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MULTI-DIMENSIONAL ANALYSIS OF PRECIPITATES IN A 12% Cr STEEL

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Background

- Creep-strength-enhanced ferritic (CSEF) steels are widely used in fossil fuel plants such as Eskom (South African public electricity utility).

- Creep is a material aging process whereby a material loses its strength and ductility.

- Power plant steels operate under high loads and at elevated temperatures which increases the rate of creep and ultimately time to failure of the component.

- It is therefore very important to replace the component before creep damage deteriorates the material to the point where failure is eminent.

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Background

- CSEF steels is strengthened by $M_{23}C_6$ (M = Cr, Fe) and MX (M = V, X = C, N) precipitates in the tempered martensite matrix.
- The parameters of these precipitates (e.g. size, shape, number density and composition) play an important role in the creep strengthening of the material.
- Precipitate strengthening quantified by the Orowan back-stress:
  - threshold stress required to cause plastic flow if particle strong enough so that not cut by dislocation.

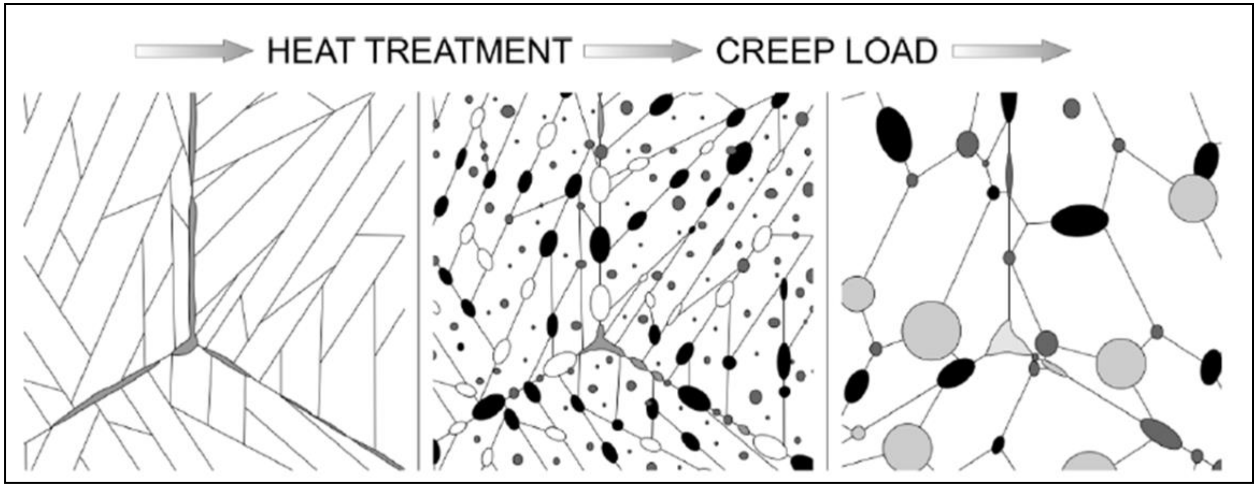

Figure 1: Schematic diagram of evolution of microstructure (*Holzer*). [Note: all images relate to same length scale]

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Background - Welding on creep aged steels

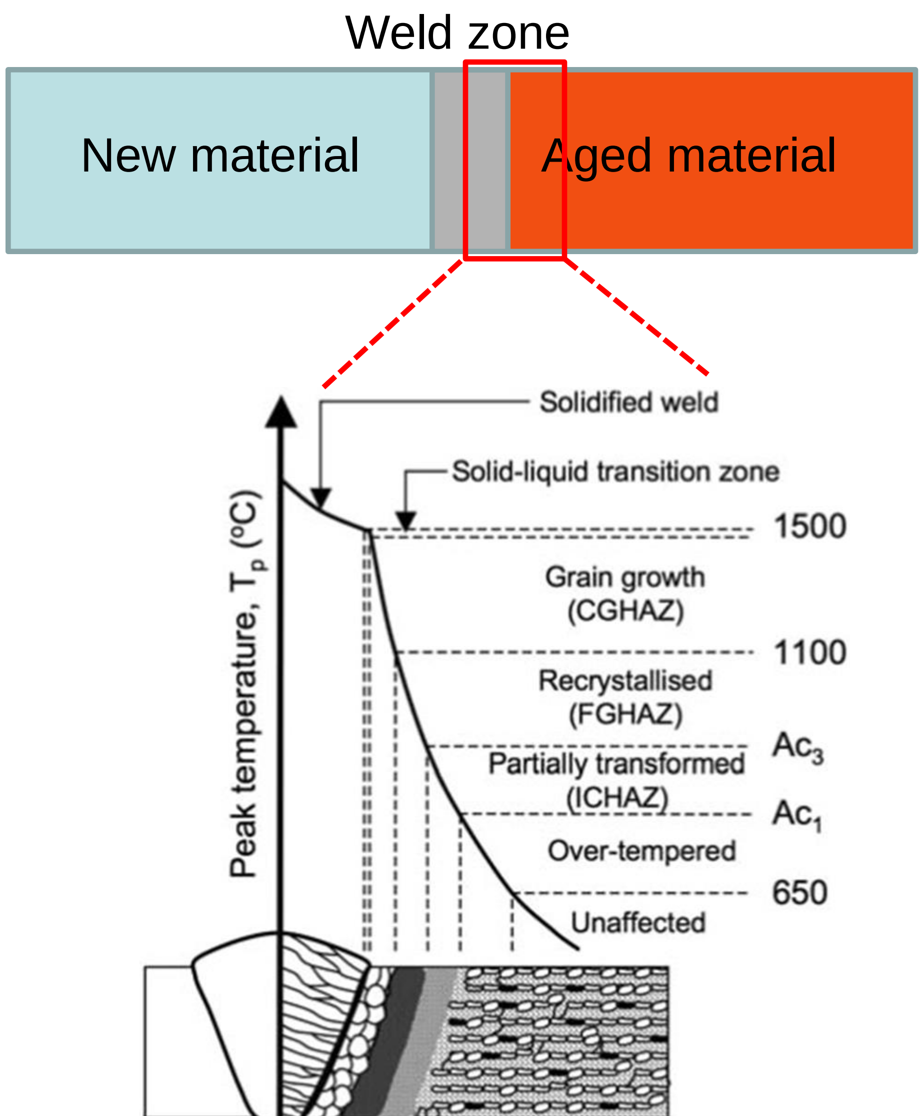

Figure 2: Regions in weldment (Francis et al.)

Motivation

- Precipitate parameters usually measured from images taken from thin-foils using the TEM.

- Thin-foil methods suffer from two drawbacks:
  1) Magnetic sample interferes with the objective lens - leads to a reduction in the spatial resolution.

  2) Thin-foil (thickness ~ 20-200nm) will section the $M_{23}C_6$ precipitates - reducing the measured precipitate size.

- Measured stereological projection of the precipitate can be corrected by several methods in order to obtain the true precipitate size distribution.

- In the case of MX precipitates no stereological correction required – assume that they are so small that they will not be sectioned.

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Motivation

- By preparing extraction replicas of the surface, the difficulties associated with the thin-foil samples are avoided.

- 2D elemental maps are only projections of the 3D precipitates - cannot sufficiently provide the precipitate shape and spatial distribution.

- Transmission electron tomography - technique capable of representing the 3D structure of the precipitates.

- If combined with EFTEM - generate 3D chemical maps, which overcomes the limitations of the 2D maps.

Objectives

- To use 3D EFTEM elemental maps obtained from the extraction replica to qualitatively determine:
  - the precipitate shape and
  - spatial distribution.

- To compare these results to the precipitate parameters that were previously obtained from the 2D maps.

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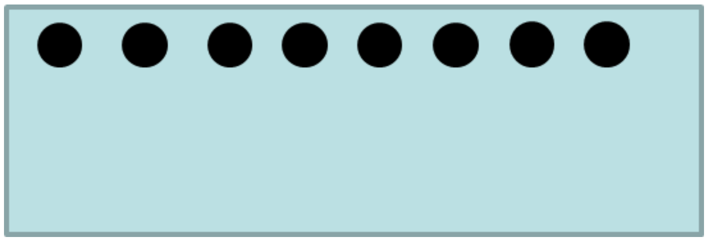
Experimental - Sampling

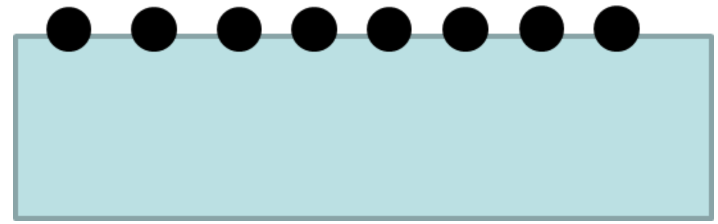
- Material: X20 (12% Cr) stainless steel (X20CrMoV11-1).
- Used for the high temperature pressure pipework (HTPP) at Eskom's coal fired power plants.
- New and service exposed (550 ºC, 208 kh) X20 steel.
- Specimens of FGHAZ obtain by physical simulation using a Gleeble 3800.
- TEM thin-foils were prepared by PIPS Ar^{+} milling.
- Extraction replicas were prepared by the bulk replication technique.

Figure 3: Main steam pipes used at Eskom coal fired power plants.

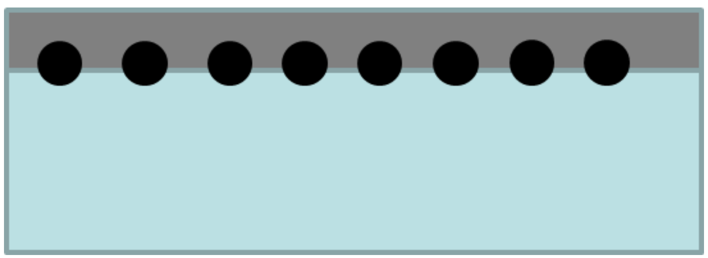
Experimental – Bulk Replication Technique



Polished surface



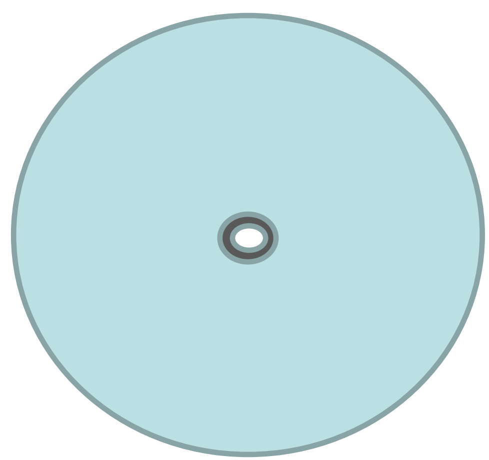
Etched surface



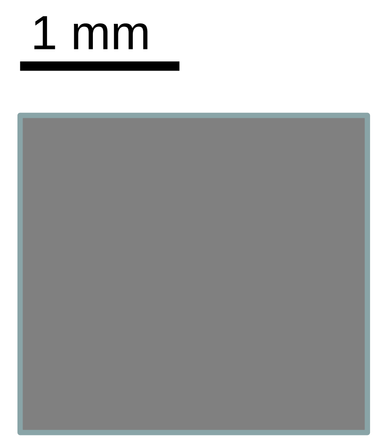
Carbon coating

Etching

FIB-SEM



Conventional



Extraction

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Experimental - Analysis

- TEM analysis performed using:
  - JEM JEOL2100 (LaB_6),
  - fitted with a GATAN Quantum GIF.
- 2D EFTEM elemental maps were acquired for Cr and V using the three window method.
- Tomographic tilt-series of EFTEM maps acquired:
  - from -60° to 60° in 1° increments,
  - using the GATAN Digital Micrograph (DM) software with a EFTEM Tomography plug-in.
- Alignment, filtering and reconstruction of the EFTEM map tilt series was performed using DM.
- Additional image processing was achieved with Amira and ImageJ.

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Experimental - Analysis

Corrected diameter of i^{th} precipitate [5]	$d_i = \frac{2}{\pi}(d_{m,i} - t_i) + \sqrt{\frac{2}{\pi}(d_{m,i} - t_i)^2 + \frac{4d_{m,i}t_i}{\pi}}$ (1)	Where: $\boldsymbol{d_{m,i}}$ ≡ measured diameter of precipitate $\boldsymbol{i}$ $\boldsymbol{t_i}$ ≡ sample thickness at the precipitate $\boldsymbol{i}$ position
Phase fraction f_V [3]	$f_V = \frac{V_V}{V_{Sample}} = \frac{1}{A_{Sample}} \sum_i A_i \left(\frac{2d_{m,i}/t_i}{2d_{m,i}/t_i + 3} \right)$ (2)	Where: V_V ≡ Total volume of precipitates $A_{Sample}\ /V_{Sample}$ ≡ examined sample area/volume A_i ≡ projected area of precipitate i
Number density N_V [3]	$N_V = \frac{N_A}{V_{Sample}} = \frac{1}{A_{Sample}} \sum_{i=1 \ldots N_A} \frac{1}{t_i + d_{m,i}}$ (3)	Where: N_A ≡ measured number of precipitates per sample area/volume
Weighted mean precipitate diameter $\bar{d}$ [3]	$\bar{d} = \frac{\sum_i d_{m,i}[t_i/(t_i + d_{m,i})]}{\sum_i[t_i/(t_i + d_{m,i})]}$ (4)	
Mean 2D surface- to-surface particle distance λ [2]	$\lambda = \sqrt{\frac{\ln 3}{2\pi N_V \bar{r}} + 4\bar{r}^2} - 1.63\bar{r}$ (5)	Where: $\bar{r} = \frac{\bar{d}}{2}$ ≡ mean particle radius of precipitates
Orowan back-stress σ_{Or} [6]	$\sigma_{Or} = \frac{\alpha \cdot M \cdot G \cdot b}{\lambda}$ (6)	Where: $\alpha = 1$ ≡ constant $M = 3$ ≡ Taylor factor $G = 65\ GPa$ ≡ shear modulus $b = 2.5 \times 10^{-10}\ m$ ≡ Burgers vector

Table 1: Summary of formulae used to calculate precipitate parameters.

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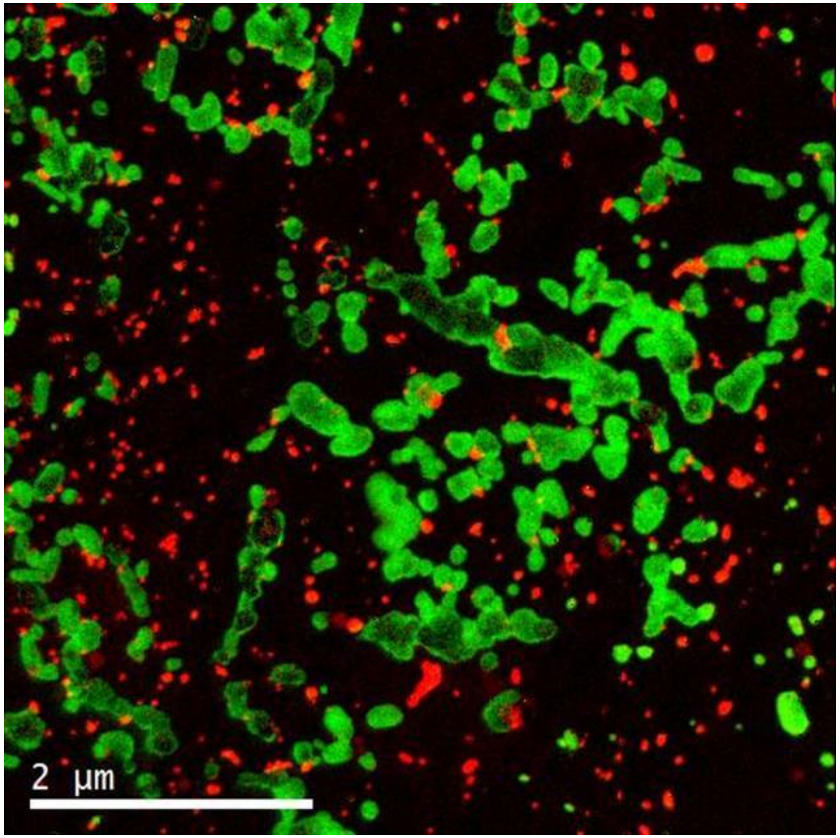
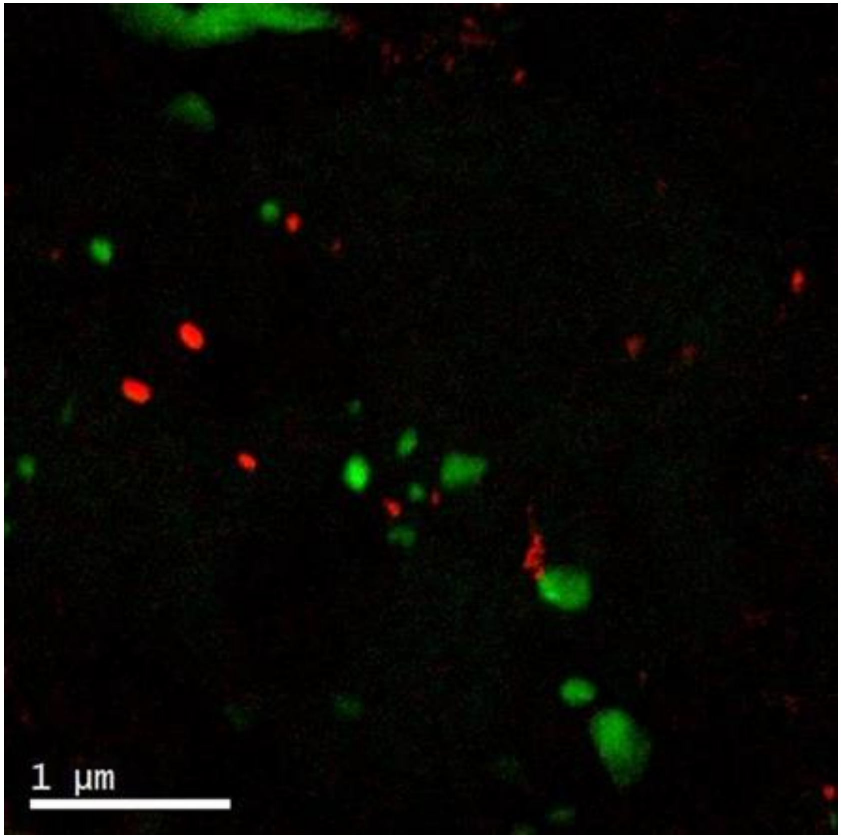
Results

Figure 4: BF-TEM images of damaged extraction replica specimen.

Results



EXTRACTION REPLICA



ION-MILLED

Figure 5: EFTEM colour map of the $M_{23}C_6$ (green) and MX (red) precipitates in the (a) extraction replica and (b) ion-milled samples prepared from new FGHAZ specimen.

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Results

- <u>Process of determining precipitate parameters</u>

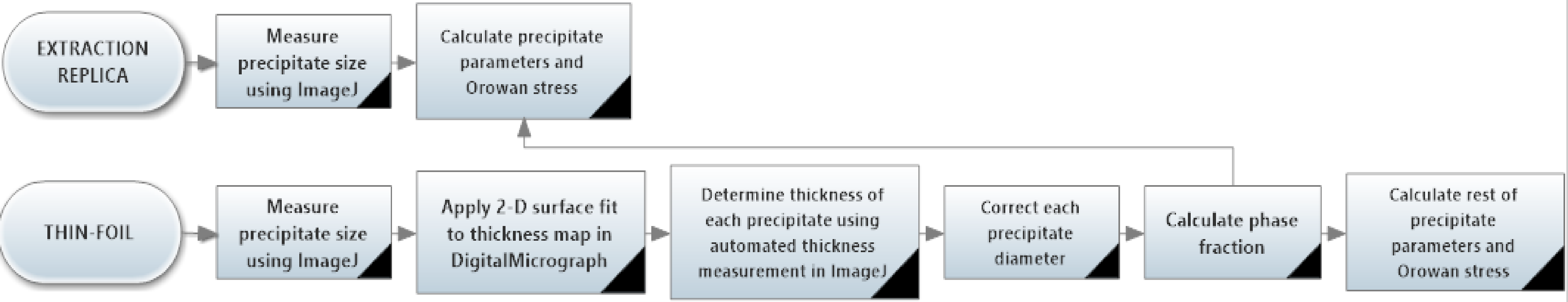

Table 2: Measured precipitate parameters and calculated Orowan back-stress values for FGHAZ of new and damaged X20 steel.

		Sample	Measured d_{mean} [ECD] (nm)	Corrected d_{mean} (nm)	f_V (%)	λ (nm)	σ_{Or} (MPa)	# Precipitates
$M_{23}C_6$	NEW	***TEM***	156 ± 5	188 ± 14	4.23	260 ± 20	147 ± 11	358
		Replica	168 ± 3			309 ± 6	123 ± 2	1182
	DAMAGED	***TEM***	166 ± 9	198 ± 12	2.69	402 ± 51	99 ± 33	224
		Replica	173 ± 4			487 ± 71	83 ± 12	1092
MX	NEW	***TEM***	56 ± 3		0.56	431 ± 96	92 ± 20	279
		Replica	45 ± 1			345 ± 45	111 ± 14	2368
	DAMAGED	***TEM***	56 ± 5		0.33	641 ± 147	64 ± 15	182
		Replica	60 ± 3			743 ± 155	52 ± 11	814

Results

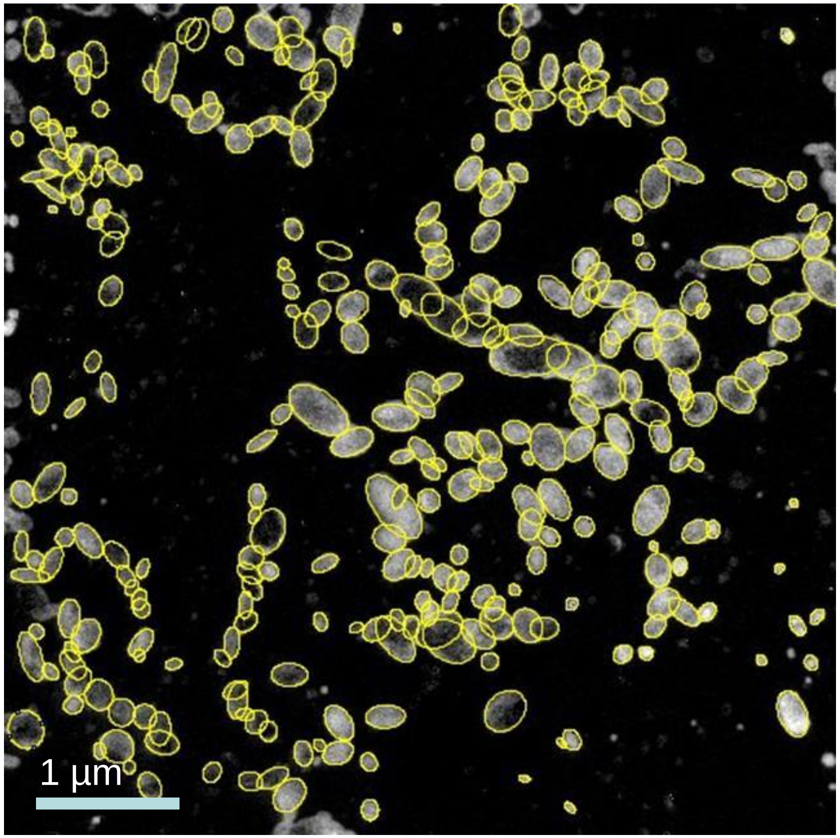

Figure 6: Measurement of precipitate size from EFTEM elemental map of $M_{23}C_6$ precipitates for a new FGHAZ replica specimen, using ImageJ.

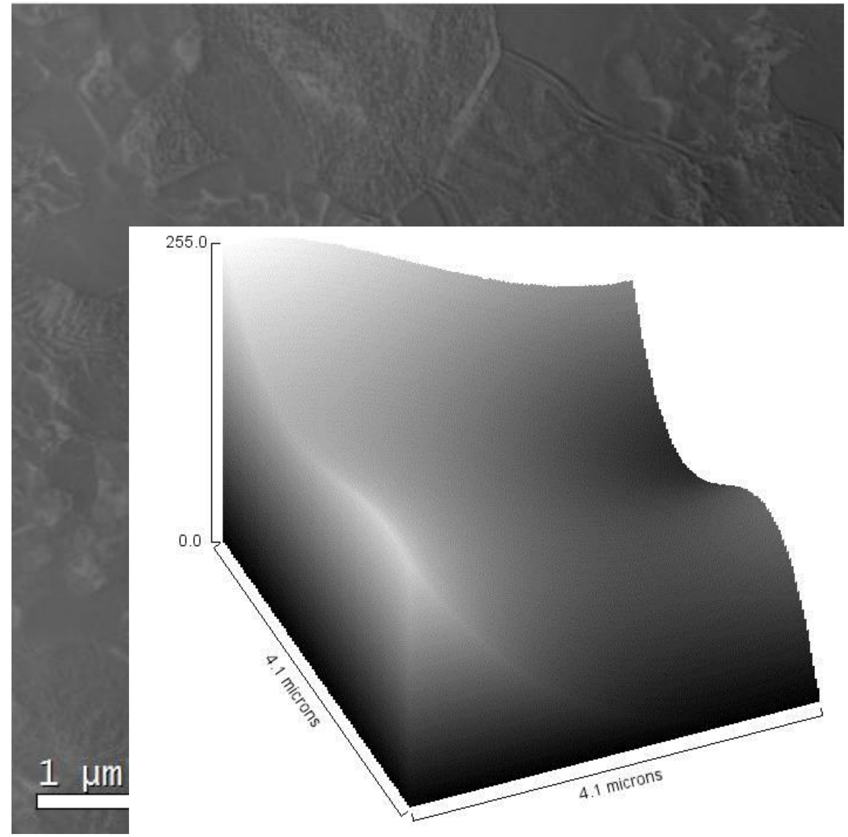

Figure 7: Thickness map of the ion-milled TEM sample obtained from the elastic/inelastic log ratio to determine the mean free path of the electrons.

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Results

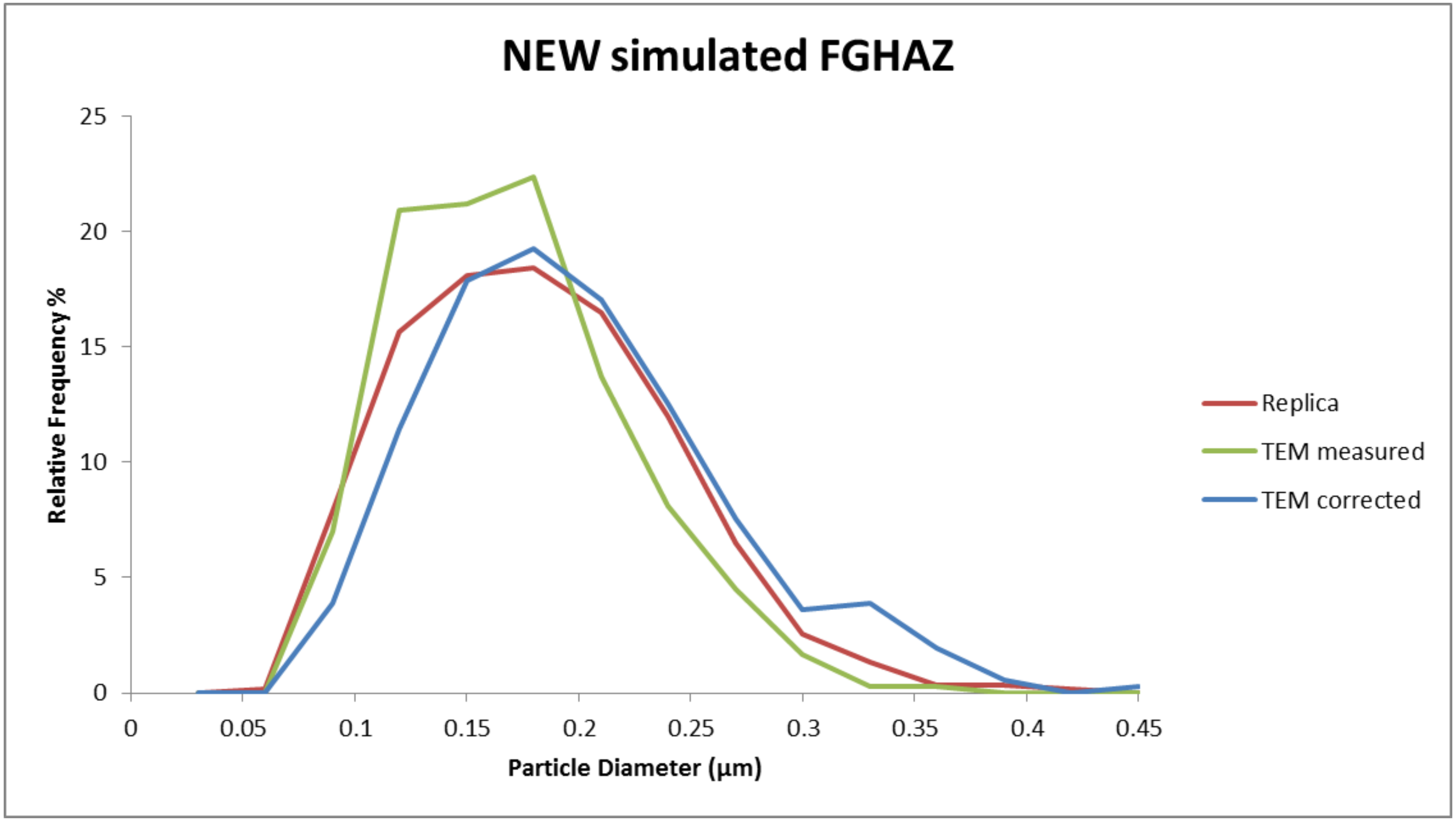

Figure 8: $M_{23}C_6$ precipitate diameter distribution plots for new simulated FGHAZ specimen.

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Results

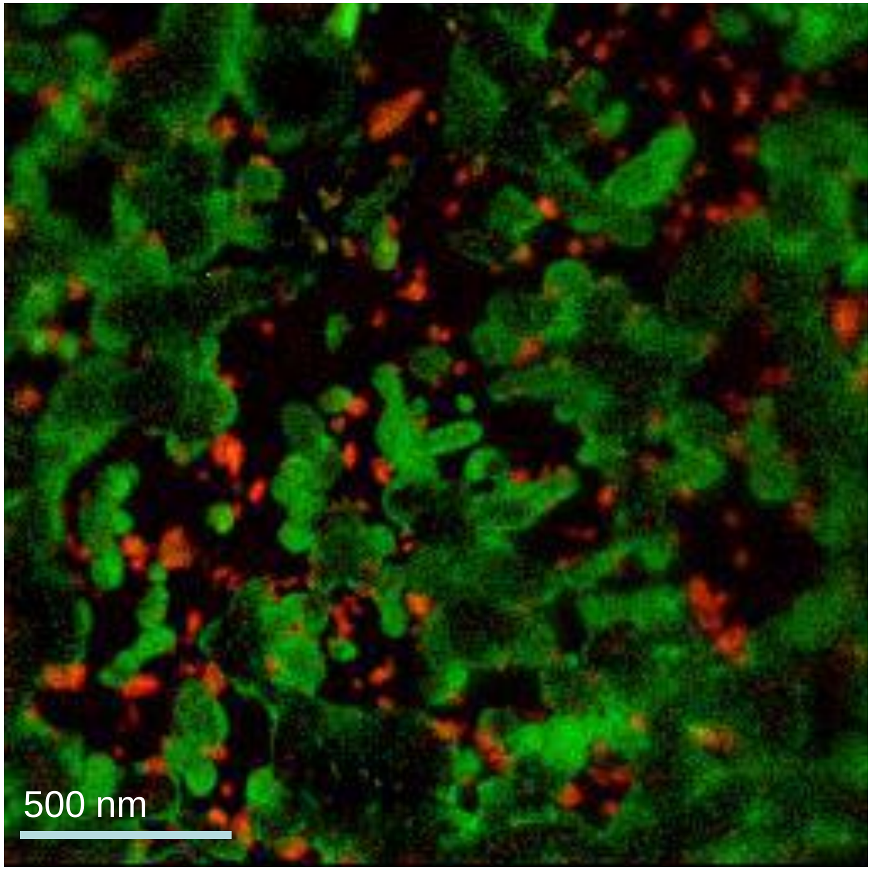

Figure 9: Video illustrating 3D structure of $M_{23}C_6$ (green) and MX (red) precipitates for the extraction replica prepared from the new FGHAZ specimen.

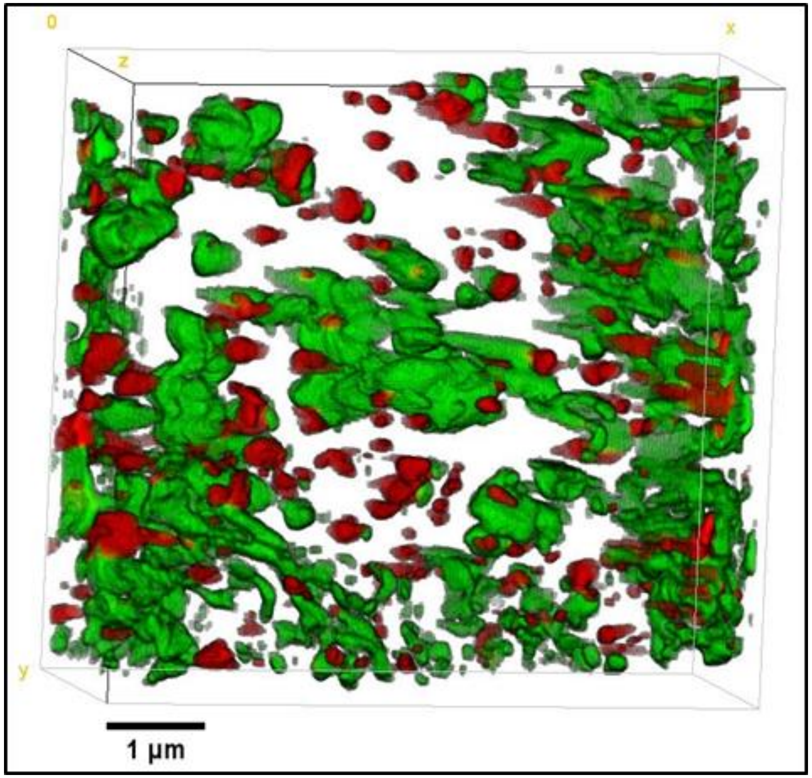

Figure 10: 3D composite image of $M_{23}C_6$ (green) and MX (red) precipitates for the extraction replica prepared from the FGHAZ specimen.

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Conclusions

- The simulated FGHAZ of the aged material had the lowest calculated Orowan back-stress. This result is consistent with the known mechanisms of coarsening of the $M_{23}C_6$ precipitates and dissolution of MX precipitates during creep aging of CSEF steels.

- Advantages of the replica sample preparation:
  - identification of inhomogeneous distribution of precipitates;
  - observation of precipitate shape;
  - larger sampling area ($\pm 4 \times 10^6\ \mu m^2$, TEM = $\pm 1.8 \times 10^3\ \mu m^2$);
  - improved image resolution.

- By using the two sample preparation techniques together, the limitations of each separate sampling technique can be minimised to obtain the precipitate parameters with improved accuracy.

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Conclusions

- The quantitative results from 2D EFTEM confirm the qualitative results from 3D EFTEM tomography – in both cases it was found that the $M_{23}C_6$ precipitates are much larger than the MX precipitates.

- It can be concluded that with 3D EFTEM tomography:

  - The projection limitation is overcome so that it is possible to determine the true spatial distribution and size of the precipitates in the extraction replica.

  - In combination with the conventional 2D maps there is the potential to obtain quantitative information about the precipitates in a 12% Cr steel with greater accuracy.

Future Work

- Optimization and hence quantitative analysis of the 3D reconstruction.
- To determine to what extend the extraction is a true replica of the steel sample.

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THANK YOU

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