sample sizes and the standard deviations. To detect differences smaller than 14,193, consider increasing the sample sizes.

Statistics

Sample	Sample Size	Mean	Standard Deviation	Individual 95% CI for Mean
450	35	52,709	9,5180	(49,439; 55,978)
75	30	115,13	7,6338	(112,28; 117,98)
125	45	117	7,0453	(114,88; 119,12)
175	40	116,68	5,1709	(115,02; 118,33)
350	35	49,971	4,0723	(48,573; 51,370)
250	35	64,843	20,558	(57,781; 71,905)

One-Way ANOVA for 450; 75; 125; 175; 350; 250
Summary Report

Do the means differ?

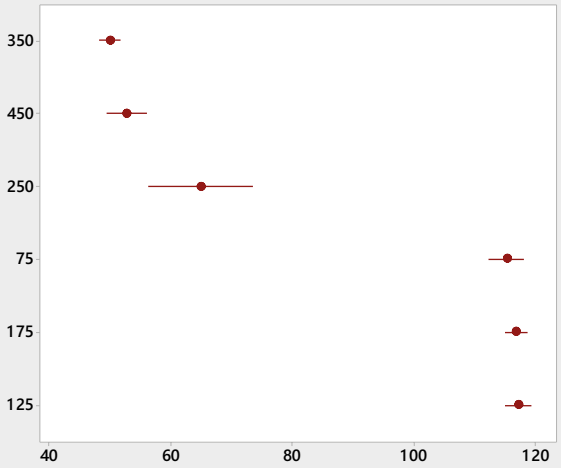
Differences among the means are significant (p < 0,05).

Which means differ?

#	Sample	Differs from
1	350	3 4 5 6
2	450	3 4 5 6
3	250	1 2 4 5 6
4	75	1 2 3
5	175	1 2 3
6	125	1 2 3

Means Comparison Chart

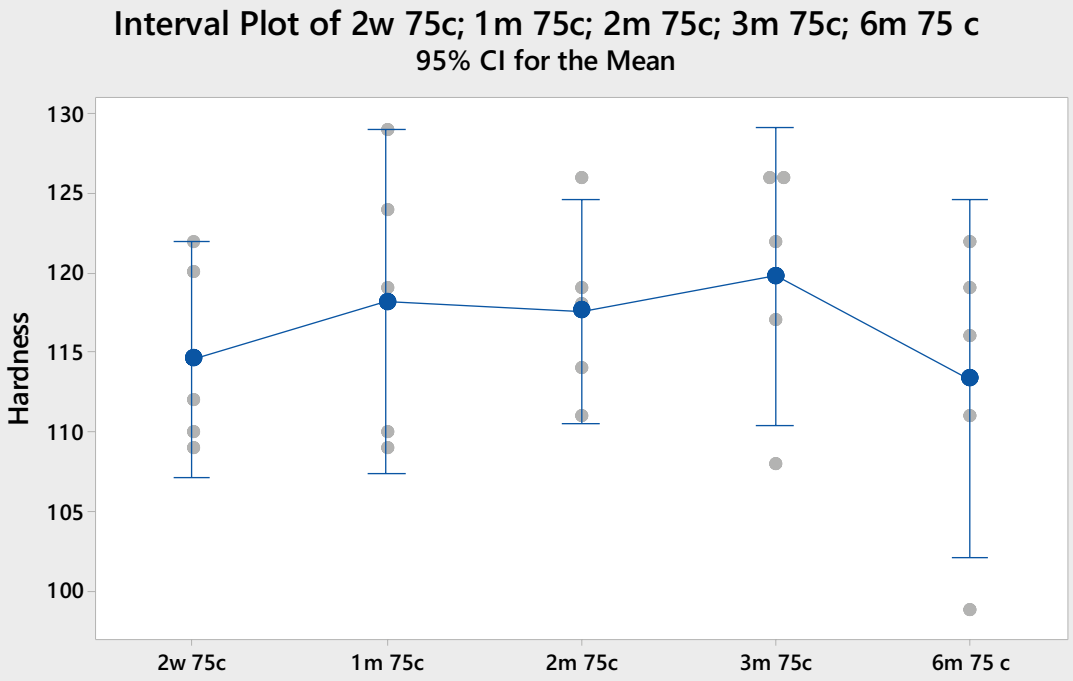
Red intervals that do not overlap differ.



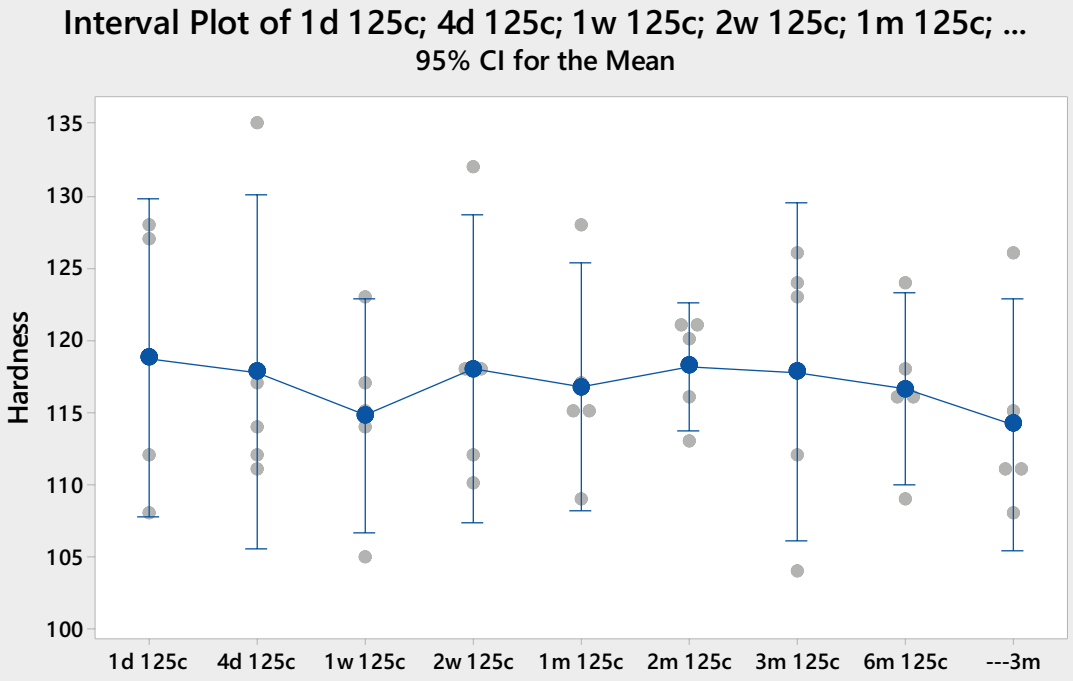
Comments

- Test: You can conclude that there are differences among the means at the 0,05 level of significance.
- Comparison Chart: Look for red comparison intervals that do not overlap to identify means that differ from each other. Consider the size of the differences to determine if they have practical implications.

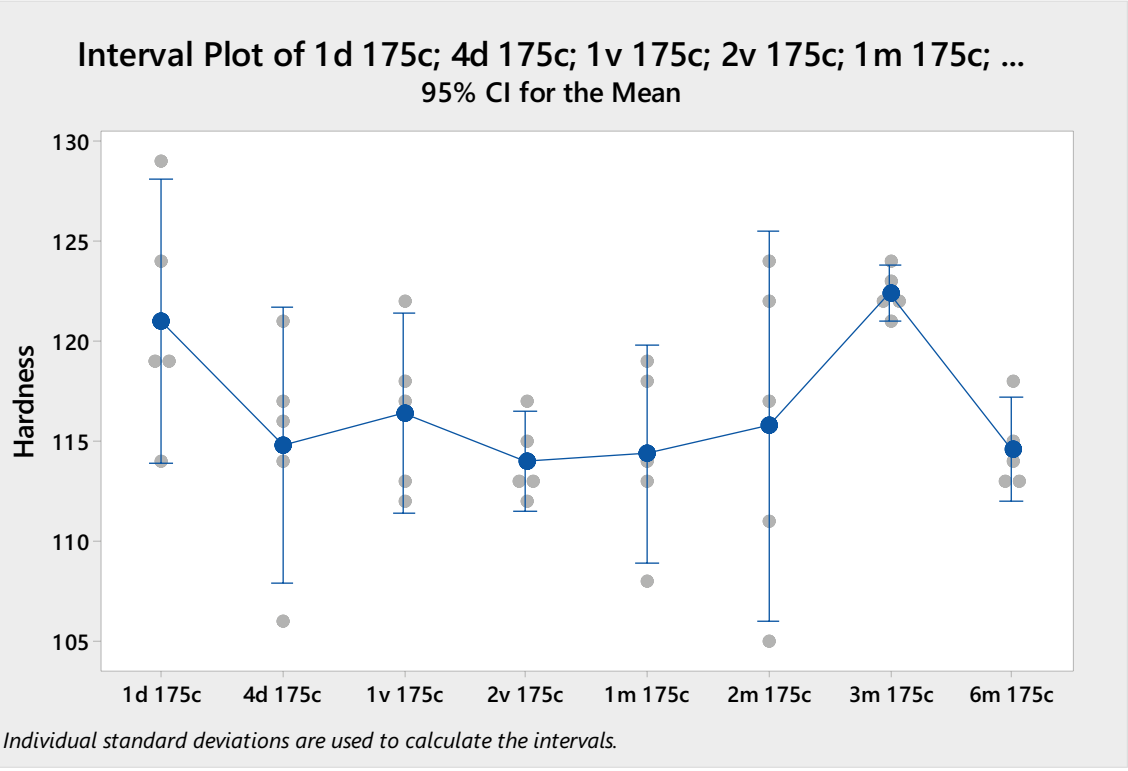
A8 Interval plots of all temperatures and durations with individual values, mean values, confidence interval for mean values at 95%



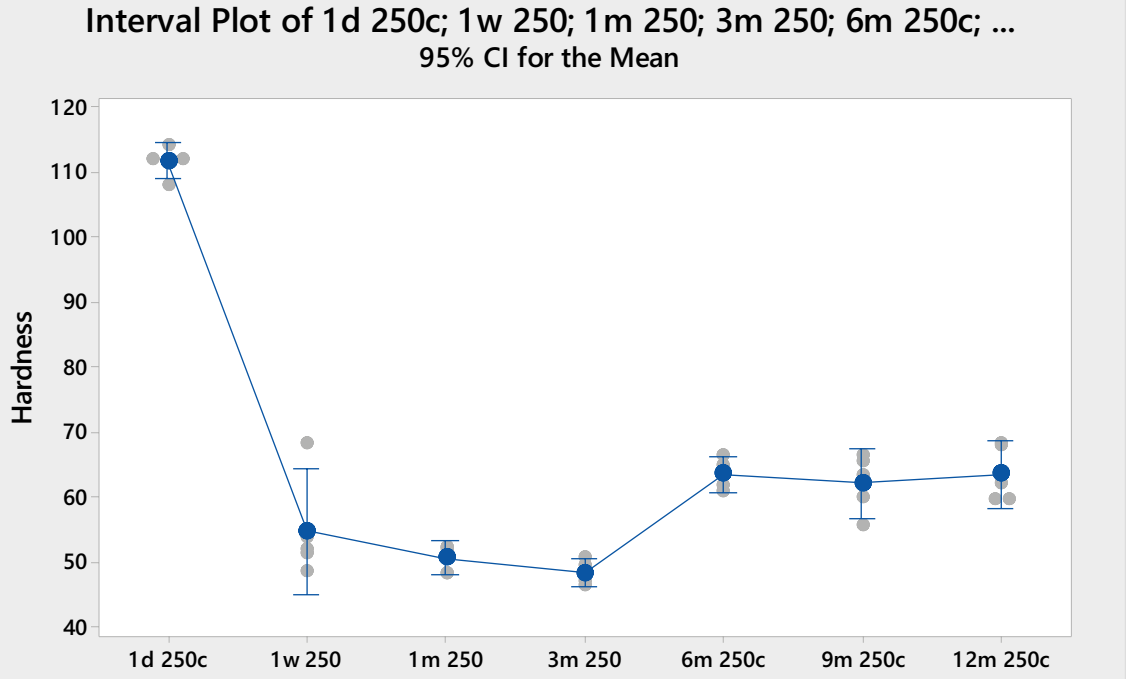
Individual standard deviations are used to calculate the intervals.



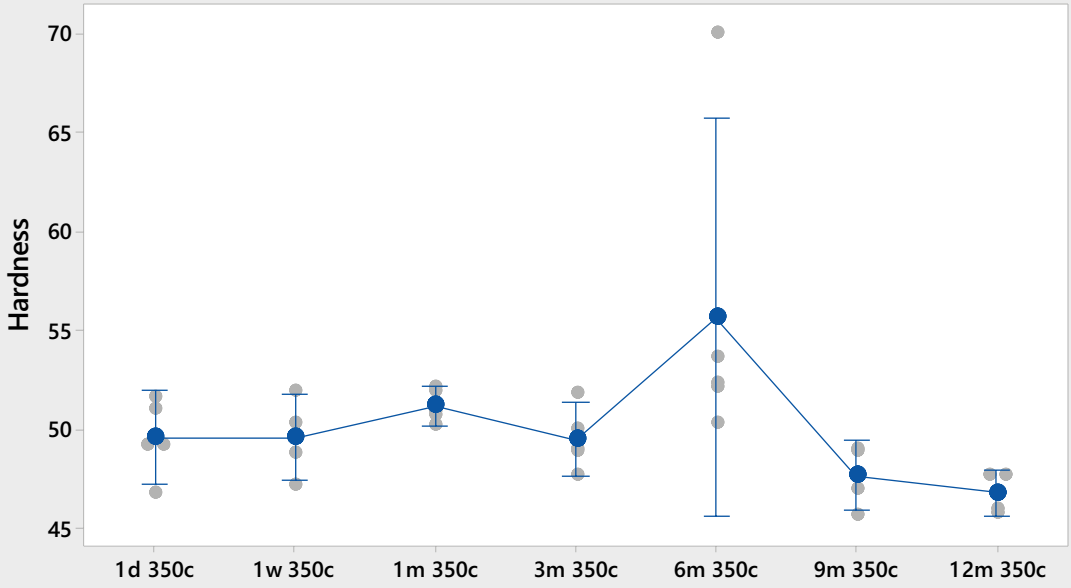
Individual standard deviations are used to calculate the intervals.



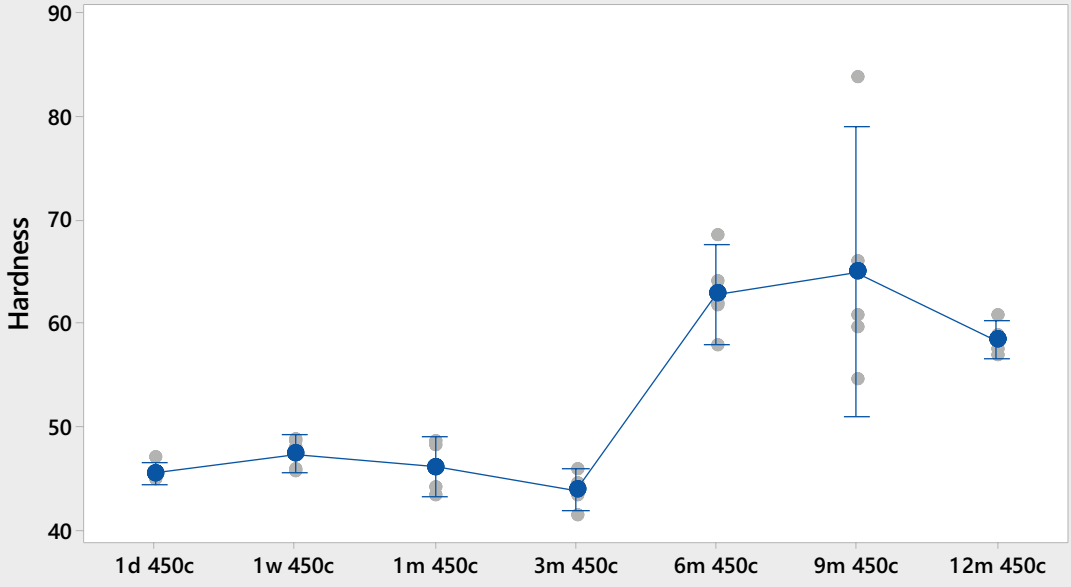
Individual standard deviations are used to calculate the intervals.



Individual standard deviations are used to calculate the intervals.



Individual standard deviations are used to calculate the intervals.



Individual standard deviations are used to calculate the intervals.

A9 Grain size measurements

Table A-1. Grain size measurements on 250 °C 1 day were not made since it was only partly recrystallized. Data for 1 month was not available.

	Temperature		
	250 °C	**350 °C**	**450 °C**
Duration	**Grain size (µm)**		
1 day	-	33.4	36.2
1 week	26.5	33.5	45.6
1 month	-	38.2	49.2
3 months	28.9	39.3	50.8
6 months	34.0	42.0	117*
9 months	32.0	43.0	66*
12 months	31.0	47.0	98*

* Calculated from images taken in LOM.

Arkitektkopia AB, Bromma, 2020

SKB is responsible for managing spent nuclear fuel and radioactive waste produced by the Swedish nuclear power plants such that man and the environment are protected in the near and distant future.

skb.se