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# Phase stability of zirconium oxide films during focused ion beam milling

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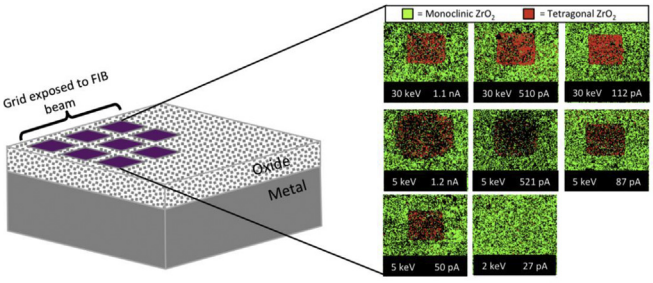
## HIGHLIGHTS

- FIB irradiation results in phase transformation from monoclinic to tetragonal $ZrO_2$.
- At a beam energy of 2 KeV no transformation was observed with either $Ga^+$ or $Xe^+$.
- The threshold beam energy for transformation is lower for $Xe^+$ than $Ga^+$.
- Final low energy cleaning step is vital and Pt layer should be maintained.

## GRAPHICAL ABSTRACT

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## ABSTRACT

Focused ion beam (FIB) is a widely used technique for preparation of electron transparent samples and so it is vital to understand the potential for introduction of FIB-induced microstructural artefacts. The bombardment of both $Xe^+$ and $Ga^+$ ions is observed to cause extensive monoclinic to tetragonal phase transformation in $ZrO_2$ corrosion films, however, this effect is diminished with reduced energy and is not observed below 5 KeV. This study emphasises the importance of careful FIB sample preparation with a low energy cleaning step, and also gives insight into the stabilisation mechanism of the tetragonal phase during oxidation.



## 1. Main text

Focused Ion Beam (FIB) milling is the most common method used to prepare samples of metal/oxide interface regions for transmission electron microscopy (TEM) examination due to difficulties preparing insulating thin film materials using more traditional sample preparation methods. One particularly important aspect is the relief of residual stresses during sample preparation, and the effect this has on, for example, the stress-stabilised tetragonal grains in oxide films formed on Zr alloys. In this case, samples prepared by FIB are typically observed to have significantly lower tetragonal phase fractions than measured by non-destructive X-ray diffraction (XRD) techniques [1–4], with the relief of the in-plane residual stresses causing transformation of the larger tetragonal grains [1,4]. This effect is also highlighted by a recent scanning precession electron diffraction (SPED) study that has shown significantly higher tetragonal phase fractions in thicker regions of a FIB-prepared $ZrO_2$ sample, where more residual

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stresses are maintained [5].

Another important aspect is the potential effect of damage introduced by the FIB on the oxide microstructure. For instance, previous studies have shown that $Ga^+$ exposure leads to phase transformation from austenite to ferrite in steel [6,7]. Although no direct effect of FIB exposure on phase transformation in $ZrO_2$ has been reported to date, ion irradiation, used to simulate the effect of neutron damage, has been observed to cause monoclinic to tetragonal phase transformation in sintered zirconia powders [8] and corrosion films [9]. It is therefore clear that charged particle irradiation has the potential to significantly change the microstructure of such materials.

The use of FIB is also becoming increasingly important for the characterisation of reactor-formed zirconium oxide films as the activity of large samples makes bulk measurements impractical. Consequently, small samples with low activity are typically shipped from active laboratories for final thinning and TEM examination [9]. This study investigates the effect of FIB irradiation on phase transformation in $ZrO_2$ corrosion films formed on Zircaloy-2 using electron backscatter diffraction (EBSD) in the scanning electron microscope (SEM) and SPED in the TEM. The effect of using different ions, namely $Xe^+$ and $Ga^+$, is investigated as well as the extent of transformation as a function of beam energy and current, on oxides formed in both autoclave and in-reactor conditions.

Non-irradiated oxidised Zircaloy-2 samples for both EBSD and TEM analysis were supplied by Wood plc. after autoclave testing at a temperature of 350 °C with simulated pressure water reactor (PWR) chemistry. After 55 days of autoclave exposure, the region used for TEM analysis had an oxide thickness of ~2.5 μm, with an average oxide thickness of ~1.9 μm calculated from weight gain measurements. The sample used for EBSD analysis was estimated to have an average oxide thickness of ~1.2 μm from weight gain after 46 days autoclave exposure. The reactor-formed oxide, supplied by Westinghouse as part of a previous investigation [9], was formed in the KKL boiling water reactor (BWR) for 6 cycles. The oxide thickness was approximately 108 μm after 6 reactor cycles with the inner ~1.2 μm region prepared for TEM examination.

In order to investigate the effect of FIB exposure on a bulk oxide sample, a 2 × 2 mm region of an oxidised Zircaloy-2 sample was prepared using 4000 grit silicon carbide paper and polished using 0.06 μm colloidal silica solution, removing approximately ~0.4 μm of oxide. This ensures the layer of equiaxed tetragonal grains, commonly observed in the outer-most portion of the oxide [1,11], was removed and that the majority of the oxide grains exposed at the surface of the prepared sample would be monoclinic prior to FIB exposure.

Following mechanical polishing, 5 × 5 μm oxide regions were systematically exposed to $Ga^+$ ions using a dual beam FEI Nova 600i FIB-SEM. Each square contained about 10,000 grains, according to the average columnar grain width of 50 nm [9]. The beam energy was varied from 2 to 30 keV at a range of beam currents from 28 pA to 1 nA for 1 s in order to match those that are typically used at each stage of TEM sample preparation (Table 1). A similar grid of 5 × 5 μm regions was exposed to a $Xe^+$ ion beam using a dual beam FEI Helios plasma-FIB-SEM. Due to the use of different apertures, it was not possible to exactly match the $Ga^+$ beam currents and so the closest available currents were chosen, as shown in Table 1.

The non-irradiated specimen was prepared from the bulk oxide sample using the in-situ lift out technique [14] with an FEI Quanta 3D dual beam FIB-SEM. A 1 μm-thick lamella was lifted out and subsequently thinned using $Ga^+$ ions at 30 keV, with cleaning steps at 5 keV and 2 keV. The TEM specimen from the reactor-formed oxide was thinned using the same method, however due high levels of residual stresses in these reactor-formed oxides, significant bending was observed during thinning. This led to direct exposure of this region to the ion beam and subsequent hole formation at the metal-oxide interface.

Scanning precession electron diffraction (SPED) was performed using an FEI Tecnai F30 TEM operated at 300 keV with a probe size of ~3 nm and step size of 5 nm. The collection and analysis of diffraction patterns, acquired with a precession angle of 0.4°, was carried out using the ASTAR automated crystal mapping system [15], more details of the experimental setup can be found in [12]. Phase maps have been overlaid with a gray scale reliability filter making low reliability solutions appear darker and with solutions with reliability less than 10 set to non-indexed points. Energy-dispersive X-ray spectroscopy (EDS) chemical mapping was performed using an FEI Talos F200X microscope operated at 200 keV with a probe current of 180 pA and fitted with the FEI Chem-iSTEM™ system. The chemical maps presented have been quantified using the Cliff-Lorimer approach [16] using calculated k-factors in the Bruker software ESPRIT.

All EBSD measurements were performed on an FEI Magellan 400 XHR SEM, operated at 10 keV with a probe current of 1.6 nA and a step size of 100 nm. The indexing rate was ~60%, which is remarkably high for bulk EBSD measurements on such a fine microstructure, with a columnar grain width of ~50 nm [9]. Researchers have traditionally struggled to get reliable indexing from nano-grained $ZrO_2$ using standard EBSD, instead relying on transmission Kikuchi diffraction (TKD), SPED or XRD in order to investigate oxide texture [1,17]. The high indexing rate in this case is achieved due to the high resolution field emission gun (FEG) source on the FEI Magellan SEM, which allows for a small spot size with a high current density. The Kikuchi patterns taken at 4 × 4 binning were indexed using the AZtec software suite.

Figure 1 (a) shows a SPED phase map of the autoclave-formed oxide. A thin region of equiaxed tetragonal grains can be observed along the top edge of the sample. It should be noted that, in this sample the protective Pt layer was inadvertently removed during sample preparation resulting in a loss of this outer region of oxide. An enlarged region of the SPED phase map, marked as region 1 and shown in Figure 1 (b), clearly shows the equiaxed nature of

**Table 1**
The energy and currents of $Ga^+$ and $Xe^+$ ion exposure used in this study, corresponding dose rate and penetration depth calculated by SRIM [13]

| $Ga^+$ | | | | $Xe^+$ | | | |
|---|---|---|---|---|---|---|---|
| Beam energy (keV) | Beam current (pA) | Dose rate (dpa/s) | Penetration depth (nm) | Beam energy (keV) | Beam current (pA) | Dose rate dpa/s | Penetration depth (nm) |
| 30 | 1100 | 53 | 48 | 30 | 2300 | 212 | 30 |
| 30 | 510 | 25 | 48 | 30 | 360 | 33 | 30 |
| 30 | 112 | 5 | 48 | 30 | 84 | 7.8 | 30 |
| 5 | 1200 | 48 | 16 | 5 | 400 | 18 | 10 |
| 5 | 521 | 21 | 16 | 5 | 66 | 2.8 | 10 |
| 5 | 87 | 3.4 | 16 | 5 | 48 | 2.1 | 10 |
| 5 | 50 | 2 | 16 | 2 | 100 | 2.8 | 6 |
| 2 | 27 | 0.7 | 8 | 2 | 9 | 0.3 | 6 |