



DPhil Thesis

Oxidation Mechanisms in Zirconium Alloys for Nuclear Applications

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Preface

This thesis describes works carried out by the author in the Department of Materials, University of Oxford, from January 2011 to January 2017 under the supervision of Professor C.R.M. Grovenor and Professor S. Lozano-Perez. No part of this thesis has been previously submitted for a degree at this or any other university. The work of other authors has been drawn upon and has been referenced and acknowledged in the text. A list of references is given at the end of each chapter.

Abstract

Oxidation Mechanisms in Zirconium Alloys for Nuclear Applications

A thesis submitted for the degree of Doctor of Philosophy

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The oxidation of zirconium alloys under aqueous conditions has been studied for more than 50 years in relation to its role as a fuel cladding element in water-cooled nuclear reactors.

The most well-known and interesting phenomenon associated with the corrosion of zirconium alloys is the cyclic oxidation rate. Oxidation initially proceeds rapidly, forming an oxide film. As this film thickens, the rate of oxidation slows before transitioning, and begins oxidising at the higher rate again. This effect has been well studied, although the cause of rate transition is not understood.

Using samples oxidised in conditions very closely matching those of a nuclear reactor, although without radiation, several techniques were used to characterise the oxide before and after the transition in oxidation rate. Comparison of these results allows some insight into the mechanism operating.

Doping samples with isotopic tracers during different points in the oxidation cycle and subsequent analysis with NanoSIMS gave insight into the porosity and protectiveness of the oxide film before and after transition. Before transition, the entire oxide film acts as a barrier, rather than a small sublayer. After transition, the whole layer of previously formed oxide

became porous and the oxidising media was admitted directly to the metal/oxide interface. Examining samples of differing oxidation times showed each subsequent transition was a close repeat of the first. Oxide thickness, rather than time under corrosion conditions, was identified as the best predictor of whether a sample would undergo transition. Oxide porosity (and thus rate transition) was demonstrated to be a local process on scales as small $< 1\mu\text{m}$.

Residual stress in the oxide and underlying metal substrate have been studied for zirconium alloys for some years. Here, a new technique is applied that largely confirms previous measurements made by XRD. Testing pre- and post-transition oxides revealed a large drop in the compressive stress after transition, showing the post-transition oxide is both porous and contains much lower compressive stresses.

Acknowledgements

This thesis, such as it is, would not have been possible without the help of the following people, to whom I am incredibly grateful

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Literature Review

Introduction

Zirconium is a group 4 transition metal used extensively in the nuclear industry for the cladding and support structures of nuclear fuel elements inside water-cooled reactors. The operating environment for the zirconium cladding is highly challenging, demanding that the material retains its structural integrity under conditions of high temperature, high neutron flux and corrosive surroundings. Zirconium alloys are the leading material used in this application primarily because of its low neutron capture cross section, which permits exchange of neutrons between fuel elements sustaining the nuclear chain reaction. In order to create a zirconium-based alloy with the required properties, careful consideration must be given to its composition, microstructure and manufacture. In order to achieve this, all production steps must be considered, and the effect they have on the final product throughout its service life [1].

Zirconium has five common isotopes, three of which occur naturally, giving it an average atomic mass of 91.224 and atomic number 40 [2]. In its pure form, zirconium is soft and ductile, solid at room temperature, alloying elements can significantly change these properties [3, 4]. It also has a high melting point of 2128.15K[5], allowing nuclear plants to operate at higher temperatures and thus more efficiently.

Zirconium is typically extracted from Ilmenite and Rutile as a by-product of titanium mining. Global zirconium production reached 1440 tonnes in 2011[6]. Refined zirconium metal is usually referred to as “commercial” purity in its naturally extracted state as it is mixed with between one and four percent hafnium[7].

Extraction of zirconium occurs mainly as a by-product of titanium refinement[8] via the Kroll process [9]. The Kroll process involves the application of chlorine gas to the ore of zirconium, which yields metal chlorides. These chlorides are extracted via fractional distillation, and can then be reduced to the pure metal. For some applications, the Hunter process [10] may be used to make ultra-pure zirconium. In the Hunter Process, impure metal is heated in the presence of iodine, which volatilises as ZrI_4 . The volatilised gas is decomposed on a high temperature filament, depositing the pure metal. The Kroll Process is the dominant extraction method of zirconium today.

For nuclear applications, the 1-4 wt% hafnium present in ‘commercially pure’ zirconium must be eliminated, as although the chemistry of the two elements is very similar, they have strongly differing neutron cross sections [11]. “Reactor grade” zirconium is more expensive but necessary, because even a small amount of hafnium in the metal will significantly increase the total neutron capture cross section of the fuel rod cladding. Hafnium has a neutron cross section 600 times greater than that of zirconium.

Separation of zirconium from hafnium is difficult due to their similar chemistry; most processes exploit the slight disparity in the solubility of the chloride compounds, zirconium compounds tending to be slightly less soluble. In order to achieve the highest possible purity, iterative purification steps may be required.

Zirconium metal consists mainly of the HCP alpha phase, though the BCC beta phase is observed at temperatures above 1155K, or at lower temperatures with the addition of certain alloying elements to stabilise it [12]. Alpha and beta zirconium have extremely different properties with regards to the diffusion and storage of hydrogen, so understanding the occurrence of these phases is of utmost importance when designing fuel cladding elements.

Zirconium possesses properties other than its neutron cross section that make it suited to use in nuclear reactors; most importantly, its corrosion resistance and its mechanical strength.

While neither of these properties are exceptional, they are sufficient to allow the fuel cladding elements to isolate the fuel pellets from the primary cooling water [11].

Zirconium has a density of 6.52 g/cm^3 , and Young's modulus of 88 GPa [13], although as the tubes used for fuel cladding tend to be very thin, the weight of zirconium is not of prime importance.

The neutron capture cross section of zirconium is 0.18 barns, which is some 13 times lower than that of steel. This has many benefits for use in a nuclear reactor, as the free neutrons produced from fission reactions can easily access the fissionable material in the other fuel rods, meaning fewer neutrons are “wasted”. More efficient transmission between fuel rods means more neutrons are able to initiate further fission reactions, sustaining the chain reaction. This allows reactors with zirconium based cladding to use less enriched fuel compared to other reactor types, which is desirable for economic and nuclear proliferation reasons.

[Applications of zirconium in the Nuclear Industry](#)

Zirconium was used very early in the history of nuclear reactors, acting as a spacer in the EBR-1 reactor in Idaho since 1957 [14, 15], although it was not until later that it was used as a fuel cladding. It had been reviewed for use in the reactors of proposed submarines as early as 1949. In many early reactors, Magnox (magnesium non-oxidising) [16] was used to protect the fuel elements. The design goal of the cladding was to concentrate the radioactivity in one place to stop the coolant from acquiring too much activity. [14]

Magnox was chosen as the fuel cladding for the same reason zirconium is used today - its low neutron capture cross section. However, Magnox was not an ideal material as it limits the temperature of operation and is reactive in the presence of water. It's reactivity in water makes storage of Magnox fuel tubes difficult, as time spent in cooling ponds can lead to excessive corrosion (cooling in service is not a concern, as all Magnox reactors are CO₂ cooled).

The Magnox cladding, similar to zirconium, allowed the use of unenriched uranium fuel, in contrast to the AGRs (Advanced Gas Reactors), which came later, and used stainless steel cladding. Despite its drawbacks, the Magnox design of power plants has been in continuous use in the UK from 1956 to 2011.

In modern times, zirconium finds use in PWRs (pressurised water reactors), BWRs (boiling water reactors), RBMKs (high power channel-type reactors) and CANDU (Canada deuterium uranium) reactors. In all these reactors, the zirconium alloys are formed into long, thin rods to contain the fuel, and separate it from the coolant [1].

Table 1 [17], showing conditions of temperature, irradiation, coolant flow and coolant chemistry for different reactor designs using zirconium fuel cladding

Parameter	Western type <i>PWR</i>	<i>VVER</i> (440/1000) MW	CANDU ¹	<i>BWR</i>	<i>RBMK</i> ²
1. Coolant	Pressurized H ₂ O	Pressurized H ₂ O	Pressurized D ₂ O	Boiling H ₂ O	Boiling H ₂ O
2. Fuel Materials (Pressure tube materials)	Zry-4, ZIRLO, DUPLEX, M5, Inconel, SS ³	Zr-alloy E110	Zry-4 (Zr2.5Nb)	Zry-2, Zry-4, Inconel, SS	Zr-alloy E110, (Zr2.5Nb)
3. Average power rating, (kW/l)	80-125	83/108	9-19	40-57	5
4. Fast Neutron Flux, Average, n/cm ² .s	6-9E13	5E13/7E13	1.5-2E12	4-7E13	1-2E13
5. Temperatures, °C					
Average Coolant inlet	279-294	267/290	249-257	272-278	270
Average Coolant outlet	313-329	298/320	293-305	280-300	284
Max Cladding OD	320-350	335/352	310	285-305	290
Steam mass content, %				7-14	14
6. System pressure, bar	155-158	125/165	96	70	67
7. Coolant Flow, m/s	3-6 ⁺	3.5/6	3-5	2-5 ⁺	3.7
8. Coolant Chemistry ⁺⁺					
Oxygen, ppb	<0.05	<0.1		200-400	<20
Hydrogen (D ₂), ppm	2-4		(3-10)	.05-.30	-
cc/kg	25-50	30-60			
Boron (as Boric acid), ppm	0-2200	0-1400	-	-	-
Li (as LiOH), ppm	0.5-3.5	0.05-0.6	1	-	-
K (as KOH), ppm	-	5-20		-	-
NH ₃ , ppm		6-30			
NaOH, ppm		0.03-0.35			

As can be seen in Table 1, the conditions zirconium alloys are used in are broadly similar, consisting of a hot, liquid water environment under high pressure.

Zirconium Alloys

Despite the fact that conditions for use are so similar, a large number of zirconium alloys have been developed and trialled (see Table 2). Initially, there were two families of alloys: the high tin, iron and chromium alloys, with or without nickel, developed for Western reactors, and the zirconium-niobium binary alloys used by Russia. Subsequently, more alloys have been developed, which have begun combining the two approaches, nearly always containing niobium and another element to strengthen the alloy.

Table 2 [18], showing the most common alloys in use commercially.

Alloy	Sn %	Nb %	Fe %	Cr %	Ni %	O %	Others alloy elem.	%	Ref.
1. Commercial alloys									
Zircaloy-2	1.2-1.7	-	0.07-0.2	0.05-0.15	0.03-0.08	0.1-0.14	-	-	ASTM
Zircaloy-4	1.2-1.7	-	0.18-0.24	0.07-0.13	-	0.1-0.14	-	-	ASTM
E-110	-	0.9-1.1	0.014	<0.003	0.0035	0.05-0.07	-	-	Shebalov, et al., 2000
Alloy E125	-	2.5	-	-	-	0.06	-	-	Solonin, et al., 1999
Zr2.5Nb	-	2.4-2.8	<0.15	-	-	0.09-0.13	-	-	ASTM
ZIRLO	1	1	0.1	-	-	-	-	-	Comstock, et al., 1996
DX-ELS-Liner	0.5/0.8	-	0.3/0.5	0.2	-	0.12	-	-	Garzarolli, 2001
PCA-2b	1.3	-	0.3	0.2	-	-	-	-	Garzarolli, 2001
M5	-	0.8-1.2	0.015-0.06	-	-	0.09-0.12	-	-	Mardon, et al., 2000

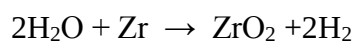
Zircaloy-2 was initially used for the cladding in BWRs while Zircaloy-4 or E110 were used in PWRs (Russian reactors used E110). These materials were found to have sufficient corrosion resistance, and so little development of further alloys was needed. However, current trends in reactor design and operation favour increased fuel burnup, higher temperatures and pressures and differing cooling chemistries. Alloys such as ZIRLO have been developed in response to this need. As well as investigation of new and experimental alloys, older alloys such as Zircaloys and Niobium alloys are still widely studied as their use will continue in reactors will continue for decades to come.

Corrosion of Zirconium Alloys

Zirconium corrosion mechanisms must be fully understood in order to formulate models for hydrogen pick-up. The oxidation process not only liberates the hydrogen that will eventually end up dissolved in the metal, but also forms a barrier layer of oxide, the properties and morphology of which can have a drastic effect on both further corrosion and hydrogen pick-up.

The oxidation of zirconium proceeds by the diffusion of oxygen ions into the oxide layer [17] (specifically, through the crystallite grain boundaries of the oxide). Simultaneously, electrons released from the metal, and oxygen vacancies formed by the formation of new oxide diffuse out through the oxide. The electrons cause the dissociation of water at the oxide/environment interface and the oxygen vacancies accept new oxygen ions. Hydrogen atoms released by the disassociation of water then find their way into the metal, through various possible mechanisms that are still not well understood. Zirconium atoms or ions are almost entirely stationary, significant movement can only occur at extremely high temperatures, as found in a loss of cooling accident. [1]

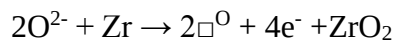
The complete reaction can be written as [18]



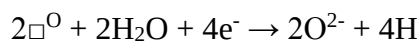
This is the same as the “zirconium steam reaction”, which usually only occurs at high temperatures, and can lead to hydrogen explosions through the rapid evolution of hydrogen gas. At normal reactor operating temperatures though, the reaction proceeds very slowly, and it is the build-up of oxide and the accompanying hydrogen pickup that present problems in this regime.

The reaction can also be viewed as an anode-cathode reaction, with two half-cell reactions occurring, one at the metal/oxide interface and one at the water/oxide interface. At the metal/oxide interface (where the metal can be viewed as the cathode and the oxide the electrolyte) the metal loses electrons, freeing a zirconium atom to react with incoming oxygen, depositing a new molecule of ZrO_2 . While at the anode (oxidant reservoir, i.e. water) oxygen and hydrogen split, oxygen ions then combine with oxygen vacancies in the oxide to move through the oxide layer, and the electrons reduce hydrogen ions to a gas. The reactions at the metal/oxide and oxide/water interface can be written as two half-cell reactions.

Cathode



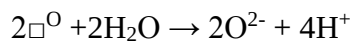
Anode



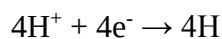
($\Box^{\text{O}}$ represent oxygen vacancies)

However, the anodic reaction can also be broken down into two separate reactions: one for the disassociation of oxygen from water, and one for the reduction of hydrogen ions into atoms.

Oxygen disassociation



Hydrogen reduction



See figure 1 for a schematic representation of this process.

The hydrogen, once reduced, is then able to travel into the metal. The species (for example, ionic or atomic) of hydrogen that migrates through the oxide is a key area of research along with which alloy characteristics affect the amount of hydrogen absorbed by the metal.

In this process, it is the diffusion of electrons out through the oxide layer that is the rate determining step [19]. This conclusion can be reached by noting the static nature of the Zr ions. This leaves only electrons and oxygen ions/vacancies as the mobile species in the lattice. It is readily deduced that electrons must be the rate limiting step by measuring the potential that develops across the oxide. The metal/oxide interface rapidly becomes negatively biased with respect to the oxide/oxidant interface. This negative potential serves to push electrons from the metal, across the oxide. Since the process requires a negative potential (increasing the rate of electron transport) in order to maintain equal flows of electrons and oxygen ions, it is apparent that the electrons must be the rate determining step.

See Figure 1.

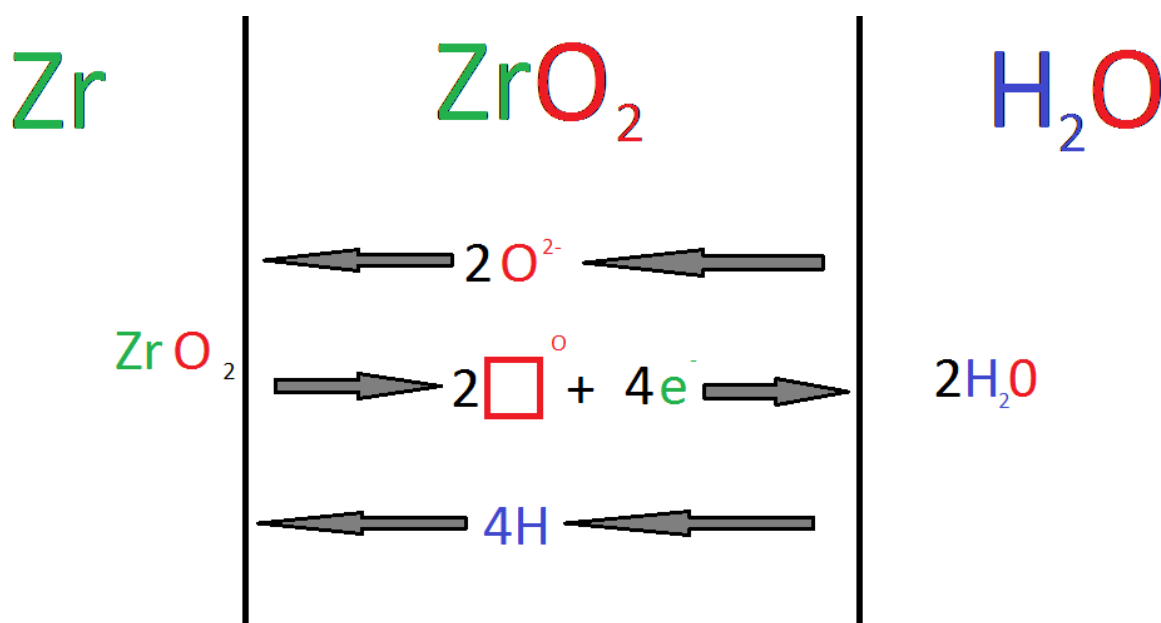


Figure 1 Schematic representation of the oxidation process and ion flow.

As well as forming oxide, oxygen is found dissolved in the metal immediately under the oxide layer [20]. In some cases, the concentration of oxygen can be as much as 30% atomic percentage in a sub-micron region near the surface.

Types of Corrosion

Oxidation can occur in different forms, which can be largely separated into nodular or uniform corrosion [18] (see Figure 2 and

Table 3). Uniform, as it sounds, is a thin layer of oxide forming on the surface, without a significant change in thickness over the sample. Nodular corrosion is characterised by the presence of local regions with greatly increased thickness compared to rest of the oxide, which macroscopically present as white spots in the black oxide.

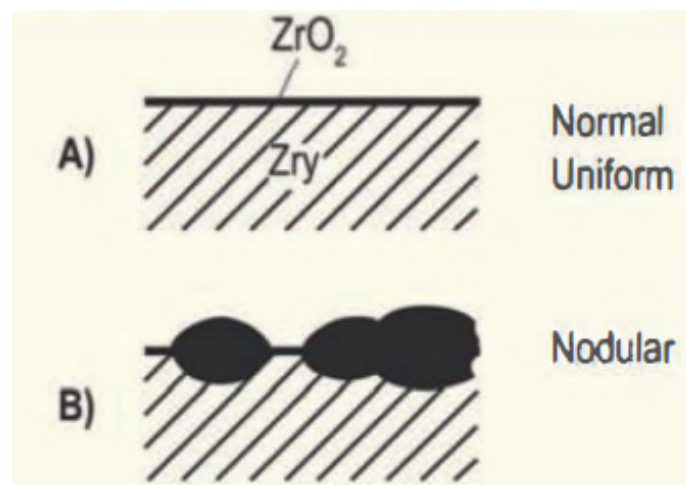


Figure 2 showing the difference between nodular and uniform corrosion.

Table 3 reproduced from [17], showing characteristics of various sub types of corrosion

Type of corrosion	Comment	Observed	Irradiation effect in oxygenated coolant (BWR)	Irradiation effect in hydrogenated coolant PWR
Uniform	Normal mode	Out-of-pile, in-BWR and in-PWR	5-10x increased from beginning, low flux dependency	2-4x increased after 1 st corrosion rate transition, low flux dependency
Nodular	Local breakdown of oxide protectiveness	In-BWR and out-of-pile >500C, Zry with large SPP	Increases almost linear with fast flux, little temp. dependency	Not observed
Shadow corrosion	Probably driven by potential differences	Only under irradiation and oxidative coolant conditions (BWR)	Increases probably almost linear with fast flux	Not observed
Crevice corrosion	Change of environment in small gaps	Out-of-pile, in-BWR and in-PWR	Observed	Observed
Increased corrosion with fine SPP	Reduction of protectivity	Out-of-pile, in-BWR and in-PWR	Increases almost linear with fast flux	Increases almost linear with fast flux, little temp. dependency
Increased corrosion at high fluences	Reduction of protectivity	In-PWR	?	Increases with increasing fluence above a critical threshold
Increased corrosion at high hydride concentrations	Lower corrosion resistance of hydride	Out-of-pile, in-BWR and in-PWR	Observed	Flux dependent but less temperature dependent

Nodular corrosion occurs mostly in BWRs in which the coolant is allowed to boil. The oxide must first reach a critical thickness, and from then nodules grow preferentially. Though the mechanisms behind nodular corrosion are not fully understood, SPPs (secondary phase particles) seem to play a prominent role in the process. It is observed that nodular corrosion is strongly affected by the presence, size and distribution of SPPs. In samples of Zircaloy with

very small precipitates, nodular corrosion is not present. Zircaloy-2 also shows a stronger tendency towards nodular corrosion than Zircaloy-4, and also has fewer and smaller intermetallic particles. Finally, the rate of nodular corrosion decreases at high fluence conditions (i.e. once the SPPs have been dissolved by the neutron flux), which again points towards SPPs playing a role in their formation [17].

This hypothesis could be tested by preparing metallographs of zirconium samples exhibiting nodular corrosion and then using an SEM to search for the SPPs in the matrix or in the oxide. SPPs do show up in high resolution SEM micrographs, and can especially be seen using the backscatter mode, as the iron and chrome that constitute these particles in Zircalloys will show different contrast due to different atomic mass.

When comparing Zircalloys to E110, which does not undergo nodular corrosion, one of the obvious differences is that E110 does not form intermetallic particles [21] unless high in iron (Nb acts as a beta phase stabiliser, so filamentous strands of beta phase are formed, which are highly enriched in Nb, with much less in the alpha Zr matrix).

Generally, PWRs can be run at higher temperatures than BWRs, which is desirable, as higher temperatures and pressures increase the thermodynamic efficiency of power generation.

However, running at a higher temperature can dramatically increase the rate of corrosion, with some tests showing a 26% increase in weight gain from just a 5K change in temperature for a static autoclave test [17]. In a real reactor, temperature must be considered in the context of coolant inflow and outflow, so different rods may heat to different temperatures. The temperature controls the rate of oxidation. A higher temperature will increase the mobility of charge carrying species in the oxide and bring the kinetic energy of the zirconium ions closer to the energy required for ionisation and electron release.

The Effect of Temperature on Corrosion

The temperature at which oxidation occurs must also be considered along with the heat flux of the system. Since heat is generated internally and escapes through the fuel rod wall, the temperature at the metal/oxide interface will be higher than the temperature of the oxide/coolant interface. The oxide acts as a heat insulator and so it speeds up corrosion by the increased temperature, but other factors caused by increasing oxide thickness may retard oxide growth rates. PWRs have a licensing limit placed upon them [17], restricting the maximum thickness of oxide growth to 100 μm . This limit is intended to prevent the insulation effect of very thick oxides (increasing temperature and thus oxidation rate), prevent excessive hydriding of the underlying metal and maintain tube wall thickness.

The oxide thickness on fuel rods is also sensitive to local conditions of temperature, where, for example, a higher position in the core will increase temperature. Alternatively, the proximity of other components can cool or heat the fuel rod by disturbing the local flow of coolant. CRUD (Chalk River Unidentified Deposits or Corrosion Related Unidentified Deposits [22]) deposits can also act to insulate the fuel rod, increasing the rate of oxidation locally.

The temperature dependence of the oxidation, rate and the effect of heat flux can be accounted for in the way a reactor is run. For example, early on in the fuel cycle when oxide is thin, a high heat flux can be maintained without raising the temperature of the metal/oxide interface too much. This is because the oxide is thin and does not insulate the fuel rod so effectively. Once a thick oxide has built up, the reactor must be run at lower temperatures so as to limit the temperature experienced at the oxidising interface.

Kinetic Transitions in Oxidation Rate

The most striking feature of the oxidation of zirconium alloys is the cyclic nature of the oxidation rate (see Figure 3). When plotting weight gain against time a clear picture of this effect emerges. Typically, these studies are done in an autoclave with samples being removed and weighed periodically. Initially, the weight gain follows a cubic or parabolic rate law with the rate of weight gain decreasing with oxide thickness. This is due to the oxide becoming thicker, and hence has a higher resistance to the movement of charged species through it, slowing the rate of oxidation. Eventually, the oxide growth rate will go through a “transition”. There is a large amount of discussion in the literature about the microstructure of pre- and post-transition oxides, or pre-transition regimes [23]), during which the rate will “reset” and the sample begin to oxidise at the higher rate again. The rate will subsequently slow down and the oxide will go through another transition. The changes wrought in the microstructure by these transitions and the events that trigger the oxide to go through them have been the subject of much investigation [24]. It is only through examining the detailed microstructure of the oxide in pre- and post-transition situations as well as having an understanding of the porosity of each layer of oxide, and through accounting for the stresses generated by each new layer of oxide forming that one can build a credible model for what is happening at and causing each of these transitions.

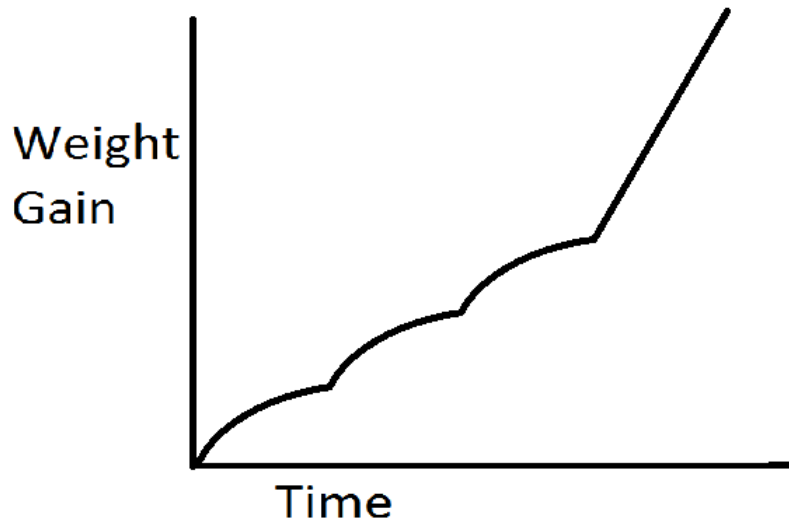


Figure 3 showing simplified graph of oxidation rate transitions, and final period of breakaway oxidation

This transition behaviour is well documented, from a phenomenological point of view, and various factors such as the alloy composition and the water chemistry are varied in order to see the effect on time of the first transition, and time intervals between subsequent transitions. It is also observed in some alloys that after several transitions, the behaviour stops, and the oxidation instead follows a linear rate law. This type of oxidation is termed “breakaway” and is extremely undesirable in a reactor, as each layer of oxide provides no protection to the surface, and so oxidation can proceed at a high and continuous rate. Pure zirconium does not show this typical behaviour. Instead it shows a short period of oxide growth following a cubic or parabolic rate law, and then after only a small build-up of oxide thickness transitions to breakaway oxidation. TEM studies of the oxidation have shown this is because of the high dependence of the oxidation rate on the crystallographic orientation of the grain being oxidised [25]. As different grains oxidise at strikingly different rates, the oxide will never

form a protective barrier due to the stresses caused by differential growth rates, and so the oxidation can proceed at a high rate.

The study of transition behaviour in zirconium alloys is made difficult by the hostile environment used for autoclave testing. The high temperatures and steam pressure render virtually any measurements of the oxide impossible. Measurements of weight gain after the oxidation have been the main method used to measure transition. A method of marking the sample during oxidation allows study of the transition behaviour as the marking can be examined later through various techniques.

Isotopic doping allows the marking of specimens during oxidation with a chemical species that can later be identified through mass resolution techniques such as SIMS (secondary ion mass spectroscopy) but which behaves chemically identically to the normal oxidising medium. Isotopic tracers were used [26] to study the transition behaviour of Zircaloy-4 and ZIRLO alloys by doping previously oxidised samples of differing transition regimes and subsequent imaging of the isotopic species to examine the sites of active incorporation. Samples were first oxidised for periods of 34, 80, 114 or 160 days in conditions closely matching the primary coolant water used in PWRs. These periods were chosen to produce samples immediately before, immediately after and near the first transition of these alloys. The addition of ^{18}O (oxygen-18) to the autoclave for a 20 day period then impressed the samples with an isotopically enriched region wherever the oxide scale was actively corroding after the differing periods of initial oxidation.

After initial oxidation and the doping exposure, samples were removed, cut and mounted to show a cross section including the entire thickness of oxide and the metal/oxide interface. This cross section was polished with colloidal silica to an extremely fine finish and examined using a CAMECA NanoSIMS, which was able to image the cross section and distinguish the

^{18}O from the natural abundances of isotopes found in the initial oxide and thus reveal the sites of active oxygen incorporation were present after differing initial oxidation periods.

On pre-transition samples the ^{18}O introduced during the final corrosion period was incorporated into the exterior of the oxide in a narrow band. This implies that at this stage the majority of the oxide layer was acting protectively and new oxide was being created through vacancy hopping of oxygen moving forward towards the metal/oxide interface and oxygen vacancies diffusing in the opposite direction.

Samples that were immediately post-transition during the introduction of the isotopic tracers showed a thick band of enrichment at the metal/oxide interface, showing that the transitioned layer of oxide above was porous and provided no protection to the underlying metal. The thickness of the oxide band combined with knowing the samples were exposed to the ^{18}O for the same time period shows that the samples were corroding much more quickly, consistent with post-transition corrosion kinetics.

Some samples showed a mixture of these two behaviours, with a very thin band of enrichment on the exterior of the oxide and a much thicker band of enrichment at the metal/oxide interface. These samples underwent transition during the introduction of ^{18}O to the system and so show both effects.

The main benefit of this technique is that it directly investigates the porosity of the oxide and hence its transition state at a local scale. Instead of depending on a time of oxidation or a macroscopic weight gain to determine the likely point of kinetic transition, there was a permanent marker to indicate which samples and which parts of samples had undergone transition.

The unique advantages of this protocol allowed the demonstration that transition occurs locally, with some areas having undergone transition and some not, even on the same

samples. It also showed that the critical factor controlling transition was not time of oxidation but instead a local oxide thickness.

Structure of Oxide layers

The structure of zirconium oxide films is important in understanding their corrosion behaviour, although the very small size of the crystallites that make up the oxide layer (equiaxed grains of 20nm -30nm are common [27]) make it difficult to get good images of the structure even with high resolution TEM techniques.

It is widely agreed that the oxide consists of several layers that have different properties and correspond to different points of transition in the cyclic oxidation [17, 18, 20]. Closest to the metal/oxide interface there may be a thin layer of amorphous oxide, composed primarily of ZrO as opposed to ZrO_2 , though this layer has not been as widely reported as others [28]. It is theorised that this layer, due to its amorphous character, may present an extremely effective barrier to the ingress of both oxygen and hydrogen.

The layers of oxide found on a sample will depend on the stage of oxidation, and this description will follow a chronological format of oxide layers as they form.

The first layer to form on an oxide will be composed of equiaxed, tetragonal grains, with a mixture of orientations, depending on the orientation of the metal grain they grow from [29]. This layer will likely provide little resistance to oxygen ingress, as the oxygen will diffuse via the grain boundaries, of which there are many. When this is the only oxide layer protecting the metal, a high oxidation rate is observed, corresponding to either the first part of the parabolic/cubic rate law at the first oxidation step or after every transition.

Once a film of equiaxed grains have built up, some of them in certain preferred orientations will continue to grow and form long columnar grains, with the long axis orientated perpendicular to the metal surface [30]. This layer corresponds to a period of decreasing oxidation rate, since as the columns increase in height, they present a more effective barrier to further oxidation, and so are responsible for the slowing down of oxidation in the latter part of a cubic/parabolic phase of oxide growth. The reason these columns grow instead of more equiaxed grains is the high Pilling-Bedworth ratio (quantifying the relative volumes of a metal and its oxide per metal atom) of zirconium and its alloys. The volume of the oxide created is approximately 56% larger than the volume of each zirconium atoms consumed, meaning the oxide occupies much more volume than the metal it replaces. This causes strains in the metal and oxide. The oxide, which will try to remain contiguous with the metal surface, will be put under compressive stress [31], and the metal at the interface will be put under a corresponding tensile stress. Understanding this stress, and how it relates to the phases of the oxide is important. As has been shown above, the oxide grows from the metal/oxide interface, and so this layer of columnar grains will be between the first layer of equiaxed grains and the metal.

Once the layer of columnar grains has grown to a certain, critical size, the oxide will undergo transition, and several changes occur simultaneously, which affect the oxide structure and subsequent growth rate. The grains (columnar and equiaxed) require a compressive stress to maintain their phase. Once the interface can no longer sustain this stress, the oxide undergoes a phase transformation into a monoclinic phase from a tetragonal one [31] (initially they shared the tetragonal phase of the small equiaxed grains that they grew from). This is accompanied by a volume change of the crystallites. Small cracks normal to the metal surface open up in them; some describe this as a form of nanoscale porosity and some as the

formation of larger cracks [4]. Either way, the effect is that the upper layer of oxide (the original equiaxed grains and the columnar grains, the base of which are still in contact with the metal) ceases to be effective as a barrier layer. Oxidant can filter through to the metal/oxide interface in fairly large quantities, enough that the metal now acts as though it is contact with the outer environment, and oxidises at the rate it did initially, with no protection. This is the root of the transition behaviour of the oxide. A new layer of tetragonal grains will now grow on the metal surface, interposing themselves between the base of the columnar grains and the metal surface. This transition leaves its mark in the oxide, as long cracks tangential to the metal surface. These cracks often form above protrusions of the metal into the oxide, and display a shape that mimics that of the outer surface of the protrusion [32]. At these protrusions the stresses are obviously concentrated, and so the phase change in order to relieve the stress must form cracks. It was well observed (see Figure 4), even in early work before the significance of the phase change was realised, that the oxide showed a layered structure after it had gone through several transitions. Each layer is a combination of tetragonal and columnar grains, separated by a network of cracks formed in the oxide.

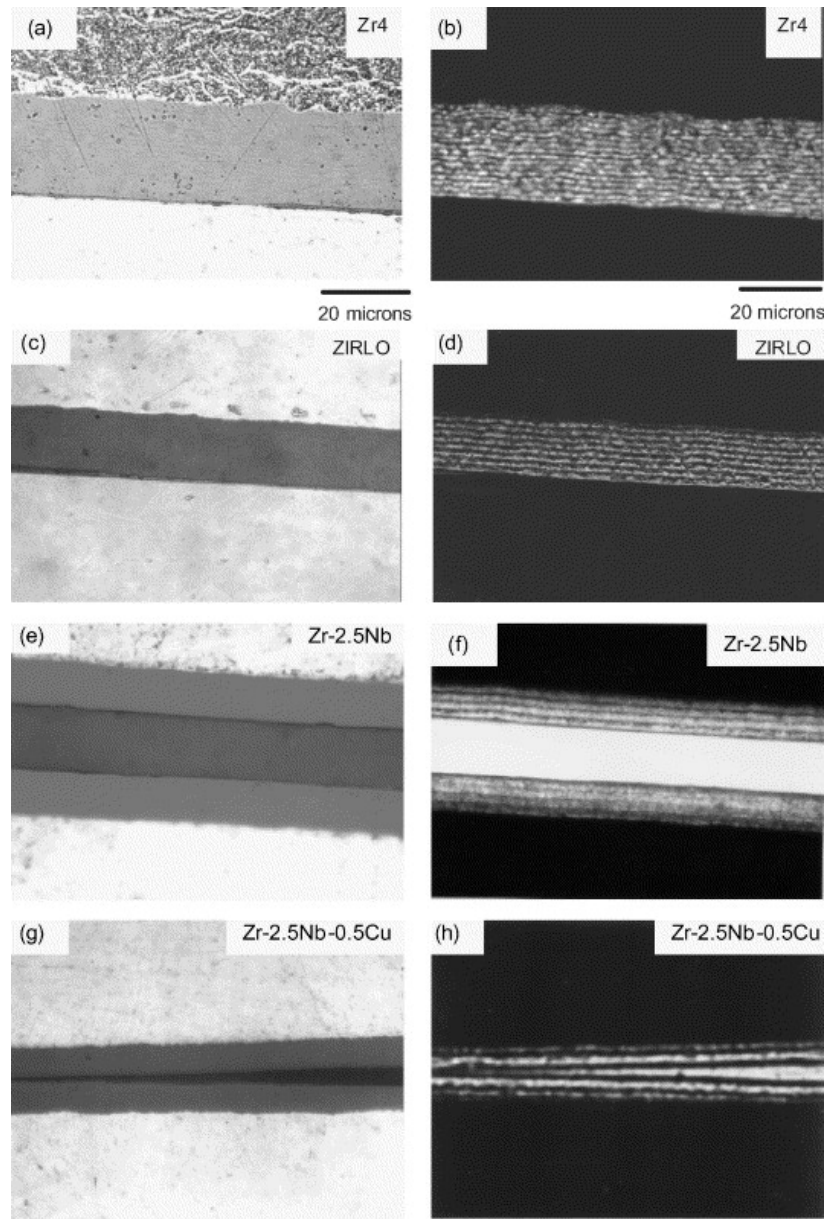


Figure 4 [23], Optical micrographs in reflected and transmitted light, showing layered oxide structure typical of post-transition samples

The new layer of tetragonal grains formed when the columnar layer has degraded will then follow on the same pattern. The oxide above a layer of columnar grains that have gone through transition can more or less be disregarded from a corrosion standpoint, as they seem to allow direct access of the oxidant to the inner layers of the metal or oxide. At each point the metal is only protected by the oxide that is still contiguous with it on the surface [33].

Figure 5 gives an overview of these layers, showing the metal surface, a layer of tetragonal

grains, the layers of columnar, and equiaxed grains that have separated and undergone phase transformation, no longer providing a barrier function.

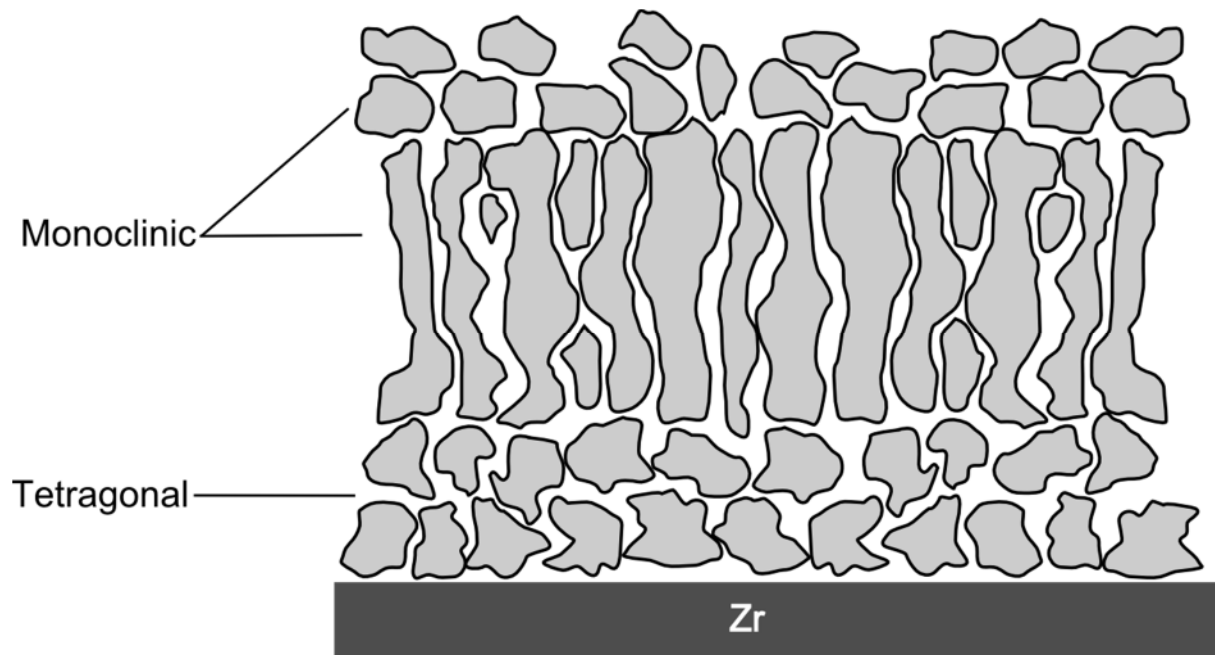


Figure 5 , showing oxide composed of three layers, after one transition

The breakaway oxidation regime is not well understood, since each layer of oxide effectively loses any barrier properties at the kinetic transitions. This should allow a new bi-layer of equiaxed and tetragonal grains to form. However, once the oxide has been through a certain number of transitions, there seems to be some effect that prevents the previous transition behaviour occurring.

Modern high resolution imaging techniques and associated chemical analysis have allowed new observation of extremely fine features in oxide layers. A study employing multiple imaging and chemical analysis techniques [34] on a well-controlled batch of samples shows both the challenges and opportunities of this type of research.

High resolution TEM of FIB (Focussed Ion Beam milling) prepared specimens produced images extremely clear images of the metal/oxide interface and the small oxide grains present

in this region. In small grains on the interface a suboxide phase was found in some samples consisting of ZrO. Careful calibration of EELS (Electron Energy Loss Spectroscopy) measurements allowed a high degree of confidence in the stoichiometry of this phase. The thickness of this suboxide phase was found to differ between samples depending on the transition state of the oxide. Samples approaching transition were found to have thicker suboxides (approaching 140nm thickness) whilst samples immediately post-transition had much thinner suboxides, suggesting the suboxide is consumed during or immediately after transition[34].

TEM analysis of these specimens also highlighted the varied nature of the interface. Even over small distance the suboxide appeared, disappeared and altered in thickness. Additionally, the phases present appeared to correlate with the morphology of the interface. This underlines the importance of repeating measurements over the interface as the character of the interface can change rapidly.

These same samples were additionally analysed with Atom Probe Tomography[34] to investigate the presence of a suboxide phase. The same correlation between transition stages and oxide thickness, in which samples nearing transition had thicker suboxides, was also found. Chemical analysis performed on the reconstructed suboxides also shows a ZrO composition for this phase. The agreement between two techniques based on different physical principles also provides confidence in the reliability of this result, despite the very small volumes being measured.

The combination of APT and TEM EELS[34] (electron energy loss spectroscopy) also permitted study of the dissolved oxygen in the metal immediately below the oxide. Dissolved oxygen up to 30% was found in samples with later pre-transition oxides, which agrees with

other values for the maximum concentration of oxygen in zirconium alloys [1]. The highest levels of dissolved oxygen were found in samples nearing transition.

The drawback of using these techniques is the extremely small area under investigation with either technique. Although the TEM foils may cover a distance along the metal/oxide interface of several microns, the individual images and EELS spectra cover regions only of approximately 100 nm. Repeating these measurements over a whole foil is extremely labour-intensive and especially so when considering repeating this over multiples foils for multiple samples and alloys. APT similarly investigates only very small volume of material and samples are even slower to produce, meaning analysis can be even more highly affected by variation between regions and samples. This limits experiments to reporting small sets of measurements rather than building a complete picture of the interface for multiple samples. Repeating these measurements as much as is practicable increases the reliability

The fact that samples nearing transition had both high levels of dissolved oxygen, and more ZrO suboxide, whilst samples immediately post-transition had lower levels of both, suggests a relationship between these factors. Creating of suboxide and the dissolution of oxygen in the matrix are most prevalent in samples with low oxidation rates. The slow advance of the metal/oxide interface means oxygen at the interface will have time to diffuse into the metal matrix creating the high concentrations of oxygen, whilst the slow transport of oxygen through the oxide supports a stoichiometry below that of the normal ZrO_2 ratio existing in the regions most starved of oxygen. After transition, when oxygen floods the metal/oxide interface, the suboxide is able to rapidly transition to ZrO_2 and the metal/oxide interface advances so rapidly that the time-limited diffusion of oxygen into the metal is overtaken by the growth of ZrO_2 . This means that samples that have just undergone transition, and thus have the highest oxidation rate, are much less likely to display suboxides or high dissolved oxygen content.

Mapping grain boundaries and determining orientation and texture in the extremely fine grained oxides present in zirconium alloys has traditionally been an extremely challenging task. Traditional EBSD (Electron Back Scatter Diffraction) lacked the spatial resolution to accurately index grains, and analysis of TEM diffraction patterns of individual grains would be almost impossible if performed manually. Recently techniques such as transmission EBSD (tEBSD, also known as Transmission Kikuchi Diffraction) and Automated Orientation Mapping (AOM) in the TEM have made characterization of zirconium alloy oxide films far more tractable.

DFT based modelling of the ZrO suboxides suggests a hexagonal structure for the suboxide grains found at the interface [35]. Further careful TEM work combining EELS to reliably identify suboxide grains by their stoichiometry and subsequently tEBSD and Convergent Beam Electron Diffraction (CBED) patterns to index them provides strong evidence for the presence of a hexagonal ZrO phase at the interface [36]. The complimentary approach of tEBSD, CBED and EELS confirms the presence of large (300nm) equiaxed grains of suboxide that show a consistent 1:1 stoichiometry. Suboxide grains larger than the width of ZrO₂ grains found elsewhere in the oxide (ZrO is only found at the interface) suggest that the suboxide forms first and is consumed by the ZrO₂ as the interface recedes.

Combining both AOM and tEBSD [37] for the detailed study of pre-transition oxides has made possible a detailed characterisation of their microstructure and microtexture. Samples of Zircaloy-4 were oxidised in an autoclave to produce samples with pre-transition corrosion kinetics after 106 days of oxidation. Cross sectional samples were prepared using a FIB to create a uniform area of electron transparency suitable for AOM and tEBSD.

A familiar structure of fine equiaxed grains on top of a monoclinic columnar layer was revealed by tEBSD. A complete indexing of this cross section found a volume fraction of only 1% tetragonal phase, which is much lower than results typically found by synchrotron or XRD measurements of phase fraction. This can probably be explained by the complete relaxation of stress caused by FIB preparation of a TEM foil. As well as phase characterisation, tEBSD is able to extract textural information, and found that most monoclinic grains had an orientation of $(10\bar{3})$ perpendicular to the metal/oxide interface. Most grain orientations were found to be within 10° of this direction.

TEM AOM results largely agreed with those obtained with tEBSD. The same grain structure of equiaxed and columnar grains was found, with the main fibre direction of the columnar grains $(10\bar{3})$. The higher resolution available in the TEM also revealed small equiaxed tetragonal grains throughout the oxide of between 5 – 30nm that were invisible to tEBSD and likely stabilised due to their small size.

Information about grain boundary misorientation can also be extracted with these techniques[37], which show a high proportion of 90° , 142° and 180° misorientation boundaries between monoclinic grains. These misorientations are associated with twin formation in zirconia and it is suggested that these twin boundaries are the result of large scale tetragonal to monoclinic transformations in the oxide. It is also suggested that the evidence presented supports the theory of a gradual transformation from tetragonal to monoclinic as a continuous process, which would be in agreement with well-established XRD and Synchrotron X ray analysis of bulk oxides. Unfortunately, the sample preparation techniques mean a complete transformation to monoclinic is inevitable as all stress stabilisation will be absent in these foils. Therefore, conclusions about the continuous nature of the transformation appear less reliable.

The sample under investigation also contained only one grain of metallic Zircaloy-4 as a substrate, so it was unfortunately not possible to derive a full relation between the crystallography of the metal and the resulting oxide growth.

Effect of Secondary Phase Particles

This late breakaway behaviour can be difficult to separate from other forms of late corrosion acceleration, such as the acceleration caused by insulation of previous layers increasing the temperature, or once a certain fluence has been reached, complete dissolution of the SPPs can have an accelerating effect on the oxide growth rate [30]. Lack of SPPs may bring the alloy back to the sort of oxidation regime experienced by pure zirconium, which will obviously lack intermetallics.

SPPs are important in understanding the oxidation behaviour of zirconium alloys. They play a role not only in the galvanic corrosion process outlined above, but can also have an effect on the stress created by volume changes in the crystallites of the oxide layer.

Typically, alloys of zirconium high in iron or chrome will form intermetallic particles of Zr(FeCr)_2 [38]. Tin does not form such precipitates, instead acting as a solid solution hardener. Nb-Zr binary alloys do not form intermetallics, instead becoming a two phase system, with a Nb rich beta phase [21]. Annealing temperatures and rates affect the size and dispersion of these particles through the metal, and also seem to have an effect on subsequent corrosion, though it can be difficult to determine how much of the effect is due to particle parameters or another factor caused by the annealing rates.

It has been shown that fine SPPs generally increase the corrosion rate [39] in high pressure steam, as long as they are well-dispersed. It has also been observed that areas without SPPs in them seem to oxidise more slowly than neighbouring regions with SPPs (in the case where

they are distributed non-uniformly [40]). In the 90s, the production process for Zircalloys began to shift to one that optimised SPP size in order to control corrosion [41].

The role SPPs may play in corrosion is a complex one. Considering the galvanic process, inferences can be made by noting that SPPs do not oxidise when at the metal surface. Indeed, they do not oxidise until separated from the metal by 1-200nm [1]. This shows that the metal will corrode preferentially to the SPP. The metal is effectively acting as a sacrificial anode to the SPPs exposed on its surface to the oxide. When an oxygen ion contacts the SPP, the bulk metal will supply electrons to reduce it, and since the intermetallic supplies no electrons, none of the metal atoms there are ionised to form an oxide. Instead, oxidation occurs faster on the bulk metal in order to cathodically protect the SPP. This also demonstrates that the initial 100-200nm of oxide is at least to some extent conductive enough to allow sufficient electron flow into the SPP.

The consequence of this galvanic couple is that in a layer above the metal oxide surface, there is a distributed number of largely metallic SPPs. It is possible during the tetragonal to monoclinic phase transition that these metallic SPPs are ductile enough to deform and relieve some of the stress. Since they take some of the stress, the crystallites will deform less due to the volume change, and the integrity of the oxide may not be affected to the same degree as in an SPP-free alloy.

However, eventually, the SPPs will corrode, and like the zirconium bulk metal, a volume change will occur. This increase in volume may add stress to the matrix of crystallites, actually reducing its integrity as a barrier. If this corrosion happens fast enough that they damage the layer while it is still contiguous with the metal surface, the barrier layer effectiveness may be disrupted, leading to a higher rate of corrosion [31].

The effect of SPPs on the microstructure of oxide grains can be studied using HRTEM (High Resolution TEM)[42]. The epitaxial relationship between tetragonal oxide and iron rich SPPs produced a stabilizing effect on the tetragonal phase. Despite this result, differing the amount of iron in the alloy did not significantly affect corrosion performance of the samples under test.

Another parameter that has been studied with regards to the oxidation of zirconium alloys is the effect of water chemistry, which can vary significantly. For example, BWR coolant is high in dissolved oxygen, while PWR coolant is high in dissolved hydrogen (to reduce the possibility of galvanic potentials forming). This can have a significant effect on the choice of alloys used, as Nb alloys will corrode much faster in oxygen rich water, while they show no increase in corrosion by adding hydrogen to the water [43].

Effect of Solid Solution Alloying Elements

Tin has been added to Western alloys mainly for improving the mechanical properties of fuel assemblies rather than as a corrosion inhibitor.

Recent work examining the role of tin in the corrosion process has shown tin can have a deleterious effect on corrosion performance [44], Transmission Kikuchi Diffraction suggested that oxide microstructure of the tin free ZIRLO model alloy was significantly different from traditional ZIRLO. The tin free alloy demonstrates stronger texture in the oxide (i.e. more grains aligned in the predominant fibre direction) and a lower tetragonal phase fraction, these effects may account for the lower rate of oxidation. The growth of columnar grains was also observed to be extended in the tin free alloy, which is a strong indicator of delayed transition.

The suggested mechanism through which tin mediates these changes in the oxide microstructure is through its effect on the stabilisation of the tetragonal phase. Further investigation of the valence state of tin atoms using XANES[45] has shown that the valence state of tin atoms in the oxide changes with depth through the scale. Tin atoms near the metal oxide interface are found in the (SNII) state near the metal oxide interface and (SNIV) further out in the oxide. It is suggested that tin stabilises the tetragonal phase through a similar mechanism employed in yttrium stabilised zirconias, namely the reduced valence of (SNII) atoms in the oxide creates oxygen vacancies which inhibit the transformation from tetragonal to monoclinic. As oxidation proceeds, the valence state of tin changes from II to IV, and thus allows transformation from tetragonal to monoclinic, and thus allowing the ingress of oxidising species. This mechanism is proposed to explain the phase transformation aspect of rate transition.

Niobium has been used as an alloying element in Zirconium primarily in Russian reactors, although more recent western alloys such as ZIRLO and M5 have started employing additions of Niobium. Generally, Niobium containing alloys are found to have superior long term corrosion performance [46] although does not give the improved mechanical properties of tin/iron western alloys.

Effect of stress on Kinetic Transitions

Kinetic transitions, the structure of pre-and post-transition oxides and the stresses present in these structures are all intimately linked. The stresses and the factors that lead to their generation are challenging to study but must be understood as well as their relationship to oxide structure (specifically the crystallographic phase) in order to fully understand the

system that governs kinetic transitions, which are very much an effect of these underlying processes.

Zirconium dioxide or zirconia can have either tetragonal or monoclinic structure when grown in reactor conditions [23]. At reactor operating temperature only the monoclinic phase is stable under normal conditions, but it has been noted that small grain size and stress stabilise the presence of the tetragonal phase [34, 37]. The tetragonal grains stabilised by small size are usually so small and comprise such a small fraction of the oxide (approximately 1% once stress has been relieved [34]) that they are unlikely to play a major role in the protective nature or breakdown of an oxide film.

The stresses present in zirconium alloys undergoing oxidation seem to be a major contributing factor the stabilisation of the tetragonal phase [34], and XRD measurements have shown that these stresses change throughout the oxidation kinetic cycle along with the tetragonal phase fraction [47]. The in-situ stresses arise primarily from the oxide attempting to accommodate the stresses caused by the high Pilling Bedworth ratio, the oxide being placed under a large compressive stress (measurements of up to 2 GPa at the metal/oxide interface) and the metal experiencing the concurrent tensile stress.

In early pre-transition oxides, the thin oxide has a high tetragonal fraction and high compressive stress at the metal/oxide interface as measured by XRD. The oxide at this stage is composed of the tetragonal equiaxed grains (which are largely stabilised by their small size) and the columnar grains growing under them, which at this early stage are still largely tetragonal. It is theorised that all grain growth begins as tetragonal, and the columnar grains that form due to favourable orientations remain tetragonal in their early growth due to the high compressive stresses.

As the oxide thickens, several changes occur. The thickening is caused primarily by the columnar grains growing in length. As these grains lengthen they provide a more effective barrier to the diffusion of oxidising species to the metal/oxide interface and so the oxidation rate slows. XRD measurements of stresses and tetragonal phase fraction show a decrease in both during this phase of oxidation. The decreases in these quantities are brought about as various stress relaxation methods occur [47], which also mean less of the tetragonal oxide can be stabilised and thus it undergoes a martensitic phase transformation to the monoclinic phase. The reason stresses and tetragonal phase fraction reduce even at the metal/oxide interface is because the stress relaxation mechanisms are active whilst tetragonal oxide is being generated at a slower rate to replace that, which transforms to monoclinic due to the diffusion barrier presented to oxidising species.

The mechanisms through which stress is relieved have been proposed as creep of the underlying metal substrate, generation of roughness at the metal/oxide interface, hydrogen lattice expansion or fracture of the oxide [47, 48]. Creep could relieve stress via the metal deforming under the tensile stress it experiences, which over time could relieve enough stress in the oxide to drop tetragonal grains below their critical stabilisation stress. In-situ XRD work [48] has concluded that metal substrate creep and hydrogen lattice dilation alone are not enough to account for the stress relaxation required to destabilise the tetragonal phase and so point towards interfacial roughening or oxide cracking as possible mechanisms.

In-situ XRD measurements have an added benefit - they account for the effects of temperature on the system. The differing thermal expansion coefficients of zirconium and its oxide are not controlled for when measuring samples at room temperature, nor the differing ductility due to temperature.

Immediately after transition the tetragonal phase fraction and compressive stresses drop dramatically. The initial layer of oxide is at this point almost entirely monoclinic and under practically no compressive strain as it will be mechanically separated from the oxide by many lateral cracks in the oxide, which have been frequently observed in post-transition samples [49].

The transformation from tetragonal to monoclinic is a martensitic phase change that involves a 6% volume expansion and significant shear stress. The almost complete porosity demonstrated by post-transition oxide layers is assumed to be due to this large disruption creating networks of interconnected porosity through which water can penetrate and begin the cycle of kinetic transition again by growing a new layer of small equiaxed tetragonal grains at the metal/oxide interface.

Cracks have been imaged using a variety of techniques, including SEM and TEM[50], appearing primarily in areas rich in monoclinic phases. The results obtained from thin film specimens must be considered in light of the fact that much of the stress will have been relieved in sample preparation, and thus likely triggered a transformation to monoclinic structure. Samples of 3 μ m thick[50] seemed to retain significant tetragonal fractions near the metal oxide interface, suggesting these samples have not entirely transformed. Cracks were not found in tetragonal rich areas, further suggesting they retained some compressive stress.

The effect of radiation on in-reactor corrosion

The vast majority of zirconium corrosion research has been performed on samples that have undergone corrosion in autoclaves in order to simulate reactor conditions as closely as possible with regards to temperature, pressure and coolant chemistry. This system does not replicate the conditions of neutron flux found in normal reactor use, which may have large

effects on corrosion behaviour. Despite the large amount of material produced from reactors each year that will naturally perfectly represent all the conditions of interest, the practicalities of studying such highly irradiated materials has limited the amount of study performed in this manner.

Two main effects are theorised to explain a slight increase in the corrosion rate of in-reactor zirconium components, both of which rely on the creation of more diffusing species in the oxide [1]. The first is the creation of extra oxygen vacancies through neutron irradiation damage of the zirconia layer displacing oxygen atoms. These vacancies could then be moved as other vacancies are to accelerate the diffusion of oxidising species. This theory is not supported by TEM observations of either pre-irradiated samples (via neutron) or in-situ irradiated samples, neither of which showed the symptoms of irradiation damage such as dislocation loops.

Another radiation-induced effect increasing the rate of oxidation could be caused by the flux of beta particles generating electron-hole pairs in the oxide, which then act as charge carriers to facilitate corrosion as an anode-cathode reaction. Measurements of conductivity have shown increases under intense electron bombardment, which then rapidly return to normal levels. The fact that this mechanism acts on the previously established rate limiting step (electron transport) also merits consideration.

Hydrogen Pick-Up

The most basic observations to be made about hydrogen pick-up in zirconium alloys are its route of entry through the oxide, the species it travels as and the interaction of the hydrogenic species once in contact with the metal.

Fundamentally, hydrogen will dissolve in the metal, because the hydrogen is more stable (lower potential) when in solution in zirconium, than as a free gas. The behaviour of gas dissolving into a metal without forming a compound of a fixed stoichiometric ratio is termed exothermic occlusion (exothermic in this case as energy is released in the process). The energy difference between the free gas, and the solution state can be thought of as the energy gained by dropping into the potential well of a zirconium atom, and is usually called the heat of solution. The heat of solution decreases as temperature increases, and this effect is responsible for the behaviour of hydrogen flowing down temperature gradients. [51]

The heat of solution also governs the relationship between the partial pressure of hydrogen as a gas, and the amount of hydrogen dissolved in the metal at equilibrium. For a given partial pressure of hydrogen, the more negative (more exothermic), the lower the resulting molar fraction of hydrogen in the metal [51].

Hydrogen atoms dissolved in alpha zirconium will flow down a temperature gradient to the coldest point of the metal, and as the hydrogen has such high diffusivity (at 400°C the diffusion co-efficient is $6 \times 10^{-5} \text{ cm}^2 \text{ sec}^{-1}$ [51]) in the metal at reactor temperatures, this process will happen extremely quickly. Hydrogen will also flow down a concentration gradient in the same way, acting to lessen the effect of a temperature gradient, as the two will effects will counteract each other. The third flux effect hydrogen is subject to is stress. Hydrogen will flow up a stress gradient to the point of highest strain. This behaviour is particularly important when considering delayed hydride cracking [52].

Zirconium Hydrides

Alpha zirconium has two important solubility values for hydrogen: the complete solubility and the terminal solid solubility. The terminal solid solubility is the maximum amount of

hydrogen that can be present (locally) in a metal before hydrogen begins to precipitate out and form hydrides, whereas the complete solubility is the amount of hydrogen required to completely convert the metal into hydride [51]. Since it is mainly the hydrides (as opposed to dissolved hydrogen in solution) [53] that have a deleterious effect on material properties, eliminating or delaying their precipitation is a desirable goal for material design, and so the terminal solid solubility is most commonly investigated.

At any given temperature, hydrogen will actually have two terminal solid solubilities in zirconium, due to hysteretic effects. Once a hydride is precipitated, it will change its volume by 17% per zirconium atom, and this additional stress will then have an effect on the amount of hydrogen that can subsequently be dissolved locally in the metal. The metal must be taken to a lower partial pressure of hydrogen in order to bring it back down to the same concentration of hydrogen in solution once hydrides have precipitated [51].

Zirconium's solubility for hydrogen can be affected by a number of factors, the most important being the phase of the zirconium metal. The beta phase of zirconium alloys shows a much higher solubility and diffusivity for hydrogen than the alpha phase, a property which is exploited in some niobium-containing alloys [54, 55].

The phase of the metal is also affected by the materials dissolved in it. In the alpha phase hydrogen occupies the tetrahedral interstitial positions, while oxygen occupies the octahedral positions [51]. Oxygen dissolved up to a few microns under the surface of the metal will stabilise the alpha phase and also lower the solubility of the metal for hydrogen [56]. At temperatures below 1200K, oxygen will increase the solubility of the beta phase to hydrogen, while the effect is reversed for higher temperatures [57]. When hydrogen is dissolved in the metal, it will stabilise any beta phase present.

Once the terminal solid solubility of hydrogen (for the particular conditions and location) has been reached, the addition of more hydrogen will cause hydrides to precipitate in the metal. This step is of key importance for nuclear fuel rod cladding, as the precipitation of hydrides is what later leads to a variety of problems that degrade performance [51].

Hydrides can be precipitated in three phases, and also transfer between these phases depending on temperature (as hydrogen is dissolved or precipitated from the metal in response to a temperature change). The known phases are: gamma (ZrH), the cubic delta phase (ZrH_{1.66}) and the tetragonal epsilon phase. It can be difficult to accurately measure the proportions of these phases (typically through x ray diffraction), because one phase can change into another due to a change in temperature. For example, it has been shown that delta phase hydrides phase may precipitate, but upon analysis, much more of the gamma phase was seen, as below 180°C the delta phase will transform into the gamma [58]. Since almost all analysis is carried out at room temperature, and a long time after initial hydriding, this is an ever-present obstacle to experiments.

Similarly, the strong temperature dependence of the heat of solution makes it difficult to study the distribution of hydrogen at reactor temperatures (360-400°C), as upon cooling, the solubility of hydrogen will dramatically drop and precipitate out as hydrides that were not present at operating temperatures. Some success has been reported with an immediate beta quench to -40°C, but on subsequent heating to room temperature, the hydrogen will gain sufficient diffusivity to coalesce and precipitate out of solution [58].

Once precipitated, the hydrides reduce both the ductility and the impact toughness of the alloy. The precise precipitation behaviour (i.e. the location and orientation of the hydrides) influence to what extent the properties of the cladding are degraded.

The precipitation behaviour of hydrides is governed by the following equation [51, 58]

$$J = -D(\nabla(C) + \frac{Q^*C}{RT^2}\nabla(T))$$

J = Flux

D = Diffusion constant

C = Concentration

Q* = Heat of Transport

T = Temperature

The flux of hydrogen through the material is governed primarily by the temperature and concentration locally. As the terms involving concentration and temperature oppose each other, temperature differences do not create large concentrations of hydrogen (as the hydrogen will flow down the concentration gradient). Once the concentration of hydrogen exceeds the terminal solid solubility locally (often at a high stress region), hydrogen will precipitate out, lowering the local concentration of hydrogen in the vicinity, therefore aligning the temperature and concentration gradients. As a result, hydrogen will flood to the area and the precipitation of the hydride will proceed rapidly until the hydrogen concentration through a larger part of the metal is sufficiently depleted to stop further precipitation.

The precipitation can be extensive, because as the volume increase during precipitation will stress the surrounding matrix, more diffusion of hydrogen to the region around the hydride occurs, which can then also precipitate [59]. Since the amount of lattice dilation caused by hydrogen interstitials is so small, the dilation of a lattice will have only a negligible effect on solubility, but a significant effect on the driving force for hydrogen flux [58]. This is compounded by the fact that 17% volume expansion is in fact caused by the collection of hydrogen dilations, which would be present while hydrogen is in solution. This can lead to the formation of dislocation loops around the formed hydrides (see Figure 6)

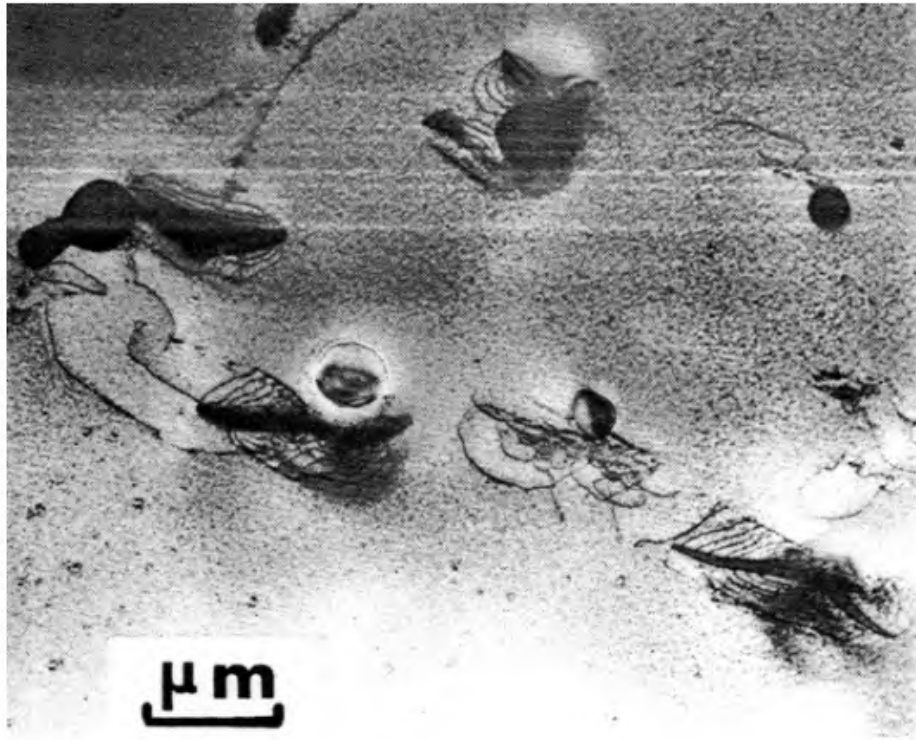


Figure 6 [58], Showing dislocation loops around precipitated hydrides, in this case near SPPs. The scalebar refers to a 1 μm distance.

The time over which the precipitation occurs has an effect on the morphology. Longer times of cooling (for instance) mean that hydrogen will be able to diffuse to precipitating regions, forming fewer, larger hydrides. Also, longer annealing times will show the various habit planes upon which the hydrides prefer to precipitate. As the temperature drops, each subsequent habit plane will be precipitated upon.

In faster anneals, the habit planes are less obvious (the hydrogen will have less time to diffuse into energetically preferred locations), and the hydride will often precipitate at the grain boundaries [12].

The phase of the metal is also important, as the beta phase has a higher solubility and diffusivity for hydrogen. When considering diffusion rate through the metal, one must take account of the volume of the beta phase and its morphology. Filaments of beta, which may be

caused by certain rolling operations in manufacture, can act as highways for hydrogen transport. In the case of long filaments of beta, a combined diffusion co-efficient can be obtained by using a pro rata combination of the two diffusivities based on the cross-sectional areas of the respective phases [58].

The Effect of Hydrides on Oxidation

Fuel rods having undergone long service in reactors will pick up hydrogen over time and form hydrides. The effect of these hydrides on corrosion behaviour must be understood to allow safer operation of reactors with high fuel burnup campaigns.

Pre-hydriding specimens of zirconium alloys allows the study of these effects with standard autoclave techniques [60]. Zircaloy-4, ZIRLO and two model alloys of low Sn ZIRLO were first hydrided via cathodic hydrogen charging and then corrosion tested in 360°C water simulating PWR conditions.

The time to first transition varied between alloys with Zircaloy-4 undergoing transition after 120 days and the low SN ZIRLO alloys going 360 without transitioning. Whilst the alloys displayed different times to first transition, the pre-transition kinetics were similar for each, indicating it is the delay of transition that gives more modern alloys their superior performance.

The presence of a hydride rim created by pre-hydring specimens accelerated corrosion with high Sn alloys experiencing a larger acceleration of their kinetics.

The purely phenomenological observations in this study (only weight gain was measured) do not allow for a mechanistic insight into the exact process that increases

corrosion, but does put forward late accumulation of hydrides as a possible explanation for late stage oxidation acceleration seen in in-service reactors.

Delayed Hydride Cracking

Delayed hydride cracking is a failure mode caused by the precipitation of hydrides in zirconium fuel rods. It most commonly occurs during a temperature decrease (for example, reactor shut down) of the fuel elements after prolonged corrosion [58]. The precipitated hydride phase has much lower fracture toughness and ductility than the alloy, which allows the formation of weak regions that subsequently crack under residual thermal stress [61].

Delayed hydride cracking is possible, only because delayed hydrogen diffuses up a stress gradient, as mentioned earlier. Where the matrix is stressed, hydrogen can sit at a lower potential compared to the undisturbed lattice, and so will migrate to these regions, counteracting temperature and concentration gradients to an extent. Once the terminal solid solubility has been reached at the crack tip, hydrides are precipitated, which provide the weakness for cracking to exploit [58].

Considerable research has gone into prevention techniques [62] and particularly the rate at which delayed hydride cracking proceeds [63-65].

The basic mechanism for delayed hydride cracking is well understood. Upon cooling, the solubility for hydrogen in the metal will drop. As the solubility decreases, hydrogen will look for somewhere to precipitate [66]. The favoured sites for precipitation are determined by where accumulates the greatest concentration of hydrogen (as mentioned, the solubility for hydrogen, and the energetic potential that drives hydrogen to a location are not necessarily related). Hydrogen will concentrate in the coldest parts of the metal, and the parts under high

stress. Notches or scratches on the outside of the cladding fulfil both these criteria, and so are preferred sites for precipitation [67].

Hydrides will precipitate at the tip of the crack (highest stress region). This process will continue, with the hydride becoming longer, following the stress field caused by the crack tip, which will be stressing the material during the cooling phase because of thermal stresses. Once the hydride reaches a critical length, and a sufficient stress intensity factor is attained, the fracture toughness will be exceeded, and the crack will propagate the length of the hydride [62]. Upon the next heating cooling cycle, during the reduction another hydride will form at the tip of this same crack, repeating the process, until eventually, the crack will reach completely through the wall of the cladding. This step-wise cracking process can leave obvious markings - see Figure 7.



Figure 7 [58], showing subsequent steps of DHC, in a complete through-wall crack.

Two of the important factors studied with regards to delayed hydride cracking are crack velocity, and crack initiation.

Crack velocity is determined by several factors. As with all cracks, the stress intensity factor is essential in determining crack growth [68]. As a results of the two phase system involving zirconium and hydrides, the crack velocity shows an interesting dependence on stress intensity factor (see Figure 8).

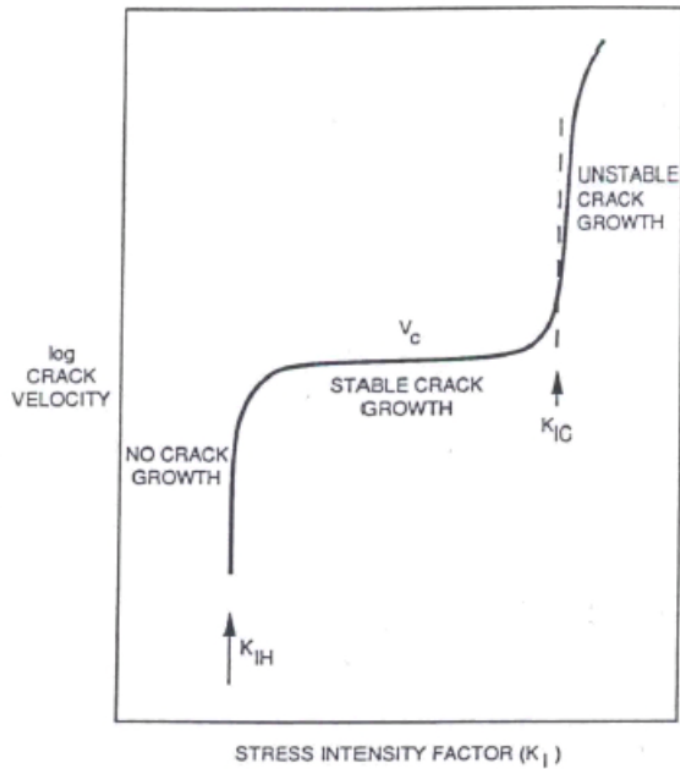


Figure 8 [58], schematic diagram showing the dependence of (log) crack velocity on stress intensity. K_{IH} is the threshold stress intensity factor for delayed hydride cracking, K_{IC} is the fracture toughness.

Figure 8 shows three regimes of crack propagation. At an extremely low stress intensity factor, there is not enough stress to crack even the brittle hydride, and no growth occurs. At extremely high stress intensity factors, there is enough stress to crack the much tougher zirconium matrix, propagating a crack through the entire thickness of the tube. The intermediate region shows stable crack growth. The gradient of this portion is so flat because of the dual phase system. The length of each crack step is limited due to the strength of the hydrides. Cracks can only propagate one step at a time, and steps (of hydride) cannot grow too long before their fracture toughness is exceeded. Once enough crack steps have taken place, the stress intensity factor will increase to the point at which the zirconium can be cracked.

Crack velocity can therefore be studied from the perspective of crack step length. The step length will be increased by higher temperature (more hydrogen will be able to diffuse to the tip of the crack, growing longer hydrides), yield strength of the material [69] (allowing longer hydrides to form before they crack), and concentration of dissolved hydrogen [68] (hydrogen, again, will find it easier to migrate to the crack tip). As well as dependence on the temperature, crack velocity will depend on the direction from which temperature is approached, due to the hysteresis effects of hydrogen solubility [64].

Investigating Oxide Transitions using Isotopically Doped Samples and NanoSIMS Analysis

Work included this chapter has also been published in the Journal of Nuclear Materials 2013 as the paper “An investigation of the oxidation behaviour of zirconium alloys using isotopic tracers and high resolution SIMS”. Some figures have been reproduced here.

Introduction

A continuing difficulty in the study of zirconium oxidation mechanisms is the impossibility of observing corrosion behaviours in an in-service environment. When samples are held at 350°C in a 10MPa steam or water atmosphere any measurements beyond local temperature and pressure become extremely difficult. Measurements of weight gain (i.e. a total measure of how much oxidation has occurred) can be made in-situ, though this can also be measured after autoclave tests with no loss of accuracy. More recently, experiments have been performed in which the electrical properties (resistance, charge held and capacitance) of the oxide film are measured under in-service conditions[70], providing important macro scale data about the effects of oxidation. Unfortunately, microscopic or microstructural investigations are more or less rendered impossible due to either sample preparation constraints or direct action of the corrosion media precluding the use of any sort of microscope.

The most promising way around this problem is the use of markers or tracers introduced during oxidation in an autoclave process closely simulating reactor conditions. These markers are introduced to the specimen in a state as close as possible to in-service conditions and so

can provide a more reliable insight into the exact mechanisms in operation. The nature of the chemical reactions is left undisturbed by use of an isotopic tracer as this behaves chemically identically[71] to the natural species. Examination of isotopic decoration in samples can then be accomplished by the use of instruments that measure mass to charge ratio to separate isotopes, rather than instruments relying on the detection of characteristic X-rays (EDX) or characteristic electronic signatures (EELS). SIMS (Secondary Ion Mass Spectroscopy) is able to detect the difference between isotopes of the same chemical species due to the difference in mass to charge ratio exhibited by different isotopes and has already been used extensively in many fields to measure similar dynamic processes[72]. Experiments can thus be designed to use isotopic markers and later examination with SIMS instruments to closely analyse the dynamics of oxidation occurring when the markers were introduced.

Sample Preparation

Sample preparation of isotopically doped specimens is similar to the standard autoclave procedure for generating oxidised zirconium alloy samples with the additional subsequent step of adding an isotopic marker while under corroding conditions. The samples under study in this chapter were supplied as bare metal coupons in either a stress relieved or recrystallised condition from the Westinghouse Electricity Company. The samples were produced as part of the MUZIC 1 project. Two alloys were supplied, Zircaloy 4, a common alloy used in Western PWRs since the 80s, and ZIRLO, a more modern alloy that has been used in Western reactors. These samples were marked with identification codes and then placed in an autoclave with an aqueous environment at 360°C and 18MPa, similar to the conditions found in many PWRs. To more closely simulate the water chemistry, 1000ppm boron and 2ppm

lithium hydroxide (both by weight) were added to the water. These chemicals are added to commercial reactors to control neutron economy or galvanic effects, and were added in this experiment to ensure as accurate a reproduction of service conditions as possible. Corrosion was allowed to proceed for a total of 160 days, with samples exchanged according to a schedule to produce specimens having undergone 34, 80, 114, and 160 days of corrosion. This was intended to produce samples with oxides of varying thickness and of varying corrosion regimes; the 34 day sample being pre-transition, the 160 post first transition and the 80 and 114 day samples near the transition point. This strategy allowed the study of the corrosion kinetics in the most commonly theorised stages of oxidation. The samples produced are summarised in .

Table 4.

Table 4: Oxidised samples used in this experiment, which varied by alloy composition, heat treatment and oxidation period.

Sample identification	Alloy	Condition	Oxidation time (days)
SZLRX17	Low tin ZIRLO	Recrystallised	34 + 20
SZLSR17	Low tin ZIRLO	Stress relieved	80 + 20
SZLRX1	Low tin ZIRLO	Recrystallised	114 + 20
SZLSR1	Low tin ZIRLO	Stress relieved	160 + 20
Z4RX17	Zircaloy-4	Recrystallised	34 + 20
Z4RX1	Zircaloy-4	Recrystallised	114 + 20

After production of the initial oxides, the samples were transferred to a second autoclave at the University of Manchester with identical conditions of pressure, temperature and water

chemistry, but with added isotopic doping. Water containing 10% ^{18}O (oxygen-18) was mixed half and half with water containing 10% ^2D (deuterium), producing a final enrichment profile of 5% ^{18}O and 5% ^2D . These concentrations are sufficiently high compared to the natural abundances (0.2% for ^{18}O and 0.028% for ^2D [73]) of each of these elements (i.e. the ratio that will be present in the initially formed oxide) that the oxide formed in the two autoclaves can be differentiated in the NanoSIMS. The purpose of adding ^{18}O to the second autoclave is so the oxygen incorporated into new oxide formed during the second exposure can be differentiated from the oxide formed previously, thus revealing the sites of active oxygen incorporation, or where the oxide is growing. The isotopic “marking” of pre, post and at transition samples in this way allows the comparison of oxidation behaviour between different corrosion stages. ^2D serves the same function, acting as a marker for the sites of active hydrogen uptake during the second exposure.

This sort of comparison would be near impossible to do while oxidation is actually occurring except in the bluntest and broadest senses, for example measuring weight gain or potential difference over the interface whilst the sample remains in the autoclave. The oxygen atoms in the oxide do not rapidly diffuse and so the markers left in the second exposure allows the subsequent interrogation of samples using much more sensitive instruments, crucially ones with sufficient spatial resolution to study local oxidation behaviour.

Using a second exposure of the same duration for all specimens has an additional advantage; the rate of oxidation can be calculated over the 20 day period by measuring the thickness and enrichment of the new (^{18}O doped) oxide and calculating the mass of oxygen added.

Comparing the rate of corrosion over a fairly short time period locally (within areas of approximately one square micron) for samples at different stages of corrosion is not possible by other methods.

The addition of deuterium to the second autoclave facilitates two different modes of investigation. Firstly, by adding deuterium only during the second exposure, the amount of hydrogen absorbed during the second exposure can be calculated by measuring the deuterium enrichment of a hydride. Hydrides formed during cooling will contain both the deuterium and normal hydrogen which are both in solution at oxidation temperatures.

Secondly, the constraints of the NanoSIMS instrument mean that some combinations of elements or ions cannot be analysed simultaneously due to the physical size of the moveable detectors. In order to measure ions of 16 and 18 atomic mass units (by comparing the distribution of the initial and subsequent oxide) the space required between the detectors necessitates a setting on the ranging magnet that would not move hydrogen ions of mass 1amu into a detectable region of the detector array. Deuterium having double the mass means a stronger field can be used and still have the deuterium enter the first detector of the instrument, whilst still giving enough separation between the 16 and 18 mass detectors set to measure at mass 16 and 18amu. This arrangement can be seen in Figure 9.

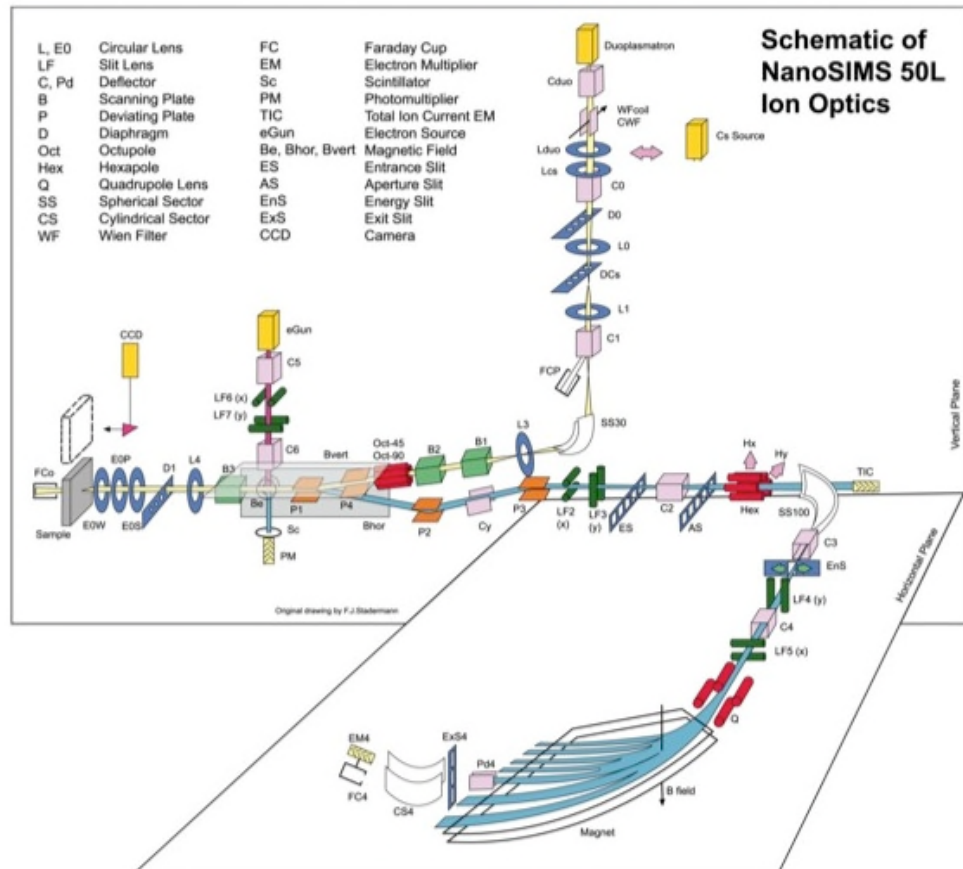


Figure 9 Schematic of the NanoSIMS optics. The diverging paths of elements with dissimilar mass to charge ratios caused by a magnetic field can be seen at the bottom of the image (image reproduced from CAMECA)

Taking measurements that contain the abundances of ^{16}O and ^{18}O at the same time as the hydrides removes the need for multiple images of the same areas to form a complete picture of the distribution of the elements of interest. Using a sample undoped in deuterium would necessitate taking images using just the 16 and 18 atomic mass peaks then recalibrating the magnet and taking an image using the 1 mass peak to pick up hydrogen. Using a deuterium doped sample removes the need for recalibration, taking multiple images and the associated problems of different volumes of material being analysed because SIMS is a destructive technique.

Unfortunately, it was not possible to take any images which simultaneously ranged the 1 and 2 mass peaks, so any discussions of hydride location are predicated on the assumption that hydrogen and deuterium behave similarly in terms of hydride precipitation on cooling. This assumption can be thought of as reasonable when considering the high mobility of hydrogen at elevated temperatures in zirconium, the difference between the solubility of hydrogen at operating and analysis temperatures[74] and the small difference in reaction rates of hydrogen and deuterium caused by the isotopic weight difference.

In order to map locations of hydrides and different oxide regions, the samples had to be presented to the NanoSIMS in cross section. The following procedure was used to make and polish cross sectioned samples that showed the metal/oxide interface.

Sample coupons were first cut to dimensions small enough to fit NanoSIMS holders (3mm by 8mm) and then a stack of samples was assembled consisting of one of each oxidation period and alloy composition. Each cut down coupon was coated in hard setting vacuum-compatible epoxy resin and stacked oxide to oxide to create a block consisting of 6 samples before being left to cure for 48 hours at room temperature. A PTFE coated clamp was used to ensure good sample adhesion and keep the samples close together.

Once fully cured, the small sample block was placed in a cylindrical mould and more epoxy resin was added to form a suitably sized and shaped sample to be easily held by the NanoSIMS sample holder, which displayed all 6 samples.

The completed cylindrical block was then mounted to a polishing plate and ground using silicon carbide papers down to 4000 grit. The close packing of the relatively hard samples in the relatively soft resin block helped to avoid issues of edge rounding, which is important as NanoSIMS analysis requires flat specimens to avoid imaging artefacts.

Once grinding was complete, the sample block was polished using colloidal silica (particle size 50nm) to form the smoothest possible surface with minimum deformation. It was found using diamond pastes after grinding caused scratching and disintegration of the oxide sections, so colloidal silica was used as the next step after 4000 grit. The 4000 grit scratches left after grinding took approximately 8 hours of polishing to remove. This produced a smooth, flat surface ideal for NanoSIMS analysis.

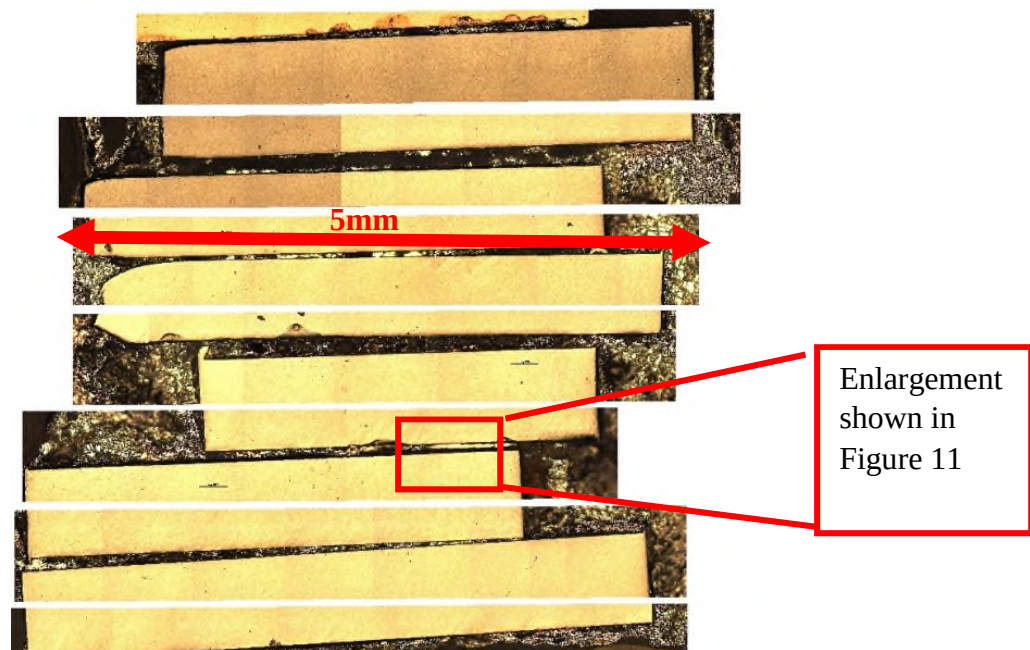


Figure 10 A composite optical micrograph showing the six alloy specimens mounted in resin. This map was used as a reference when imaging samples as the NanoSIMS has an extremely limited field of view. The constituent micrographs are sufficiently high resolution to determine locations of hydrides and identify oxide features for closer examination. At this scale the oxide is not visible but is present on the exterior surfaces on all sample coupon cross sections.

Zirconium alloys are known to form a native oxide immediately on exposure of a freshly polished surface to air; this oxide was undesirable for NanoSIMS analysis and so samples were polished and then coated in 1 nm of platinum immediately prior to insertion into the NanoSIMS. The platinum coating not only helps to avoid oxidation of the specimen surface, but also acts as an essential grounding path for current to flow away from the samples as the resin used conducts very poorly. 1nm of platinum is thick enough to provide an adequate

charge pathway, but thin enough to be easily removed in the instrument to facilitate image capture.

All the samples were mapped by optical microscopy prior to NanoSIMS analysis in order to identify areas of interest, as shown in Figure 10. In these images, hydrides are clearly visible on the polished cross section. The hydrides in optical images correlate well with NanoSIMS 2D scans of the same areas, which is another indicator that pure ^1H hydrides are not present.

The maps produced previously were used to identify regions of interest and navigate the sample as the NanoSIMS internal optical microscope has a limited field of view.

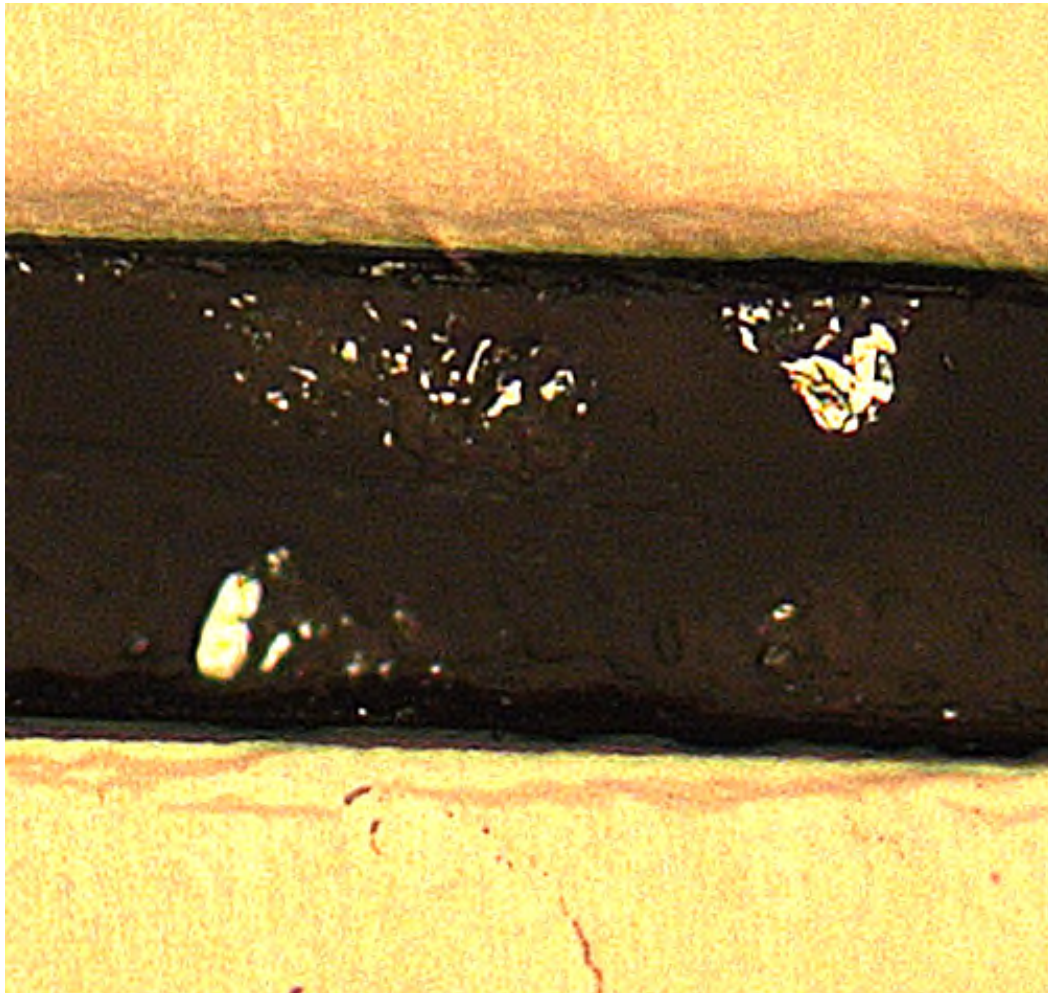


Figure 11 An enlarged micrograph showing the oxide scale on the exterior of the sample coupons. Also visible are hydrides that have precipitated below, near the metal surface and

are viewed in cross section. The oxide on the lower coupon is visible as a thin grey region; the region on the left is well preserved although the region on the right suffered damage during polishing. Micrographs aided the selection of suitable regions for NanoSIMS analysis.

NanoSIMS Instrumentation

All SIMS images in this chapter were taken on a Cameca NanoSIMS 50. The NanoSIMS is a dynamic SIMS instrument with sub 100nm lateral resolution and is able to detect chemical and isotopic species in the parts per million range. These capabilities allow for an entirely new insight into corrosion mechanisms when partnered with isotopic doping sample preparation.

Fundamentally, the NanoSIMS is capable of the analysis of isotopically doped specimens because it relies on the difference in mass to charge ratio of secondary ions to discriminate chemical and isotopic species. This makes the NanoSIMS uniquely suitable for this task where other chemical imaging technologies (such as those relying on the detection of characteristic x-rays) which measure solely the electronic structure of the sample atoms are unable to differentiate between isotopes of the same chemical species.

The NanoSIMS, compared to most other commercial SIMS instruments, has very good lateral resolution. In the context of this experiment the high lateral resolution allows for extremely local characterisation of corrosion behaviour. The resolution is sufficiently high that local corrosion behaviour can be correlated with features present in the oxide scale (such as cracks) or in the underlying metal substrate features (grain boundaries, secondary phase particles etc). The resolution, however, is not sufficient to directly measure porosity in the oxide scale, for which nanometer scale resolution is necessary.

The ion source used for this run of experiments was a 16kV caesium source. Caesium is used as an ion source due to the high yield of secondary ions liberated from the sample surface. Due to the co-axial secondary ion extraction arrangement of the NanoSIMS optics, the source ions must be positive and the secondary ions negative in order to direct the primary ions to the sample surface and the secondary ions to the detector respectively. The advantage of the co-axial ion optics is that they can be placed extremely close to the sample surface, thus providing a fine focussed primary beam high lateral resolution due to the small working distance. This also allows the primary ion beam to be directed normal to the sample surface, reducing the interaction volume. The primary Cs^+ ions are accelerated into a beam which is then scanned across the specimen in a raster pattern similar to conventional FIB or SEM imaging. Secondary ions removed from the sample surface are extracted through the same optics.

Another capability boasted by the NanoSIMS is extremely high mass resolution, which allows the reliable discrimination not only of ^{16}O and ^{18}O , but also between ^{18}O , and ^{16}O with two attached hydrogen atoms (which differ slightly in weight due to the nuclear binding energy) or other species of approximately the same mass to charge ratio. The extremely high mass resolution allows much more confidence in species identification and therefore vastly lowers the signal to noise ratio. The low signal to noise ratio aids in the accurate determination of enrichment percentages of different regions in the sample by comparing the number of collected ^{16}O and ^{18}O ions.

In order to determine the mass to charge ratio, the NanoSIMS uses a Mauttach-Herzog mass analyser which offers the highest possible mass resolution ($M/\Delta M > 10^4$). The specific arrangement employed uses a magnet to separate different ions based on their mass to charge ratio. Beams of ions are directed onto movable carriages equipped with electron multipliers to measure the signal of a specific ion from a specific pixel. The magnetic field can be altered to

range different mass ions, although due to the physical size of the carriages there are limitations on the combinations of mass to charge ratios that can be measured simultaneously. Specifically, this restricts the measurement of ions with similar mass to charge ratios while also measuring a much higher mass ion. This restricted the current experiment from being able to measure ions of atomic mass 1, 2 and 18 simultaneously as sufficiently spacing the trolleys to measure both mass 1 and 2 ions would require a magnetic field so weak that it could not direct a mass 18 ion into the measuring region of the detector.

Data Collection

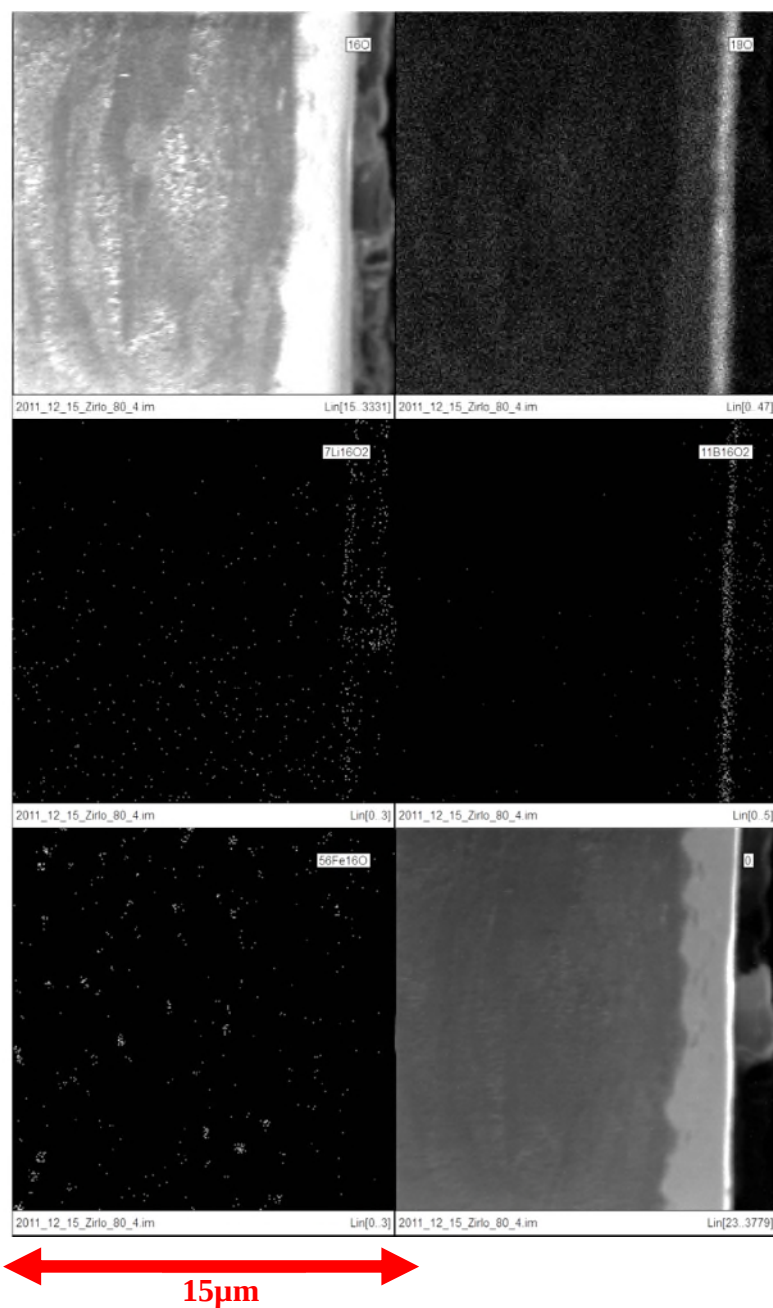


Figure 12 NanoSIMS output image showing (clockwise from top left) ^{16}O signal, ^{18}O signal, $^{11}\text{B}^{16}\text{O}_2$ signal, secondary electron signal, $^{56}\text{Fe}^{16}\text{O}$ signal and $^{7}\text{Li}^{16}\text{O}_2$ signal. These are the base images from which composite images can be formed and analysis performed upon.

The NanoSIMS detects five ions (one channel for each detector carriage) and so can generate five images of up to 256 x 256 pixels up to 50µm square, with each channel representing the number of collected secondary ions of a particular mass to charge ratio. These five channels can be displayed on one image to show the localization and distribution of particular elements in the sample. A secondary electron image is also captured at the same time. A typical set of images is shown in Figure 12.

To maximise the lateral resolution of the instrument, the smallest possible aperture was inserted ($d_1=4.5\mu\text{m}$) resulting in a primary beam current of 30-40 pA.

To obtain reliable data about the ions under investigation, the mass analyser must first be calibrated on samples of known elemental composition and the moveable trolleys adjusted accordingly. In this case, the 160 day sample was used as a calibration specimen as it had a high concentrations of ^2D , ^{16}O and ^{18}O . The boron signal was calibrated on a doped silicon wafer.

Prior to each scan, the 1nm platinum coating had to be removed; this was accomplished with a defocused Cs^+ beam scanning the area of interest for approximately 20 minutes immediately before each scan was acquired. Maintaining the protective layer until this point was necessary due to the extreme speed with which bare zirconium surfaces oxidise even inside the high vacuum (1×10^{-10} atmospheres in the sample analysis chamber). With the previously described beam conditions, each scan took approximately 10 minutes to complete.

The 20 minute cleaning exposure left a clean sample surface for analysis and also implanted the surface with the necessary quantity of caesium ions which aids in the extraction of secondary ions of other species when imaging occurs[75]. This effect is due to the implantation of caesium ions changing the work function of atoms at the surface. Due to the

inherently low erosion rate of 16kV caesium ions at these low beam currents, there was minimal milling of the sample during this period, although some small surface topography was introduced which was evident later under SEM analysis.

Data Analysis

Raw data is collected as 5 different 256 x 256 pixel images with each image representing a different channel and hence different selected ions. Simply inspecting these separate images can reveal information about the distribution of elements in the sample.

Data processing was carried out using ImageJ, a free Java based program with a wide range of capabilities[76]. By use of a plugin (OpenMIMS) the raw data could be directly imported and analysed. Once the five channel maps were imported, the images could be manipulated and combined using features of ImageJ and OpenMIMS in order to display the data in more intuitive ways and perform subsequent analysis to extract quantitative data from images.

To obtain information about the relative enrichment of ^{18}O over the imaged area of the sample, ratio images were used. Since the main area of interest was the uptake of ^{18}O from the second oxidation exposure, it was crucial to know the ratio of ^{16}O to ^{18}O to see which areas of oxide had grown during the second exposure. In order to do this the two images representing ^{16}O and ^{18}O are combined in such a way that the intensity (pixel value or count rate) of the ^{18}O image is divided by the intensity of the ^{16}O image on a per pixel basis, and then normalized to show the fullest greyscale possible. The resulting image (Figure 13) shows bright white areas where ^{18}O is enriched, i.e. the oxide formed during the second exposure. This is superior to simply looking at the ^{18}O image as it will take into account variations in the signal intensity caused by real variations in the local concentrations of the different oxygen isotopes but also remove spurious contrast from depleted or enriched

regions around precipitates or step edge contrast. As both oxygen signals will be similarly affected by edge contrast or other phenomena that create artefacts in SIMS analysis, it reduces the chance of misinterpreting a normal part of the image as an ^{18}O enriched feature. Using the ratio instead of merely the counts per pixel of the ^{18}O signal is also a better measure of oxide enrichment and allows comparison of enrichment between data sets.

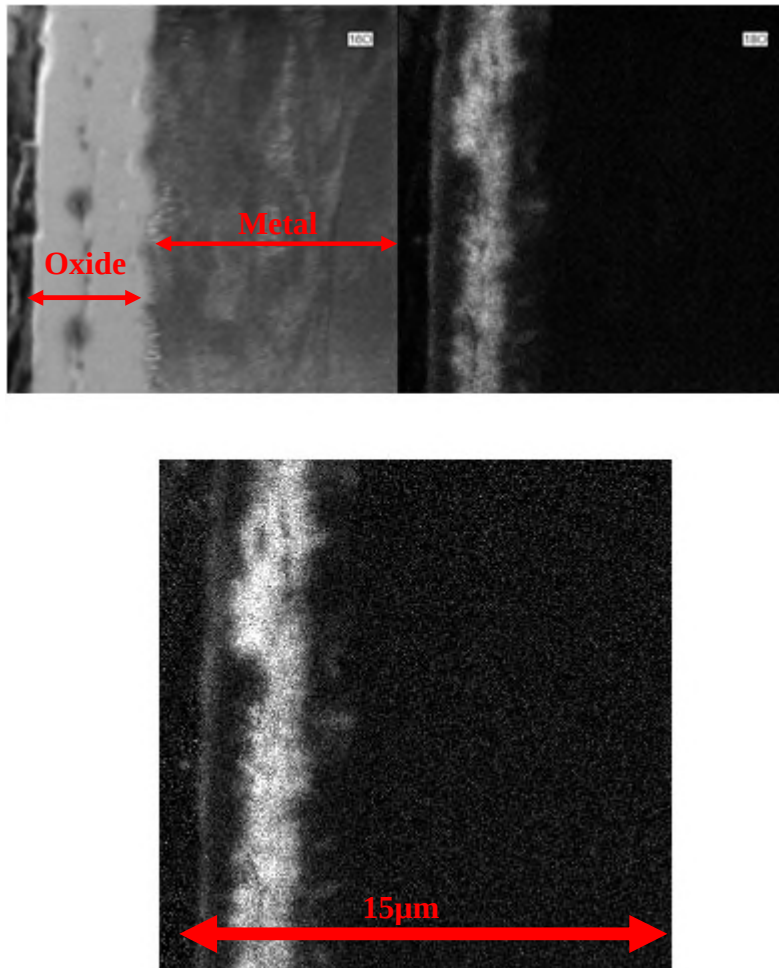


Figure 13 The ^{16}O signal (left) and the ^{18}O signal (right) are combined by dividing the ^{18}O signal by the ^{16}O signal on a per pixel basis to form the ratio image (bottom). The ratio image removes certain charging artefacts seen around the crack in the middle of the oxide and also provides a more reliable figure for enrichment percentage.

In order to study the distribution of multiple elements over the sample surface, without necessarily taking into account relative enrichments, colour merge images were used. Colour merged images simply superimpose each image onto a single picture as a different colour for each element. This allows the study of the distribution of multiple elements (for example ^2D , ^{16}O , ^{18}O and boron simultaneously), so the correlation between elements can be examined. While this is useful for showing for example the relationship between hydrides and intermetallic particles in the matrix and oxide, it does not allow ready interpretation of relative concentrations.

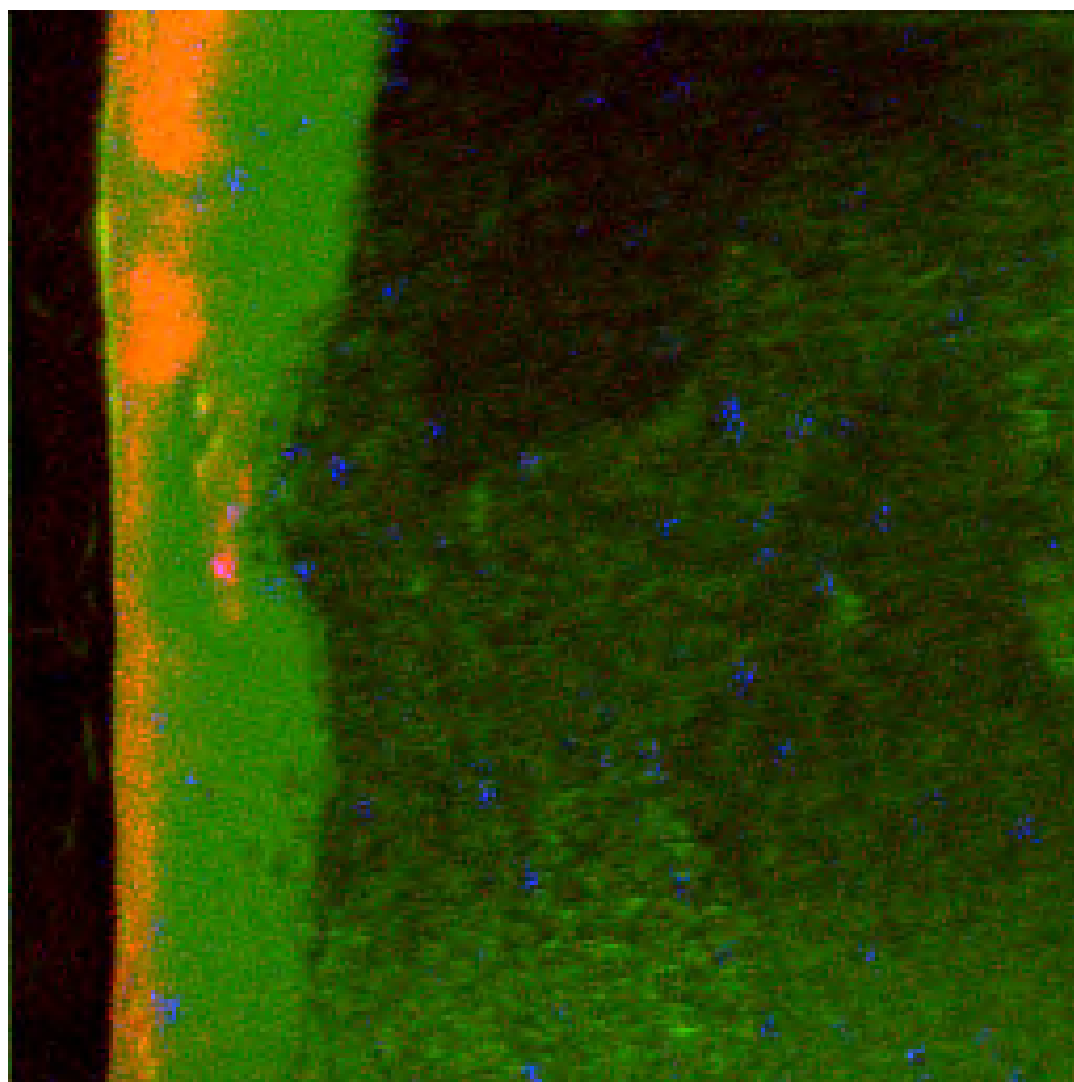


Figure 14 A colour merge image of a 114 day ZIRLO sample, showing ^{16}O in green, ^{18}O in yellow and FeO in blue. This colour merge image allows the study of multiple element traces

simultaneously. Here the enrichment of ^{18}O in the oxide does not appear to correlate with the distribution of iron rich precipitates, although they are still visible in the oxide.

A third way of displaying multi element information is as HSI (Hue Saturation Intensity) images. These images show the ratio of two species (for instance ^{16}O and ^{18}O) as a colour scale and the concentration of the species as the saturation of colour. This type of image shows similar data to ratio images but will also show areas that are depleted or enriched in the two elements studied. For example Figure 15 is an HSI image showing the ratio and concentration of ^{16}O and ^{18}O , a small area of the oxide with lower saturation would indicate an area with lower oxygen counts such as might be expected from a partially-oxidised intermetallic particle.

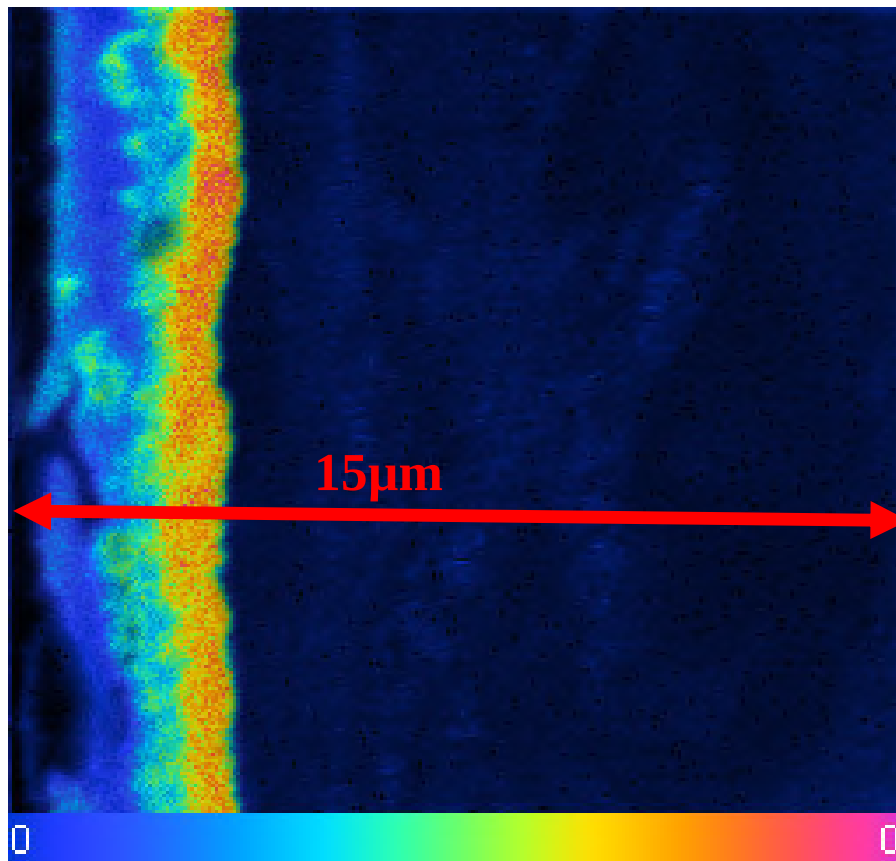


Figure 15 HSI image of an 80 day ZIRLO sample. The red regions of the image show areas with a high ratio of ^{18}O to ^{16}O . In this particular image the ^{18}O is located at the metal/oxide interface.

Additional data can be extracted from these images, either raw or processed into HSI or ratio images. As each pixel of the image contains the count of collected ions for each of the five channels it is simple to create line profiles or to count the total collected signal over an area.

Results

Over 100 images were recorded over approximately 10 days of machine time covering all the samples shown in Figure 10. In order to quantitatively analyse the data and explore

correlations between sample oxidation phenomenon, images were grouped by sample and the metrics of the images were measured to generate statistical data about oxidation behaviour.

^{16}O and ^{18}O Analysis

The oxidation and doping treatments described above were designed to produce an oxide enriched in ^{18}O only at the sites of active oxygen incorporation during the final 20 days of exposure. By introducing samples of different corrosion histories into the final 20 day exposure, the difference in oxygen incorporation behaviour at different oxidation stages can be revealed. By using the same exposure time for the doped corrosion period, it also allows data to be collected on the instantaneous rate of oxidation during the last 20 days separately from the oxidation rate over the entire sample exposure as would normally be the case when using a raw weight gain figure.

In order to study the difference between corrosion regimes, the two main factors under consideration are the thickness of the oxide and the location of the ^{18}O within the oxide. Measuring the thickness of the oxide and the location of the ^{18}O peak were both determined by drawing line profiles perpendicular to the metal/oxide interface for the ^{16}O and ^{18}O images as shown in Figure 16. The oxide shows in a line profile as a large, flat topped region in the ^{16}O signal and oxide thickness was measured by taking the full width half maximum of this feature. The position of the ^{18}O peak is simply read off using the highest ^{18}O count and the distance to the start of the oxide (i.e. the metal/oxide interface) measured to the start point of FWHM chosen earlier. By using this approach, subjective estimation of thickness and peak location is eliminated.

Line profiles generated in imageJ used line widths of 3 μm in order to reduce the noise observed in a single pixel line by improving the counting statistics. The small undulations

present in the metal/oxide interface that are covered by this line will cause a slight reduction in resolution of the interface location, but the oxide FWHM and ^{18}O peak position should not be significantly altered. On samples that presented localised behaviour corresponding to different stages of corrosion a separate line profile was drawn for each area.

Measurements of all images were taken and compared, and the data seemed to cluster into three distinct behaviours correlating to pre-transition, immediately post-transition and long term post-transition. Typical examples of these three behaviours are shown in Figure 16.

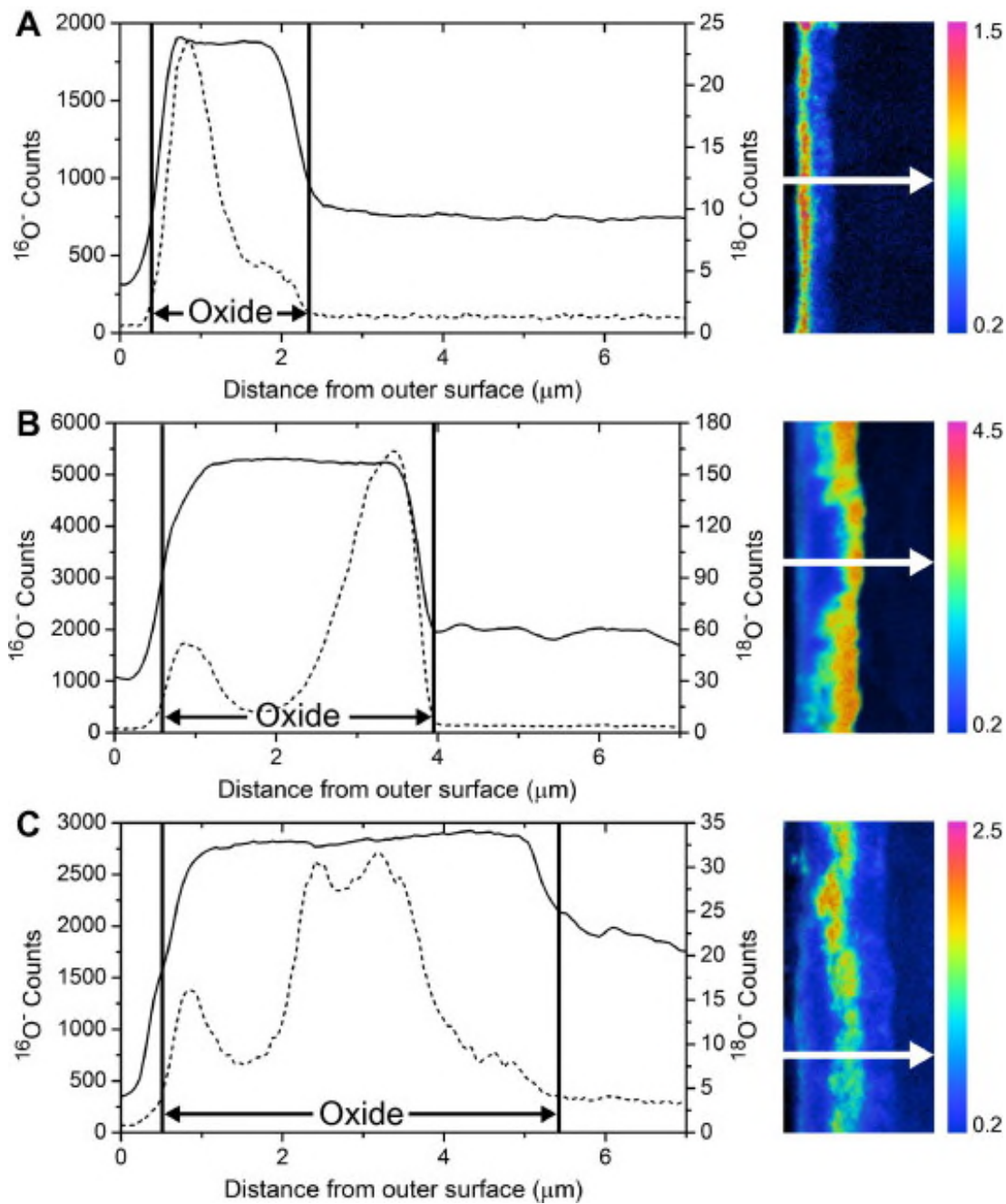


Figure 16 HSI images and accompanying line profiles showing the position of the ^{18}O peak in oxides on different samples. (A) shows a thin (2 μm) pre-transition oxide on a 34 day sample, showing the ^{18}O peak near the exterior surface of the oxide. (B) Shows a thicker (3 μm) oxide on an 80 day sample where the ^{18}O peak is at the metal/oxide interface. (C) shows the thick oxide of a 160 day sample where the ^{18}O peak is in the middle of the oxide scale. Comparing (B) and (C) shows the position of the ^{18}O peak is at a similar position relative to the exterior oxide surface for both of these cases.

Behaviours were for the most part easy to categorise into three regimes based on the location of the ^{18}O peak. Pre-transition oxides showed a thin band of ^{18}O enrichment on the external surface of the oxide. Samples immediately post-transition showed a thicker band of ^{18}O enhancement at the metal/oxide interface. Samples from long oxidation exposures that were long past the initial transition showed a wider band of ^{18}O enriched oxide at or near the middle of the oxide scale.

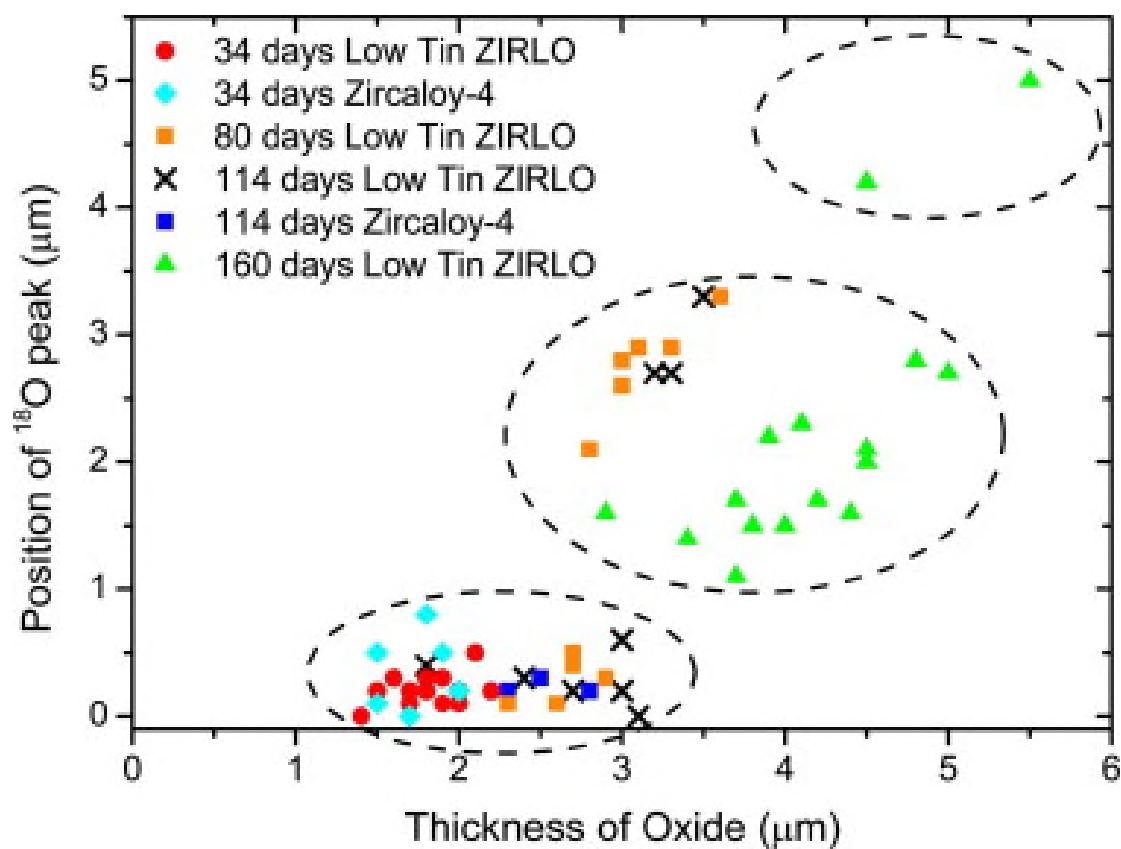


Figure 17 This graph shows the clustering behaviour of samples according to their transition states when the thickness is plotted against distance of the ^{18}O peak from the exterior oxide. Thick oxides exhibit ^{18}O further from the exterior of the oxide, and some distinct clustering can be seen. Some of the samples show measurements in more than one group.

Figure 17 shows the clustering of these measurements for the full set of six samples, which clearly show the differing behaviour of samples based on their transition stage. The pre-transition samples show an enriched band of oxide on the exterior of the oxide and fairly thin oxides. Samples that have undergone one transition show the band of ^{18}O enrichment below the first layer of oxide which has now undergone transition and become porous. In the case of the 80 and 114 day samples this transition occurred very close to the time of ^{18}O introduction, and so the band of enriched oxide formed right at the metal/oxide interface during the period of rapid oxidation that occurs at transition, whilst for the 160 day samples present in the middle group a layer of presumably protective oxide had formed under the porous first scale and thus the ^{18}O was found on the exterior of this new layer in the middle of the oxide. Some samples had undergone two transitions during the corrosion period and show the thick oxide one would expect and the ^{18}O peak once again near the metal/oxide interface.

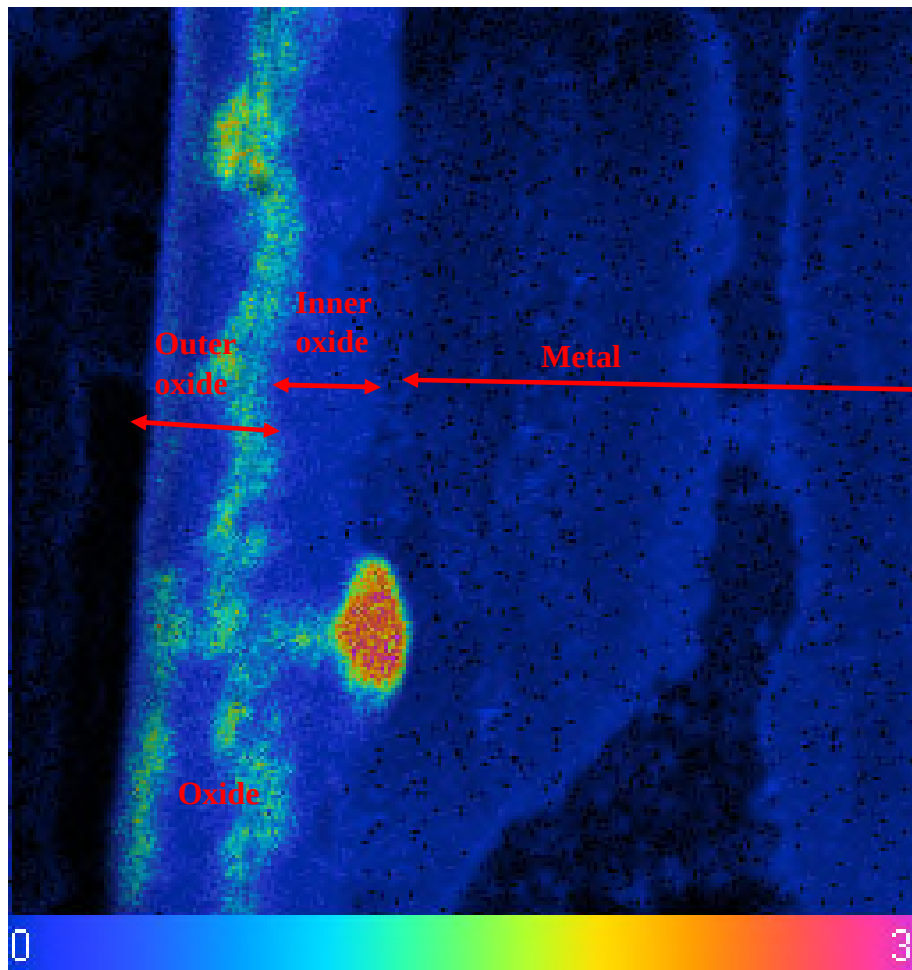


Figure 18 An HIS image showing a 160 day ZIRLO sample where a second transition has occurred. The band of enriched oxide in the middle of the oxide scale shows that the oxide exterior to this band has transitioned, whilst the oxide under it is still protective. The large enriched feature at the metal/oxide interface shows that the second, inner layer of oxide has also transitioned at this location and is no longer protective. Red arrows show the metal and oxide, the oxide can be further divided into the inner and outer layers.

Closer examination of the data in Figure 17 can yield more information about the variance in oxidation behaviour between samples which had undergone similar exposures to corrosion conditions. All sets of samples showed a range of oxide thicknesses created during the experiment, from the 34 day samples (1.8 μm average with 0.2 μm standard deviation) to the 160 day samples (4.2 μm average with a 0.8 μm standard deviation). As expected, the

samples which had undergone longer corrosion periods had a higher standard deviation as differing conditions and the resulting effects on corrosion rate will have had time to accumulate for these samples.

It can also be seen that there is some overlap between different transition groups. For example, the thickest pre-transition sample has an oxide thickness of 3.1 μm whilst the thinnest post-transition oxide has a thickness of 2.8 μm . In this case a post-transition sample can be identified by the appearance of the ^{18}O peak below the outer layer of oxide, rather than on the exterior. It should also be remembered that the 2.8 μm oxide will include some of the post-transition oxide, so the critical transition thickness would have been even less than this value. This variability in transition thickness is not well explained although it may be caused by different metal grain orientations or SPP concentrations supporting a pre-transition, protective oxide for longer before transition[77]. The overall difference in thickness attained during the corrosion period is likely due to a combination of local sample effects such as metal matrix orientation and also changes in local conditions. The fact that more measurements on the 80 day sample show transition than 114 day samples suggests that there was some significant variation on the corroding environment between samples.

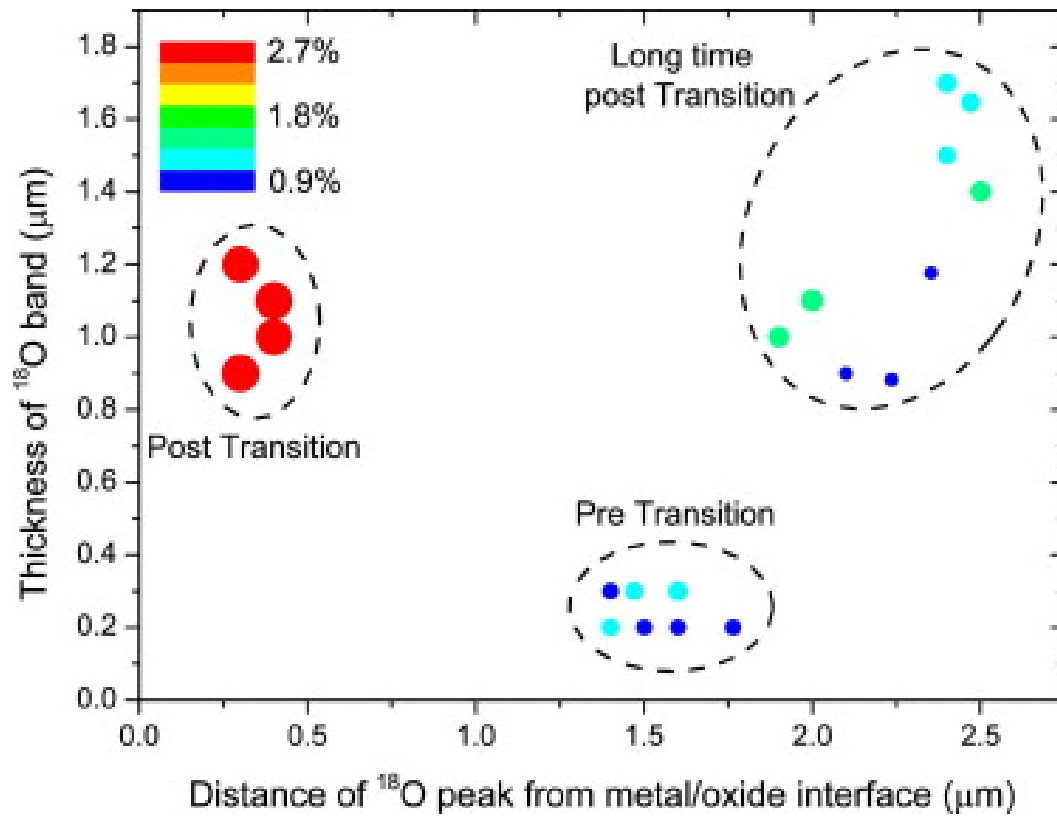


Figure 19: Thickness of the ^{18}O band plotted against the distance of this band from the metal/oxide interface. The size and colour of the points represent the enrichment percentage of the ^{18}O band, with red larger points signifying a high enrichment of ^{18}O .

The different behaviour of pre and post-transition samples can also be seen by examining the thickness of the ^{18}O band formed and the isotopic enrichment percentage, as shown in Figure 19. This measurement is essentially a measure of the amount of ^{18}O incorporated and so total amount of oxidation occurring during the 20 day period of doped oxidation, with all specimens undergoing the same period of doped oxidation. As is immediately obvious, samples that present a band of ^{18}O near the metal/oxide interface produce fairly thick bands of ^{18}O with a very high enrichment percentage ($>2\%$, ten times the natural isotopic abundance of ^{18}O of 0.2%). Pre-transition samples produce a thinner band of oxide with low enrichment near the surface of the sample. The isotope decorated bands present in the 160

day samples which were well past their first transition showed a thick band but with a low enrichment percentage.

The differing thickness and enrichment of bands fits well with established ideas of mechanisms of zirconium oxidation [78, 79] and thus make the identification of the factors controlling the sample kinetics more certain. Pre-transition samples are oxidising slowly and so during the 20 days of final oxidation produce a thin band of oxide with low enrichment (this translates to only incorporating a small amount of ^{18}O from the spiked water). The faster oxidation found in post-transition samples produces a thick band of oxide with high enrichment due to the large amount of ^{18}O incorporated during this period.

The 160 day samples show a thick ^{18}O band, similarly to post-transition samples, but a low enrichment, similarly to pre-transition samples. This is likely caused by the porosity present in the middle of the oxide (i.e. the dividing line between pre-transition barrier oxide and the post-transition porous oxide on the exterior). This highly porous region is incorporating ^{18}O both as an oxidant to grow the barrier layer of oxide, but also passively as an isotope exchange with the porous oxide layer. This passive exchange explains the large band of ^{18}O enrichment as it does not require an inflow of oxygen ions towards the metal - just the presentation of a large surface to the doped oxidising media. 160 day samples also exhibited a thin band of enrichment on the very exterior portion of their oxides in the small equiaxed grain region which is not actively growing, again pointing to passive exchange of ^{18}O and ^{16}O in regions of high porosity driven by the large surface area exposed to the corroding medium.

When rapid oxidation is occurring, the oxide formed will likely be similar in isotopic ratio to the water from which the oxide is being formed, whereas slow oxidation as found in pre-transition samples allows time for the newly incorporated ^{18}O to diffuse into the oxide and form a band of lower enrichment but greater extent. This will be discussed more below.

Some samples exhibited oxides of intermediate thickness (approximately 2 μm) with a band of oxide enrichment both on the exterior and at the metal/oxide interface (Figure 20). These samples underwent transition *during* the second exposure, and so initially showed pre-transition behaviour with the ^{18}O at the outside of the oxide, followed by post-transition behaviour with ^{18}O at the metal/oxide interface. The fact that both these behaviours were captured and remained visible in the final samples is a good indicator of the reliability of this technique as it shows that ^{18}O localisation is preserved through at least the final 20 days of oxidation.

This exterior band of oxide should not be confused with the thin band of enrichment seen on the outside of some of the 160 day samples, which is most likely caused by the natural exchange of oxygen ions between water and oxide. This effect is exacerbated by the high surface area, small grain size and proximity to water of the outer oxide which allowed it to pick up ^{18}O atoms during the second exposure despite not being actively oxidising. This determination can be emphasized by comparing the enrichment and total counts of the exterior bands. ^{18}O found on the exterior of 160 day sample scales can be assumed to be wholly due to passive exchange, as we know the exterior oxide scale is no longer actively growing in this region. This effect can be seen in Figure 18, where a thin band of enriched oxide is visible at the very exterior of the scale, despite a certainty that this scale is no longer oxidising.

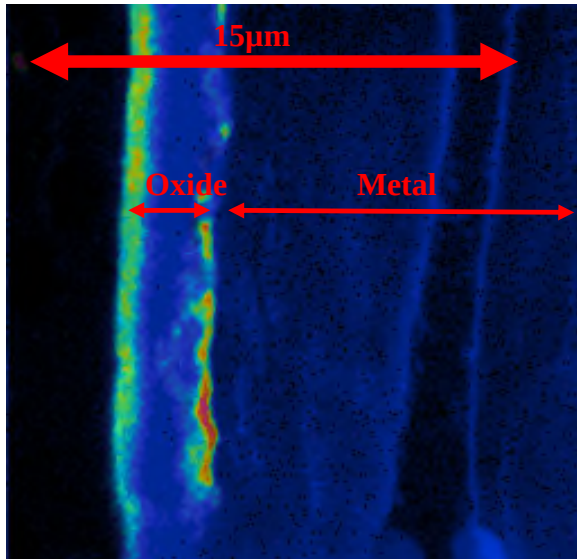


Figure 20 A HSI image from an 80 day ZIRLO sample showing initial ^{18}O incorporation on the exterior of the oxide and subsequent penetration of the ^{18}O to the metal/oxide interface at some locations. Note the higher enrichment of the post-transition ^{18}O incorporation at the metal/oxide interface.

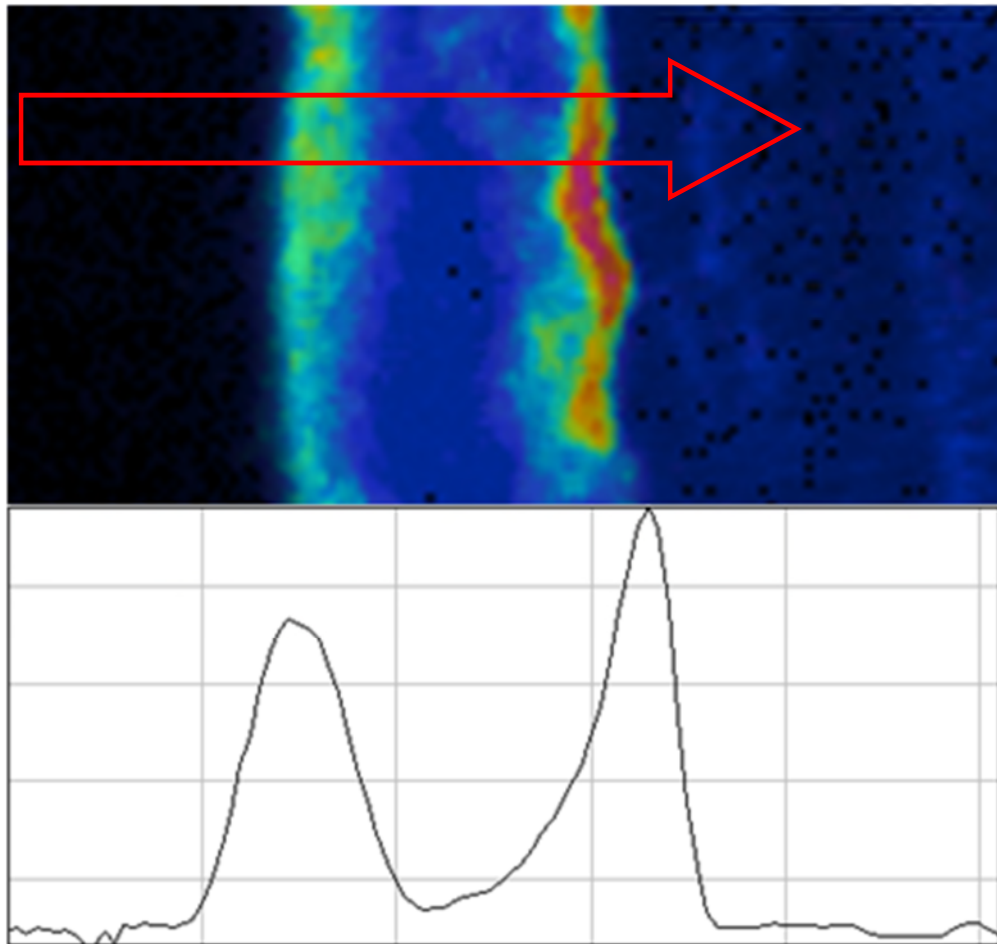


Figure 21 Close up of transitioned area showing a line profile of ^{16}O to ^{18}O ratio over the oxide. The red arrow shows the line profile region. As can be seen from the image this ratio is somewhat saturated right at the interface, suggesting a value close to maximum enrichment of 1.8%.

The series of comparisons that can be accomplished by measuring the oxide thickness, position of ^{18}O bands and their enrichment allow extremely reliable distinction between pre and post-transition oxides.

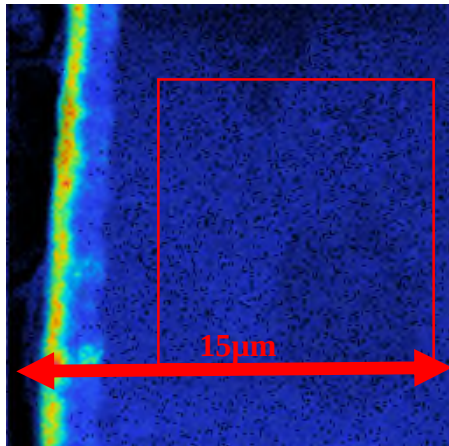
Calculating ^{18}O enrichment

It was found that the enrichment of ^{18}O bands varied with different locations of the band in the oxide. To gain a greater understanding of the significance of this result, it is desirable to have an accurate picture of the enrichment in each band. As previously, if the ^{18}O band is defined as the FWHM of the ^{18}O peak on a line profile, the enrichment of this band can be determined by summing the counts under this area on the graph, and comparing them to number of ^{16}O counts over this same region. However, this assumes that the yield of ^{16}O and ^{18}O secondary ions collected will be the same. This assumption can be broken down further into two parts, assuming ^{16}O and ^{18}O have the same likelihood of producing secondary ions under bombardment by the caesium ion source, and assuming these secondary ions are equally likely to be collected and counted by the mass analysing detectors of the NanoSIMS.

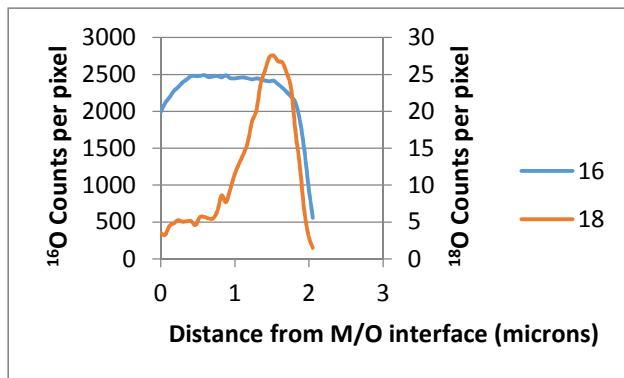
The sensitivity of the detectors can be calibrated by measuring the ratio of two ions coming from a sample with a well-known composition. However, tuning the sensors to measure two ions from a well-defined reference sample and then tuning them back to look at ^{16}O and ^{18}O is unnecessary as the sample images themselves provide such a reference. The surface of the metallic zirconium in the NanoSIMS begins to oxidise as soon as the protective platinum coating is milled away prior to measurement. This oxygen is present in the residual gas in the sample chamber and so represents a good reference for the natural abundance of ^{18}O .

Assuming that any opportunistic oxidation in the sample chamber is caused solely by this atmospheric oxygen means that analysis of the ratio of opportunistic ^{16}O and ^{18}O will provide a good reference sample from which the sensors can be calibrated.

Another benefit of performing the calibration by using this opportunistic oxidation is that it also will account for the possible variance in secondary ion yield caused by the different mass of ^{16}O and ^{18}O ions. An example of this procedure is shown in Figure 22.



Total ^{16}O counts in region = 46673802
 Total ^{18}O counts in region = 71802
 Measured Ratio = 0.15%
 Natural Ratio = 0.2%
 Concentration Correction Factor = 1.33



Uncorrected peak enrichment = 1.0%
 Concentration correction factor = 1.33
 Corrected peak enrichment = 1.3%

Figure 22 An example of calibration of the ^{18}O to ^{16}O ratio for a 34 day ZIRLO sample. Note, in this image the line profile is measuring the distance from the metal/oxide interface, showing the ^{18}O peak on the exterior of the oxide. A large area of opportunistic oxidation of the metal surface was chosen to try and average yield and growth effects from different surface grain orientations.

Performing the calibration on all samples allowed a more reliable determination of the true $^{16}\text{O}/^{18}\text{O}$ enrichment ratio and so allowed more confidence in correlating enrichment and oxidation behaviour. Every measurement of the opportunistic oxidation ratio showed an undercounting of ^{18}O compared to the natural isotopic abundance. The average correction factor was 1.27 over all samples, and is caused by the difference in sensitivity of the detectors

mounted on the two trolleys used for these measurements since it is unlikely that the secondary ion yields for ^{16}O and ^{18}O under caesium bombardment will be significantly different.

An initially unexpected result of this analysis is the relation between transition stage, oxide thickness and oxidation times. All images of 34 day samples showed only pre-transition behaviour, whilst some images from 80 day samples showed pre-transition and some post-transition behaviour. Images taken from samples having undergone 114 days of oxidation showed almost entirely pre-transition behaviour. One would expect that the samples having been exposure to a longer corrosion period would show a more advanced stage of corrosion, but this has not been observed in these samples. Whilst the relationship between corrosion time and kinetics was not as expected, there does seem to be a strong relationship between oxide thickness and corrosion stage.

Oxide thickness seems to be the main predictor of corrosion stage. The only sample group which showed both pre and post-transition behaviour (the 80 day group) showed that samples with oxides less than $2.0\text{ }\mu\text{m}$ had not undergone transition, whilst samples with thicker oxides universally had. The 114 day samples one would expect to have undergone transition all had oxides thinner than $2.0\text{ }\mu\text{m}$ and had not undergone transition.

This discrepancy in oxidation time and oxide thickness in which samples that were oxidised for shorter times showed thicker oxides even on the same alloy could be caused by differing conditions in the autoclave, where one set of samples may have been exposed to, for example, higher temperatures causing more rapid oxidation. Interpreting data in light of differing oxidation conditions requires the assumption that corrosion kinetics were not significantly altered by whichever condition varied, but were merely accelerated.

The discrepancy between oxidation time and thickness does however allow one to draw other inferences about the corrosion kinetics. The only samples that had passed through transition had oxides thicker than 2 μm , regardless of their oxidation time. This strongly suggests that oxides thickness is the critical predictor of transition, not oxidation time. Acknowledging that the total amount of corrosion is the important factor governing transition eliminates time-limited mechanisms of transition as the major determinant of oxidation stage, and is also supported by the fact transition behaviour can be localised, whilst corrosion time is constant across a sample.

Determining this critical thickness of the oxide must account for the oxide formed immediately after transition, which is obviously not a factor in determining the thickness at transition. Measuring samples that showed clear evidence of transition during the second exposure ensures the data is most appropriate, since we can be sure that no post-transition oxidation occurred before the doping with ^{18}O . Since the oxide that formed after transition will form under the layer of pre-transition oxide, the total oxide thickness minus the thickness of the ^{18}O enriched band at the metal/oxide interface will yield the critical oxide thickness for transition for a particular location.

Due to the high lateral resolution of the NanoSIMS, it is possible to study local transition events even when looking at areas of only 15 μm x 15 μm . Two samples showed localised transition events, the 80 day sample showed images where the 15 μm length of oxide was entirely pre-transition, entirely post-transition, or a mixture, with some areas post-transition and some areas pre-transition. On the 160 day sample, most images showed entirely post-transition kinetics, but in some images there was localised breakdown of the post-transition oxide (the oxide that formed after the first transition) creating areas of second transition oxide. It is appropriate to compare these two groups of oxide and study them together as they show essentially the same phenomenon repeating itself.

The double transition 160 day samples showed only an extremely localised transition and the accompanying oxide was very thick (5 μm). These were likely amongst the fastest oxidising sites on the entire specimen.

The existence of localised transitions strongly suggests that local oxidation stage differs across the sample on the scale of a few microns. The localised differences in oxidation rate and transition behaviour also provide a possible explanation for the observation of linear weight gain (as opposed to cyclical) in samples that have undergone multiple transitions. As different parts of the sample oxidise at different rates and thus undergo transition at different times, the cycles begin to decohere (run out of phase with one another) from one another. After several cycles this effect is completed and the average corrosion rate across the sample (as measured by bulk weight gain measurements) becomes linear in time. This effect would be particularly marked in reactor conditions due to the different temperatures, water flow rate and neutron fluence of the cladding tubes along their length due to the inhomogeneity of the reactor core environment.

With further study it would be possible to draw conclusions about the relationship between the variance of corrosion rate and the time to complete cycle decoherence. The higher the variance in oxidation rate, the faster a linear average rate would be established.

Variance in the local oxidation rate could possibly be connected to several factors, such as grain orientation of the underlying metal substrate, density of secondary phase particles in the oxide or metal substrate[77], or presence of cracks in the oxide. It seems unlikely that local variations in temperature could cause such localised transition events (some were as small as only 2 μm), although it is well understood that temperature can locally affect oxide thickness (as seen for instance over the length of a fuel rod cladding tube).

NanoSIMS images sometimes produce contrast between neighbouring grains due to ion channelling contrast, in much the same way a conventional FIB does. Whilst the instrument is not operated in order to maximise this effect, some images in which this effect is apparent show interesting phenomena associated with neighbouring grains of different orientation.

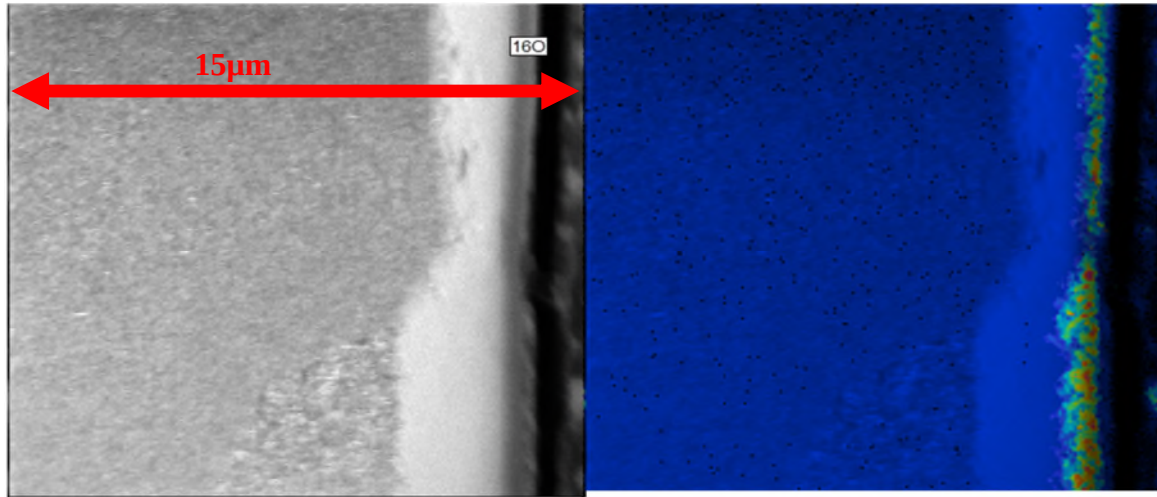


Figure 23 The image on the left shows the ^{16}O signal of a Zircaloy 4 sample having undergone 114 days of oxidation. This image clearly highlights two different grains by means of different “texture” caused by ion channelling. There is also a clear difference in the oxidation rate between these two grains, with the grain in the lower right oxidising much more rapidly. On the right is the associated HSI image again showing the step in oxide thickness, but also showing that the oxide had not transitioned at this point as the incorporation of ^{18}O is purely on the exterior of the oxide. This shows that the usual vacancy hopping method of pre-transition oxide growth is operating, but the thickness of the scale shows that the process is occurring more rapidly in this portion of the oxide.

Most strikingly, some images showed a marked difference in oxidation rate for different grains (Figure 23), with the step occurring right at the grain boundary of the metal substrate. This difference in oxidation rate is governed by a complex relationship involving the epitaxial growth of different oxide and metal orientations, and the resulting structure of the

oxide formed with regards to porosity and diffusion co-efficient. This relationship is not well understood for zirconium, but has been exploited for “heat tinting” techniques to reveal microstructure after short oxidation periods of polished samples[80]. Recent work involving automated, high spatial resolution orientation mapping has provided some insight into the structure of zirconium oxides in stress relieved conditions[81].

The channelling effects present in these images are not suitable to conduct a full investigation into these relationships, other than noting the maximum variance in oxidation rate correlated with grain boundary changes.

A full investigation of this effect would involve both TEM of the metal/oxide interface to index the metal surface grains and the resulting oxide grains grown on them, and EBSD of the metal/oxide interface presented in cross section to compare grain orientation of the metal substrate to oxide thickness.

Analysis of Hydrides

The NanoSIMS tuning allowed simultaneous analysis of hydrides (as indicated by the presence of deuterium) and ^{16}O and ^{18}O signals, in order to investigate possible correlations between them. Hydrides were found in all specimens, usually running roughly parallel to the metal/oxide interface, and in some cases deeper into the metal substrate as identified by optical microscopy.

Deuterium was found to be strongly localised in the hydrides with relatively small amounts found in the surrounding metal matrix (as shown in Figure 24). Whilst the exact composition

of hydrides was not determined, the count density of deuterium in the hydride was approximately 18 times higher in the hydride than the surrounding metal.

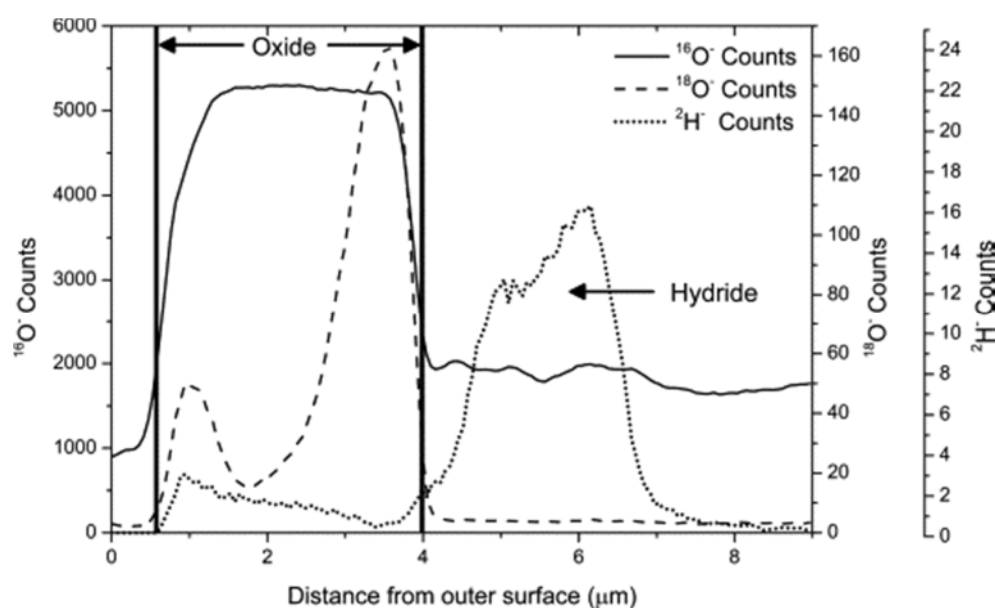


Figure 24 Line profile showing the ^2H concentration through the oxide, metal and a hydride on a ZIRLO 80 day sample. The concentration of deuterium in the metal matrix is approximately 18 times lower than that detected from the hydride. There also appears to be a gradient of hydrogen concentration over the oxide, with a peak near the oxide surface and near zero at the metal/oxide interface.

Hydrides were found in all samples although they ran along a greater length of the surface in the longer exposure samples, as confirmed by optical microscopy.

The apparent gradient of ^2H through the oxide is not easy to explain. The solubility of hydrogen in the oxide is extremely low[22] and so seeing counts as high as 20% of those recorded from the hydride is unexpected. Unfortunately, reliably quantifying the actual concentration of hydrogen in the oxide is not possible. The hydride cannot be used as a reference as it is not possible to determine the isotope ratio between hydrogen and deuterium, nor can it be assumed that the oxide and the metal have the same yield of hydrogenic species when analysed with SIMS. The concentration seems higher in the outer part of the oxide,

which will be post-transition with a higher monoclinic fraction and more porosity, possibly explaining some of the gradient, but conclusions drawn from this data must be extremely tentative.

Boron analysis

As part of the sample preparation process, boron was introduced into both the first and second autoclaves in order to more closely simulate the conditions of in service reactor water chemistry. The NanoSIMS can be tuned to pick up BO^- ions and provide a spatial mapping of boron concentration.

This mode of analysis provided another method to determine the possible mechanisms of oxidation. It was found that oxide layers which had undergone transition always had a layer of boron under the oxide, whilst pre-transition oxides had a layer of boron on the exterior surface. The transition state of these oxides could also be determined by the position of ^{18}O enrichment which was measured simultaneously.

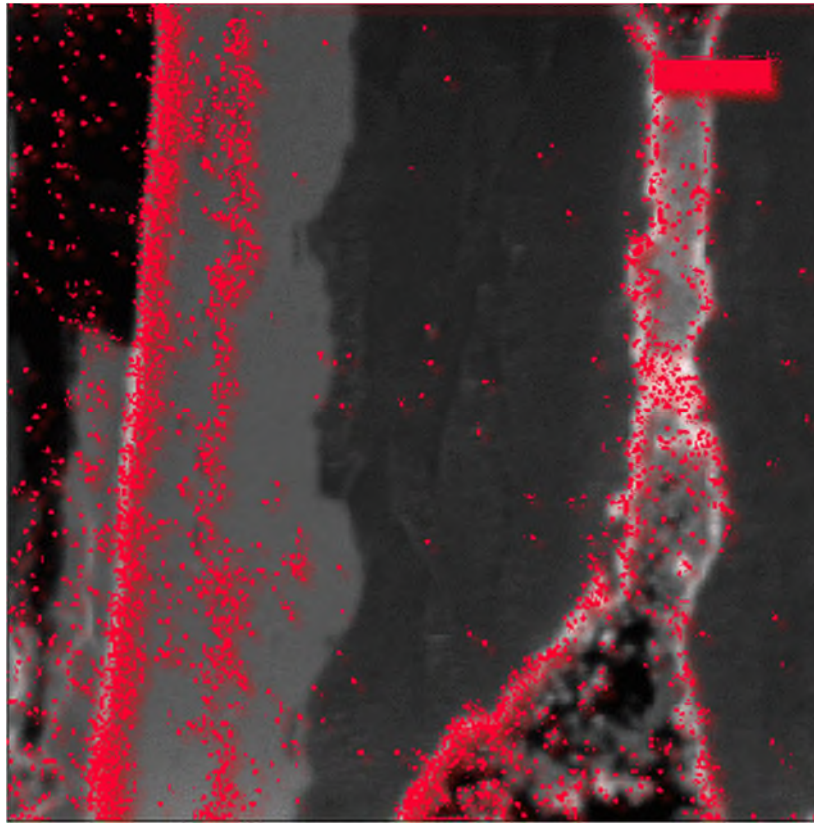


Figure 25 A 160 day ZIRLO image where the boron signal has been overlaid onto a secondary electron image. A large deposit of boron is seen on the exterior of the oxide, but also boron is detected in a thin band in the middle of the oxide, corresponding with the location of ^{18}O enrichment. This shows that boron penetrates the outer layer of non-protective oxide, suggesting that this location is fully accessible to water or steam, rather than oxygen reaching this location through another process.

This effect is also present in the 160 day samples, in which boron is deposited under the outer (transitioned) oxide and on the exterior of the protective pre-transition oxide. This is another demonstration that the same process whereby a protective oxide thickens to the point of transition before becoming porous and a new layer of protective oxide grows under it, is repeated over each transition cycle.

The extremely reliable correlation between boron location and ^{18}O band location lends credibility to both markers as reliable indicators of transition in this experiment as it is unlikely that both would be altered in the same way through sample preparation or other experimental techniques.

Finding boron under post-transition oxide layers indicates that whatever porosity develops at transition is large enough to admit dissolved boron ions as well as the accompanying water. The flood of water right down to the metal/oxide interface this suggests would be consistent with the high oxidation rate observed in samples immediately post-transition.

Boron is found in relatively thin bands on the exterior of protective oxide bands, either on the outside of the sample or under a post-transition layer, but not dispersed throughout the porous layers it travels through. This observation could imply either a driving force that attracts the boron to the exterior of protective oxide layers, or that the porosity of the layers is concentrated in thin bands where the boron is later found (i.e. the boron travelled through “thin tubes”). Since the concentration of boron in the autoclave water is known, one can work out the amount of displaced boron per unit of oxide formed. This of boron captured by the oxide and the amount rejected back to the surrounding water. Unfortunately, could then be compared with the concentration of boron found on samples to gain an insight into the amount the NanoSIMS cannot be relied upon to give quantitative data about ions without extremely careful set up and calibration, as the yield of secondary ions can vary between different ionic species. Due to time constraints this calibration was not performed.

In all cases boron does not seem to be incorporated into the oxide but is present in locations with the highest porosity, perhaps indicating boron species left behind after the removal of water from the specimens.

Elemental analysis of boron in zirconium oxides (where the oxidising medium contains sufficient quantities of boron) could provide a more accessible means to obtain similar results to ^{18}O isotopic doping, as it does not require expensive isotopic oxidising media and can be detected on instruments relying on other techniques to identify elements. Sensitivity may prove a problem as even with the NanoSIMS very high sensitivity, the count of secondary boron ions detected was still low.

Analysis of SPPs

Both Zircaloy and ZIRLO contain Secondary Phase Particles (SPPs) in the metal matrix. In Zircaloy 4, these particles are rich in iron and nickel, whilst in ZIRLO the SPPs are rich in iron and niobium. Both alloys contain tin which is more widely dispersed as a solid solution hardener[82]. The effect of these particles on oxidation is still poorly understood, with the mechanism through which various alloys gain their oxidation performance advantage over pure zirconium at least partially unidentified.

The high iron content of these SPPs allows easy identification of their location, distribution and to some degree their size. Tuning the NanoSIMS to pick up FeO^+ ions allowed for the analysis of SPPs in both ZIRLO and Zircaloy 4 without retuning. Unfortunately, due to the arrangement of the sensor trolleys in the mass analyser it was not possible to arrive at a configuration which allowed simultaneous imaging of the FeO^+ , ^{18}O , ^{16}O and ^2D ions, so ^2D was omitted. Whilst this precludes interrogation of the relationship between SPPs and hydride formation, it allows investigation into the relationship between SPP distribution and oxidation phenomenon.

The SPPs are preserved in the oxide, oxidising more slowly than the zirconium matrix. The local concentration of alloying elements is maintained so that they can be imaged even after oxidation. Some research has shown SPPs persist in the oxide in a metallic state (i.e. unoxidised) although the resolution available in the NanoSIMS is unable to distinguish this.

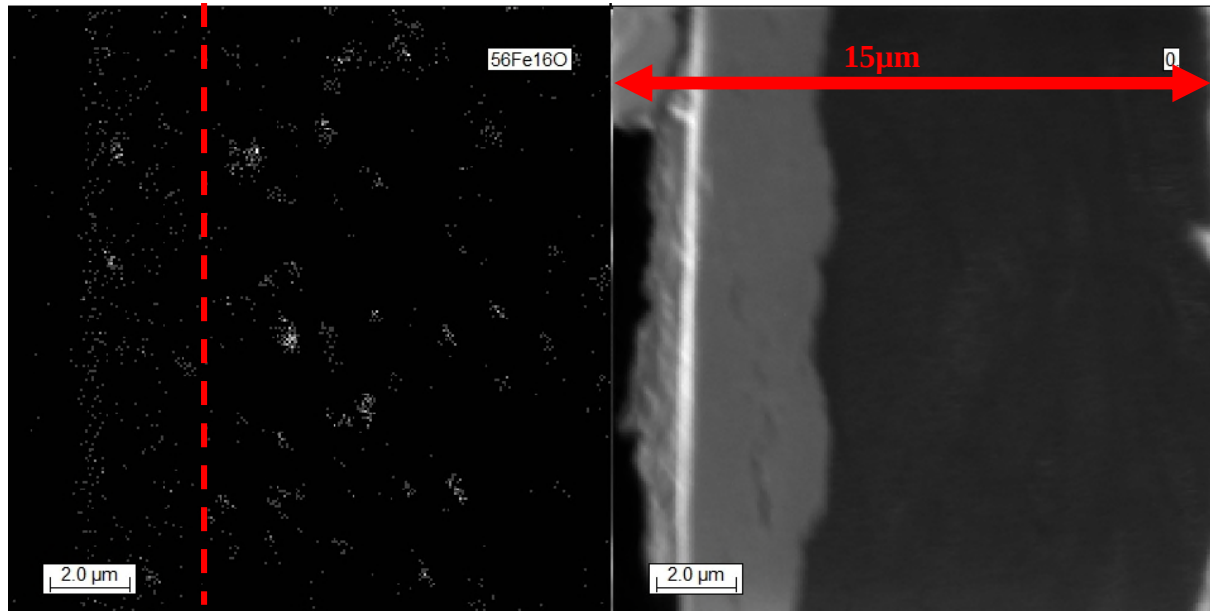


Figure 26 This figure shows the FeO signal (left) and the electron signal (right) obtained from a ZIRLO sample having undergone 80 days of oxidation. The dashed red line indicates the position of the metal/oxide interface. The secondary phase particles are clearly visible in the matrix. When considering the oxide region, two large particles can be seen to persist in the oxide whilst a more diffuse FeO signal is also present in this region.

The nature of SPPs after their incorporation into the oxide varies. In nearly all images a band of diffuse FeO counts coincides with the oxide layer whilst the FeO signal in the metal matrix is more concentrated into small particles. Some images also show clear FeO particles maintained in the oxide layer. This suggests some particles remain after oxidation whilst the majority are sufficiently dissolved after oxidation to be irresolvable. It is not clear which factor controls whether the elements remain well defined in particles after oxidation or are dispersed.

Most images showed an even distribution of SPPs over the metallic region of the cross section with few areas of increased SPP density.

A large enough sample of FeO images was not available to conduct a comprehensive evaluation of the relation between SPPs and local oxidation mechanisms, although some images do show notable features. For example, Figure 27 shows an image in which it appears that a cluster of SPPs coincide with a region of slow oxide growth. There are also several small cracks in this region of the oxide. It seems possible they caused the slow oxide growth, which then subsequently caused the horizontal crack due to the differing growth rates between the slow growing section of oxide and its neighbours[83].

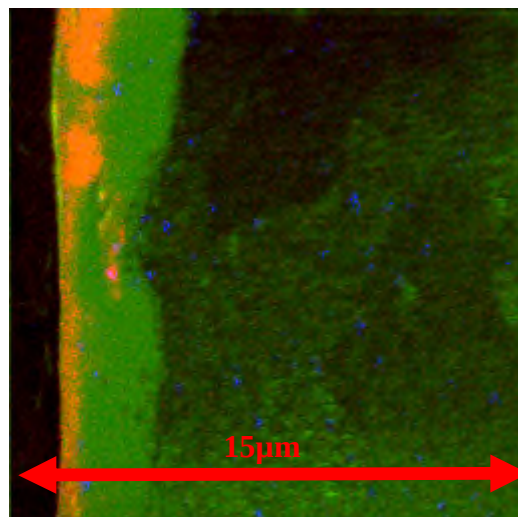


Figure 27 A colour merge image showing SPPs (blue), ¹⁶O (green) and ¹⁸O (orange) signals collected from a 114 day Zirlo sample. In this instance it appears the cluster of SPPs under the oxide have slowed oxide growth (the oxide is notably thinner here)

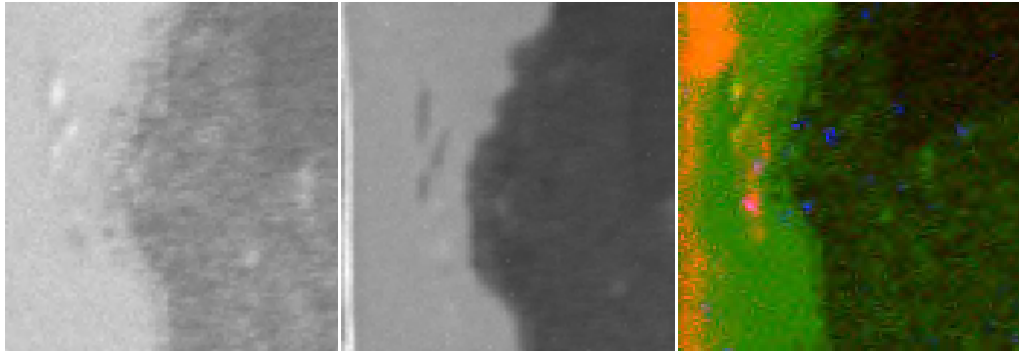


Figure 28 An enlarged view of the data in Figure 27 showing the region of slower oxide growth and the concentration of SPPs in the metal matrix below this protrusion using the ^{16}O signal, electron signal and a colour merge image showing the SPPs in blue.

The lateral cracks observed in Figure 27 and Figure 28 directly above a protrusion in the metal/oxide interface are not uncommon, as has been shown in a 3D FIB tomography study[27], and the mechanism behind their formation has also begun to be understood in recent years. Various modelling studies have also begun to address this phenomenon. Closer examination of Figure 28 shows also that the lateral crack above the interface protrusion contains a high concentration of ^{18}O , whilst the oxide under shows no penetration of the oxidising species in the second oxidation stage. This could indicate either the oxide above the crack has become porous (the crack may be isolating it from the compressive forces originating from the metal/oxide interface) or that interconnected porosity out to the oxide surface allows the influx of water which is decorating the interior of the crack surface with ^{18}O .

Work correlating SPP distributions and lateral crack formation performed by Tejland and Andren [83] has shown that higher densities of SPPs seem to produce more lateral cracks in the oxide (by crack volume), the suggested method being that unoxidised SPPs at the metal/oxide interface when found at the peak of a protrusion in the metal/oxide interface act

as a stress concentrator and crack nucleator. This could be the mechanism in operation here, although it should be noted that the SPP in question which may have nucleated this crack would have been oxidised by the time this image was taken. The Tejlund and Andren work ascribes waviness in the metal/oxide interface to a variance in the diffusion rate of the oxide grain boundaries and does not consider that it may be factors in the metal matrix or larger scale stress relaxation behaviour which contributes to the development of the interface shape. Creep of the metal matrix under oxide-induced stress may also be affected by the distribution and size of SPPs. Examining the metal beneath the oxide using TEM of FIB-prepared foils [84] found extensive evidence of plastic deformation in a layer 1-2 μm beneath the metal/oxide interface in the form of dislocations structures, sub grain formation and twinning. The authors were careful to contrast the dislocation density between an oxidised specimen and an unoxidised specimen so as to eliminate sample preparation as a source of plastic deformation, and chose to take specimens from the pickled surface of a tube to eliminate manufacture as a source of plastic deformation.

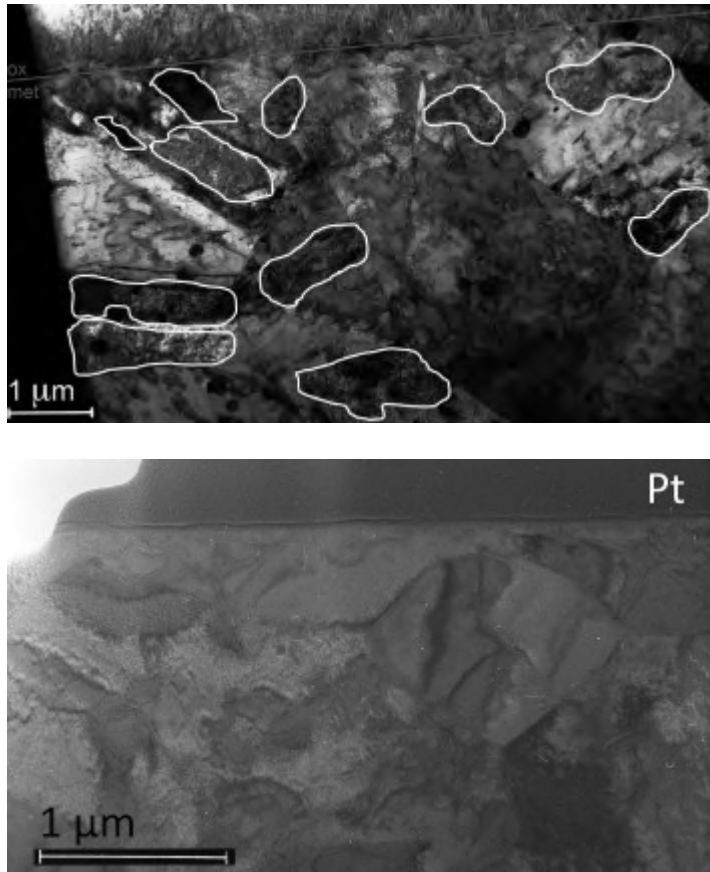


Figure 29 The top image shows metal matrix under an oxidised specimen, showing high concentrations of dislocations and sub grains. The lower image shows a much cleaner microstructure of a sample that has not undergone oxidation. Reproduced from Tejland & Andren 2014[83]

The dramatic contrast between the micrographs and the careful selection and control of specimens strongly implies that the difference in plastic deformation is caused by the oxidation process (as shown in Figure 29), and thus it is likely some stress-induced creep occurs during the oxidation process.

This layer of plastically strained material was found not to vary between samples with differing SPP distribution or differing oxide thickness. The fact that a material with a higher density of SPPs showed the same pattern of plastic deformation as a material with many fewer would seem to imply that the SPPs are not the main determinant of the extent of the

plastic deformation, or that this technique cannot distinguish between the two cases. It was also claimed that the material with fewer SPPs exhibited superior corrosion performance as measured by weight gain, although this difference was slight in samples with thicker oxides that had undergone multiple transitions (2%)

Penetration profile differences between alloys

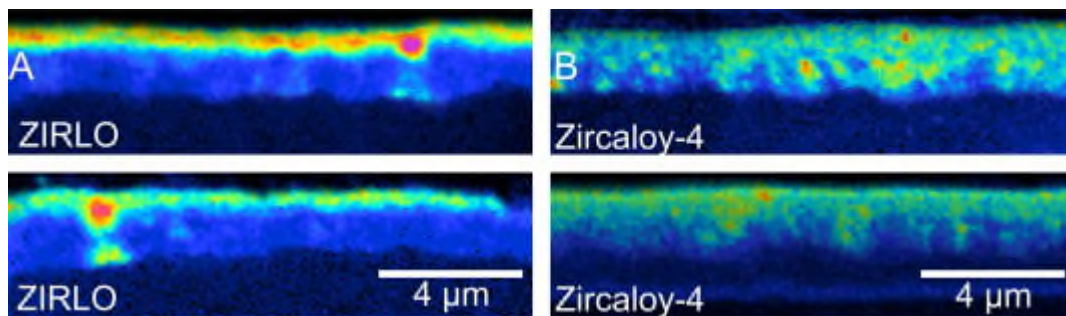


Figure 30 This image compares the distribution of ^{18}O in oxides formed on Zircaloy 4 and ZIRLO, showing a thin, concentrated band in ZIRLO 34 day specimens and a thicker, more diffuse band in Zircaloy 4 samples.

The 100nm lateral resolution of the NanoSIMS allows a close inspection of the penetration profiles found in samples of different alloys. The comparison in Figure 30 of Zircaloy 4 and ZIRLO pre-transition samples shows that the shape of the penetration profile of ^{18}O are characteristically different between these two alloys. ZIRLO samples show a thinner, more concentrated band of ^{18}O in the outer oxide, and in some samples there are occasionally features that show a large enrichment of ^{18}O at the exterior and well-defined regions of

penetration towards the metal/oxide interface. The Zircaloy 4 samples always showed a more diffuse band of ^{18}O , which seems to extend towards the metal in many thin “fingers”.

The difference in incorporation of ^{18}O has not been noted before and the NanoSIMS isotope doping technique is uniquely suited to examining it. Interpreting this difference relies on the fact that surfaces to which the ^{18}O doped water is exposed will passively exchange oxygen atoms with the corroding media, thus pick up some ^{18}O).

Looking at these pictures suggests that the Zircaloy 4 samples may develop an oxide that is more porous in its upper layers than that formed on ZIRLO. However, the weight gain for both samples was very similar, so it appears this difference in oxide morphology does not adversely affect corrosion performance. Since the ^{18}O was introduced during corrosion it can confidently be said that these differences were not caused due to sample preparation issues as might be argued with other methods of crack or porosity examination.

The ZIRLO images selected for the comparison show infrequent features where it appears that the local protective nature of the oxide breaks down causing rapid oxidation. The red colour and thick doped region, however, does not appear at the metal/oxide interface where one would expect a post-transition sample to oxidise, but high up in the oxide on the surface. Under the area of increased activity is another region of doped oxide directly under and next to the metal/oxide interface. This secondary patch is less enriched and looks to be separate from the upper patch of oxide growth, with no appreciable penetration into the metal matrix as would be seen if a large volume of new oxide were being created there. This phenomenon then does not fit with the pattern of transition that is usually seen, but instead seems to be a rapid taking on of ^{18}O in certain regions of the oxide without the growth of large quantities of new oxide as would be expected if a full transition was occurring. This may be the start of a

local transition, with the oxide losing protectiveness in this small region, but the oxide does not seem to have appreciably thickened in this area.

The combination of a sudden enrichment and no appreciable oxide growth suggests that some form of porosity has developed rapidly in that area, exposing a large surface area for passive oxygen exchange. However, the porosity may not reach down to the metal/oxide interface and so no rapid creation of new oxide occurs.

Additional TEM was carried out on these specimens before the NanoSIMS examinations took place and no significant difference in the microstructure was found between ZIRLO and Zircaloy 4 oxides, which might explain the difference in penetration profiles. Both oxides showed the characteristic layer of small equiaxed grains on the outer surface which would provide a large surface for the entrance of ^{18}O , but no obvious paths or porosity were found in the columnar layer. This may explain the diffuse penetration in Zircaloy 4 oxides.

Additional sample investigation

One of the 160 day ZIRLO samples investigated showed a range of interesting behaviours and was selected for additional investigation using SEM and TEM techniques.

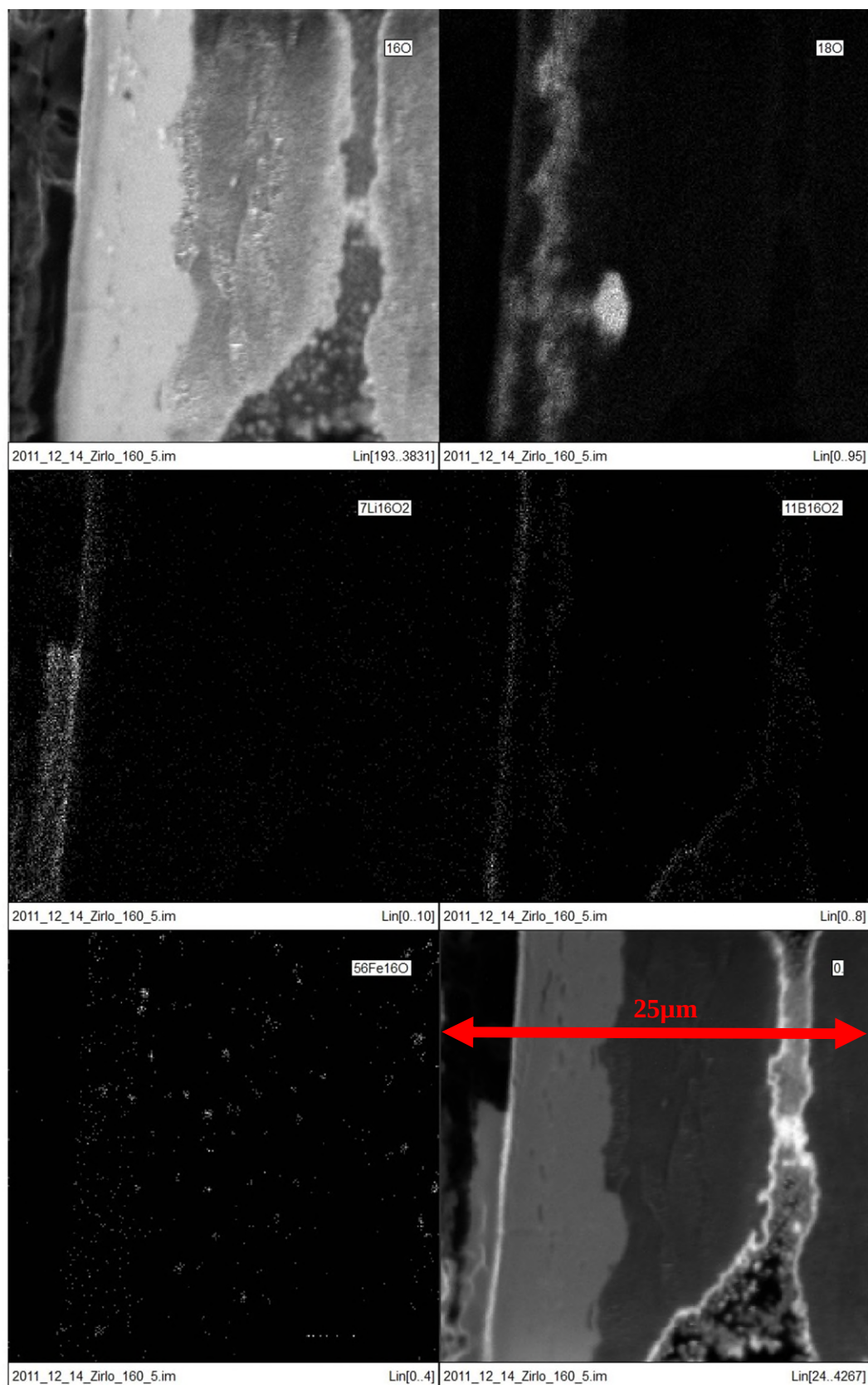


Figure 31 Base images of a double transition sample. Showing ^{16}O , ^{18}O , $^{7}\text{Li}^{16}\text{O}_2$, $^{11}\text{B}^{16}\text{O}_2$, $^{56}\text{Fe}^{16}\text{O}_2$ and secondary electron signals.

This sample showed a thick oxide that had transitioned a second time, producing a large band of ^{18}O enriched oxide at the metal/oxide interface under this local transition and a protrusion in the metal/oxide interface. The interface in this sample was also significantly wavy in regions away from the local transition. Closer examination revealed the presence of a vertical crack running through the oxide near the point of second transition, which was not found in any other samples. The data captured in the NanoSIMS contained information about ^{16}O , ^{18}O , boron, SPPs (iron rich) and the secondary electron images. Due to the combination of interesting behaviours and the collection of multiple data types about this sample, it acts as a good discussion point and also as a demonstration of previously observed behaviours.

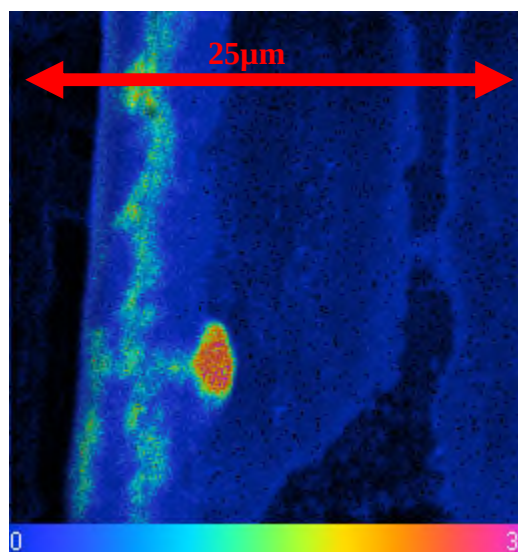


Figure 32 HSI image of the double transition sample. The red patch of highly enriched oxide is a clear demonstration of a second, local transition.

The HSI image in Figure 31 obtained by combining the ^{16}O and ^{18}O images and shows a dramatic ^{18}O rich feature right at the metal/oxide interface, which is consistent with a large amount of oxide forming in the later 20 days of oxidation, suggesting that the oxide above this point is porous to water. There is also a protrusion in the metal/oxide interface caused by

the oxide growth consuming metal at a faster rate than elsewhere at this interface.

Additionally, there appears to be a crack or porosity feature running perpendicular to the metal/oxide interface above this growth of oxide, which is suggestive of the water entry path, and will be discussed in more detail below.

The rest of the oxide follows the common 160 day sample behaviour, with an outer porous layer and the ^{18}O incorporated into the exterior of the inner protective band. In this instance the ^{18}O band in the middle of the oxide is wavy and irregular, highlighting either differential growth rates leading to differences in the thickness of the protective inner oxide or perhaps varying porosity in the internal region of the oxide. Above the local transition there is also a thin line of ^{18}O enriched oxide that appears on the exterior of the porous oxide. It is not immediately obvious why this would occur, although it appears to be linked to changes in the oxide occurring down near the metal/oxide interface.

Analysis of the boron signal confirms this porosity distribution, showing the usual deposition on the exterior of the oxide, a band in the middle of the oxide that corresponds to the exterior surface of the protective oxide and a thin trace down the local transition feature right to the metal/oxide interface

SPPs are shown clearly using the FeO signal and display an even distribution across the metal surface. A small number of SPPs are preserved in the oxide along with a more diffuse signal indicating oxidised SPPs. There is no cluster or void of SPPs associated with the double transition feature.

Additional investigations were carried out using a ZEISS NVision dual beam FIB. Areas that had been imaged in the NanoSIMS were visible in the SEM using backscatter mode as the redeposition of milled material around the crater and the implantation of caesium provided good contrast. These sites could then be matched with NanoSIMS images to get a better

picture of the sample than that provided by the low resolution SEM in the NanoSIMS. No additional sample preparation was performed, which preserved the sample surface and the markers left by caesium implantation. The platinum coating applied previously provided enough of a current drain, and opportunistic surface oxidation was not considered a problem.

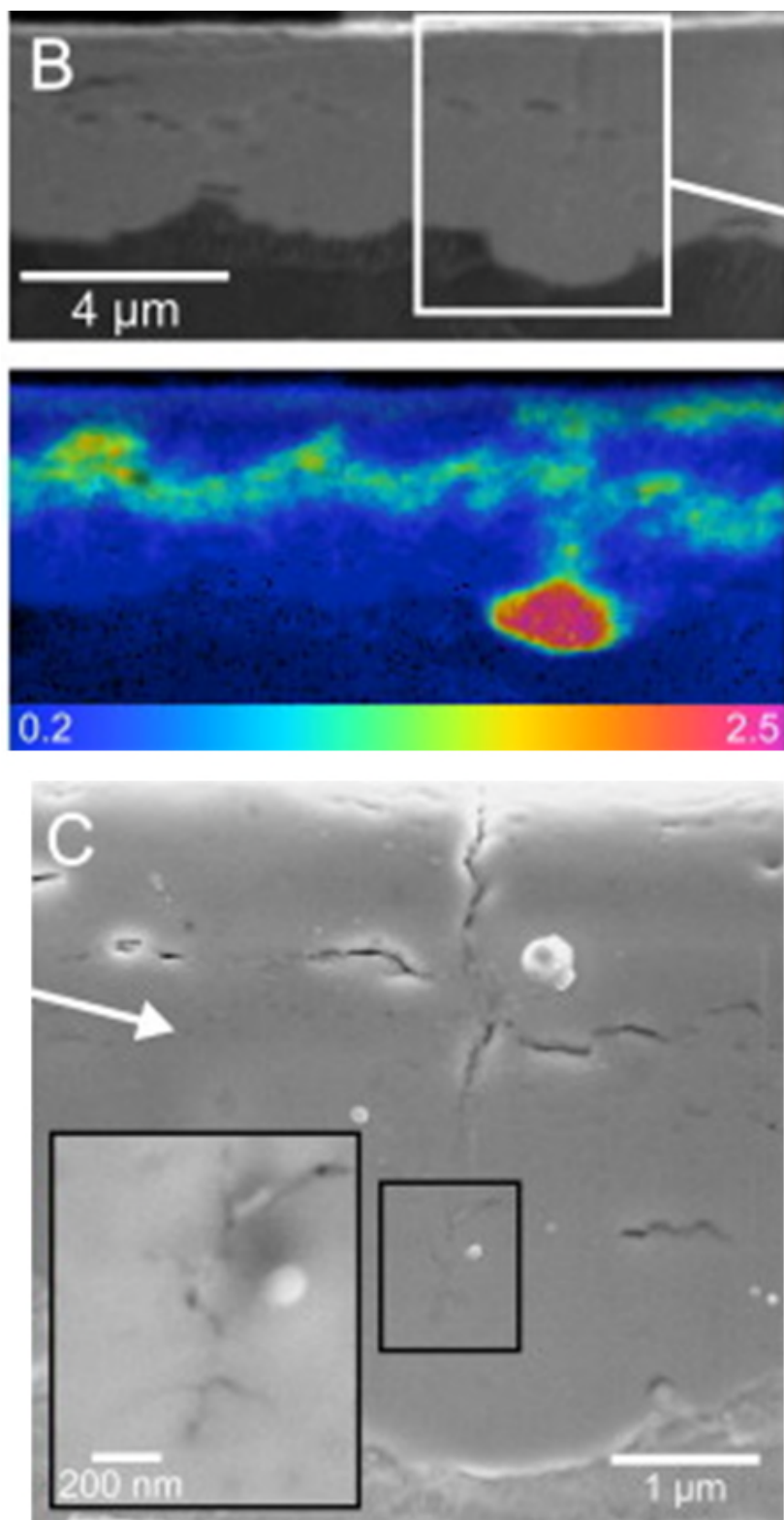


Figure 33 The top image shows the secondary electron image of the double transition sample captured inside the NanoSIMS, and the middle image shows an HSI image highlighting the second local transition, as well as the incorporation of ^{18}O in the middle of the oxide scale,

which corresponds to the exterior of the protective oxide. The final image shows a high resolution SEM image of the crack captured after NanoSIMS analysis

The high resolution of the SEM column (approximately 3nm when operated at 2kV) allowed examination of the fine surface features of the oxide, including the cracks running both laterally and vertically. The low accelerating voltage also allowed fine examination of these features due to the smaller interaction volume. SEM examination showed clearly that the vertical trail of ^{18}O and boron shown in the NanoSIMS images was associated with a large crack running from the exterior of the oxide to approximately $1\mu\text{m}$ from the metal/oxide interface. The presence of ^{18}O and boron suggests that this crack was present from the sample oxidation period and is not a result of sample preparation techniques.

Close examination of the crack tip shows a fine branching structure, which terminates at the start of the newly formed oxide. This newly formed oxide is likely to still be under a compressive stress as it is in contact with the metal/oxide interface, whilst the layers above seem mostly disconnected by layers of horizontal cracks. These vertical cracks are not commonly seen, and a review of all the NanoSIMS images reveals no other obvious candidates for such features. This large scale vertical cracking appears to have happened in addition to the normal process of porosity development rather than as the necessary step. Possibly the extremely localised and rapid growth of the newly formed oxide at the interface was sufficient to cause this cracking by rapidly creating a volume expansion, which needed to be accommodated in the overlying oxide.

Using this sample to analyse cracks has the advantage that the sample is at least partially constrained by the bulk media around it, and thus will not suffer as much distortion once excess free surface has been created. The extent of the cracks can be determined with more

confidence, as creating free surface may allow cracks to extend to positions where they were not when in situ.

Additional examination of this sample was performed using TEM (Jeol 2010) in order to gain a better understanding of the microstructure and look for anomalous features, which may explain the sudden localised growth or the rare cracking feature in the oxide.

TEM liftout is widely used to study zirconium oxide samples, but the usual preparation technique involves taking a liftout from the sample perpendicular to the surface to create a small cross section. In this sample, the surface needed to be preserved and lifted out parallel to the surface in order to study the same surface that the NanoSIMS imaged.

The result of this technique after usual thinning and sample cleaning treatments was a thin (approximately 100nm) TEM foil encompassing the most interesting region of the NanoSIMS image. Sample thickness was judged by checking the transparency of the thinned foil in the NVision operating at 7kV.



Figure 34 Composite TEM micrograph of the double transition sample liftout. This image clearly shows the vertical crack, which extends from the exterior of the oxide to the edge of the oxide formed during the secondary exposure. The metal substrate shows features that indicate the build-up of dislocations as suggested by Tejlund [84].

When viewing the TEM micrograph of the oxide, it must be remembered that this sample is thinned to approximately 100nm and thus has had almost all internal stresses relieved and it is likely any phase transformations (for instance from tetragonal to monoclinic phases in the oxide) that could have taken place will have already occurred. The cracks visible in the oxide correspond well to those observed in the NanoSIMS and SEM imaging, while a number of finer cracks are now apparent, it cannot be inferred that these cracks were necessarily present during the sample oxidation period.

The area of highly ^{18}O enriched oxide near the metal/oxide interface seems to have undergone minimal cracking during the liftout and thinning procedure. The area is clearly columnar in grain structure and is well attached to the metal substrate. Immediately above this layer is a horizontal crack that corresponds to the end of the fine branching cracks imaged with the SEM. the increase in size of these cracks is an indication of the extent to which liftout procedures can affect sample morphology.

Above this crack the layer possesses cracks that have opened up along grain boundaries and existing cracks have widened. Unfortunately, the width of this electron transparent sample is limited so this region cannot be compared to parts of this layer where it had not undergone a transition.

The metal substrate shows a variety of dark features that are most likely creep-induced dislocations caused by the high tensile stress on the metal during the rapid oxidation.

The barrier layer

This work strongly suggests that different layers of oxide are protective or porous during different stages of the oxidation process because the location of ^{18}O band shows areas of active oxide incorporation during the 20 days of exposure to spiked water. This provides a new way to measure the thickness of the “barrier layer”, which has been much discussed by researchers for several years now, often ascribing its protective character to entirely different physical or microstructural effects.

The thickness of the barrier layer is also revealed in images of samples with thick oxides with an entirely protective character (80 and 114 day samples). The main columnar region (as seen in the TEM sample) of oxide clearly remains protective in the later stages of pre-transition oxidation. This does not agree with impedance spectroscopy measurements, which imply a thinner barrier region, but is consistent with the theory of a continuous phase transition maintaining protectivity right up until transition[85]. The images showing incorporation of oxygen at the very exterior of the oxide demonstrate that for pre transition oxides, the entire thickness of the oxide is acting as the barrier to oxygen ingress.

Also evident is the similarity between pre- and post-transition oxides, which show exactly the same behaviours and grow via the inward diffusion of oxygen ions meeting oxygen vacancies diffusing to the exterior of the oxide.

The relationship between porosity of oxide layers and boron location has not been demonstrated before, and whilst this research does not examine the role of boron in the corrosion process, knowledge of the location and incorporation of boron within oxides will contribute towards this understanding.

The unique scale at which these observations have been carried out (larger than volumes analysed by TEM or APT but smaller and with much higher resolution than techniques such

as XRD) has been perfect for revealing the localisation of transition events and the related corrosion events. The lack of clear transition markers and the small volumes of material studied hamper TEM and APT analysis of local transition, whilst XRD and similar techniques are unable to interrogate the sample in sufficient detail for determination of local transition events. The imaging of clear localised transition at the scale of 1-2 μ m laterally in the oxide layer is a new observation, and shows that it is likely that local factors affect transition rather than, for instance, sample-wide electrochemical effects.

The creation of isotopically doped specimens used in this experiment have allowed the use of novel techniques for the direct imaging of the oxidation phenomenon. The sample formulation meant that direct comparison was possible between different alloys in the 114 and 34 day samples, as they all used recrystallised material. ZIRLO specimens were made for every oxidation period and so provide a good record of sample behaviour which can be compared against the Zircaloy 4 specimens. Figure 30 shows that there is not a significant difference between the two alloys studied in overall corrosion performance, although as noted there seems to be difference in the character of ^{18}O incorporation between the alloys.

Heat treatment seemed to play a lesser role in the corrosion process, although the recrystallised specimens did show larger grains, which may have led to more instances of uneven oxidation growth across grain boundaries. The lack of samples that had the same alloy composition and oxidation time but differed in heat treatment unfortunately meant a direct comparison was impossible between the recrystallised and stress relieved states. This is a possible area for future work.

Residual Stress Analysis by Ring Core Milling and Digital Image Correlation

Stress plays a crucial role in the oxidation of zirconium alloys. The Pilling-Bedworth ratio of zirconium is 1.56 [86, 87] leading to high compressive stresses in the oxide. Oxides formed on metals with Pilling-Bedworth ratios in the range 1-2 are normally passivating, and while pre-transition zirconium oxides follow cubic or parabolic kinetics with a decreasing oxidation rate as the film thickens [79], at transition this behaviour changes and the oxide becomes non-passivating. There appears to be a relationship between compressive stress in oxide films and their protective nature; this link may be explained by stress stabilisation of the tetragonal phase or through mechanical cracking of the oxide, or both.

It has been demonstrated that stress in pre-transition oxides is high, especially for thin oxide films, and reduces immediately post-transition [88]. Unfortunately, “transition” is not well understood or defined, so it is difficult to determine whether it is caused by or causes this drop in internal stress, or even which comes first. The drop in compressive stress coincides with the drop in phase fraction of tetragonal oxide. Some authors report a slow decrease in tetragonal content occurring uniformly through the corrosion process [88], while others report a reduction in tetragonal phase more closely linked to the transitions [89, 90]. The tetragonal-to-monoclinic transformation is accompanied by a 3% increase in volume [91]. This increase in volume maintains the compressive stress at the level required to stabilise some of the tetragonal oxide [91]. When the oxide transitions from protective to non-protective behaviour, porosity is generated that allows the oxidising media to reach the metal surface [92, 93].

The conditions under which tetragonal or monoclinic oxides form are important when considering the role of stress on the phase change, and the resulting development of porosity. Tetragonal oxide is not stable at normal reactor operating temperatures and pressures, requiring 1200°C [94] or pressures of 3 GPa. Most of the tetragonal oxide present at normal operating conditions is either stress stabilised or stabilised by the small grain size [94] or a combination of the two. The stress stabilisation of the tetragonal phase combined with the expansion of the monoclinic phase presents an explanation for the smooth decrease in tetragonal phase noted in XRD studies [88]. When the tetragonal phase transitions to monoclinic, the resulting volume increase results in compressive stress applied to the remaining tetragonal oxide and thus prevents it from undergoing the spontaneous transition to monoclinic expected from the phase diagram until further relaxation occurs.

Relaxation of the compressive stress in the oxide generated during corrosion is important to the transition phenomenon, but this process is still not well characterised or understood. Stresses present at high temperature suggest creep in the metal substrate as a possible factor as zirconium and its alloys have been shown to undergo creep at temperatures found in typical reactors[95]. As the metal substrate stretches to relieve tensile stress (in comparison to the compressive stress in the oxide) the oxide attached to it will be allowed to relax and undergo transition. This model for the distribution of the different oxide structures relying on the build-up of stress marries well with observations that oxide thickness is more important in predicting transition (even locally) than time spent under corrosion conditions [96].

Experimental Measurements of Residual Stress in the Oxide Layer: Previous Work

One method used to measure residual stresses in zirconium oxides is the curvature produced by one sided oxidation of a thin zirconium sample. In this technique a thin (50-100 μm) zirconium sample is oxidised on one side only and the growth of oxide causes a deflection of the whole sample coupon due to the compressive stress caused by the high Pilling-Bedworth ratio. The specific methods of how to oxidise one side only vary (such as masking the surface, only exposing one side, or removing an oxide on one side only), though all such experiments rely on Stoney's equation [97], which translates a radius of curvature into a residual in-plane stress [98]. Using this technique, researchers have made several measurements of residual stress. Kim [98] et al measured oxide films of thickness ranging from 40 nm to 1 μm grown on 99.2% pure zirconium (impurities unlisted) and found a peak stress of 5.1 GPa for extremely thin films (40 nm), dropping to approximately 0.5 GPa for thicknesses more than 300 nm. Since the deflection is caused by the total stress through the oxide film the calculated residual stress represents an average value, and there is almost certainly a strong dependence of stress on depth in the film. Roy [99] and Burgess found stresses of up to 1.7 GPa in oxides grown on pure zirconium and Zircaloy 4 though measuring thicker oxides (in excess of 1 μm). The use of thicker oxide films likely results in the measurement of lower stresses because the effect of lattice mismatch at the metal-oxide interface will be diluted. Garzarolli milled the metal away from Zircaloy 4 samples and measured stresses of 0.9 GPa for oxides 0.5 μm thick [91]. This study compared the instantaneous corrosion rate with the stress present, and found a peak in the stresses immediately before and during transition. It is unclear if these studies account for tensile stresses in the metal, which would act simultaneously with the compressive stresses in the oxide. Later papers [100] have suggested the result may be somewhat high in these studies

due to no consideration being paid to the directionality of expansion caused by the Pilling-Bedworth ratio (I.e. the free surface at the exterior of the oxide will accommodate the vast majority of the expansions and the resulting in-plane stress values will be reduced accordingly).

Another method of measuring residual stress in the oxide is by X-ray Diffraction. XRD produces a profile of diffracted X ray intensity with angle of diffraction, and combined with a knowledge of the material structure and Bragg's law this can be used to determine interplanar distances. Residual stress in a sample can be inferred by measuring the change in lattice parameter caused by elastic deformation and using the Young's Modulus of the material. In this way XRD provides a non-destructive way to measure residual stresses in zirconium oxides, though with some problems in interpretation. For instance, the samples do not have uniform stress profiles, and so determining the stress at different depths in the oxide is difficult due to beam size of the instruments. Normally different depths are interrogated by using glancing incidence beams of differing angle, with shallower incidence angles examining smaller depths, this allows the study of stress and crystal phase at varying depth in the oxide. Additionally the spectrum produced by ZrO_2 produces peaks of interest which lie close to peaks from the matrix [101] complicating data extraction. Using this technique, Petigny found values as high as 1.8 GPa for Zr-1Nb samples and 0.5 GPa for Zircaloy 4.

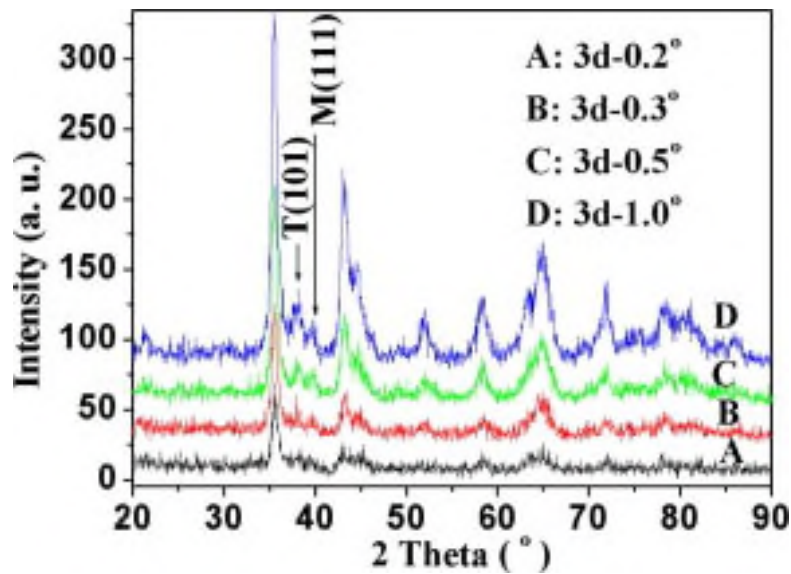


Figure 35 A graph of diffracted x-ray intensity with diffraction angle for the oxide on a zirconium alloy sample from an XRD study [88]. In this instance the relative strength of the peaks corresponding to known planes in either the tetragonal or monoclinic phase can be compared to estimate the phase fraction of each.

A study using Synchrotron XRD correlating phase fraction, stress levels and transition kinetics [102] is particularly helpful in elucidating the interactions between all three features of an oxide layer. It was found thin films known to be protective (by their instantaneous weight gain when removed from the corrosion environment) had high compressive stresses and high tetragonal phase fractions. Additionally, separate stress profiles for each monoclinic layer (i.e. layers that have fully transitioned) were obtained and showed an increase in stress towards the metal oxide interface in thicker films.

A range of destructive or semi-destructive techniques exist to estimate stress. These operate by creating a free surface and measuring the deformation of the remaining material in proximity to this region as a result of removing the mechanical constraint on the stressed region of the sample. One such technique is called the contour method[87] where a sample is cut carefully cut in half using a technique such as electro discharge machining. As the

material is removed the stresses in the sample are relaxed, and markers placed on the surface are tracked to find which parts of the sample move towards or away from the cutting surface. The displacements are then used as the boundary conditions of a finite element analysis model to extract the stress field existing in the material prior to cutting. This method can be used for large components, but samples smaller than 1cm require too great a precision to obtain accurate results.

Ring Core Milling

A small scale application of the contour method called Ring Core Milling [103] allows the local determination of in-plane stress in small regions (1-10 μm) on a sample surface. This technique is an execution of the contour method on a scale much smaller than those traditionally used, taking advantage of the high precision available in modern FIB instruments in both imaging and material removal modes.

Ring core milling has not been applied to the study of zirconium oxides before, but has found extensive use in the examination of numerous thin films [104, 105] on dissimilar substrates. Its application to zirconium oxides (or any metal oxide in which residual stress is of interest) will provide the zirconium corrosion community with another technique to measure residual stress in oxides.

Ring core milling relies on the comparison between two images of the sample before and after the creation of the free surface and the resultant stress relief. A dual beam FIB such as the Zeiss NVision is ideal for this task, as it contains an extremely high resolution SEM column capable of taking detailed images. In the case of the NVision, image resolution of approximately 2 nm is routinely achievable under a range of conditions. A high resolution image is taken before milling commences, and then an annulus is milled such that an “island”

is created in the sample surface. This island is disconnected from the rest of the sample surface, and so can relax, relieving any residual stress. After milling, another high resolution image is taken using the SEM column and the two images are compared to determine the change in dimension of the island, giving a value of the residual strain present. This process can be performed in steps of incremental depth to obtain a stress profile through the oxide[104].

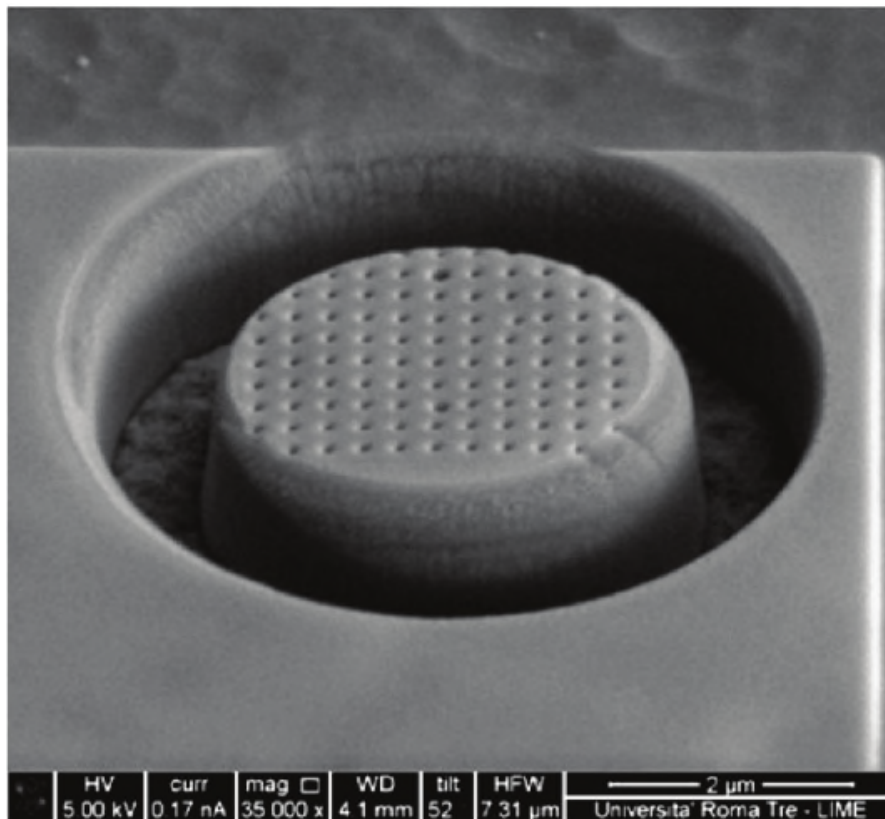


Figure 36 The island created by ring-core milling. The small dots on top are fiduciary markers milled to a shallow depth in order to aid the DIC tracking of movements in the image. The movement of the markers compared to an initial image is used to estimate the stress relieved in the milling process.

Measuring Residual Stress: Digital Image Correlation

Comparison of the before and after images to determine the strain requires more precision than a simple measurement of island width. Digital Image Correlation is a method used to compare two images and by tracking certain features in the images between the two exposures determine their relative displacements[106]. DIC first reads the initial state image as a greyscale, and then each pixel is mapped to an entry in the matrix (so a 1000 by 800 pixel image will produce a 1000 row by 800 column matrix) with the value of the entry being the intensity or brightness of that pixel. The final state image is similarly input and converted to matrix form. Subsets of these matrices are compared by calculating and trying to maximise the correlation coefficient between them. The correlation coefficient then yields the deformation of dimension change between the two images. This process is repeated over the image with multiple subsets producing a full map of the deformation between the first and second images.

This map of deformation then reveals movement in the x and y directions of the surface plane. The movements (strains) can be directly related to the stresses present by using the Young's modulus for the material under study, E .

Calculating Stress

Inputting a single value of E and the relevant strain extracted from the DIC analysis will give a stress assuming a completely elastic interaction. In the case of a zirconium oxide film this is not an entirely straightforward choice, as there are several stress-related phenomena occurring during oxidation and during the stress relief procedure. The phase change from

tetragonal to monoclinic could occur during stress relief. Once the stress is reduced to a critical level, if a phase change takes place it will produce movements whilst maintaining a constant stress. In addition the oxide film is nanocrystalline with many grain boundaries, so a value of E derived from testing larger single crystal specimens of ZrO_2 will likely be inapplicable. The nanoscale grains of the oxide are also not isotropic, having a columnar habit that again will likely affect the value of Young's Modulus.

Other research into residual stress levels in zirconium oxides has used an elasto-plastic self-consistent model developed by Tome and Oliver [102]. This model predicts a Young's Modulus of 253 GPa for both the tetragonal and monoclinic phases. This value of Young's Modulus does not account for anisotropy in the structure, but provides a rough estimate.

Experimental procedure

Sample preparation

Sample preparation is relatively simple for ring core milling as the only requirement is a flat sample with sufficient surface features for DIC tracking and small enough to fit in the FIB chamber.

The samples used in this work came from the same samples produced under the MUZIC program used in earlier chapters. However, in this chapter the samples will be referred to with the full period of oxidation, as the second exposure used to dope the specimens with isotropic tracers has no special relevance for this work.

Coupons of ZIRLO that had been oxidised for 54 or 100 days at 360°C, 18 MPa in water with additions of 1000 wtppm of boron and 2wtppm of lithium, were cleaned in sequence with

acetone, ethanol and isopropanol, then rinsed in distilled water. This left a clean surface free of carbon based contaminants that can become ionized under electron beam instruments and deposit on the sample at the area of interest.

Once clean, the coupons were mounted on a 12.5 mm aluminium stub with silver dag. Silver dag is an acrylic based paint containing 50% by weight silver particles to provide a highly conductive grounding pathway for SEM samples. Silver dag proved superior to carbon based grounding products both in reduction of contaminants (preventing deposition) and in reduction of drift due to charging of the sample.

The stub-mounted coupons were then treated in a gold sputter coater for 45 seconds with a sputtering current of 0.85 amps. This produced a thin coating of gold approximately 2 nm thick. The purpose of the gold coating is to improve the grounding of the sample by providing a pathway for electrons to leave the highly insulating surface of the zirconium dioxide surface under investigation. In order to capture good images for DIC it is vital that the image does not drift due to specimen charging. To obtain the highest detail images, imaging was conducted with the highest possible digital resolution, low SEM beam current (small aperture), and long scan times. These conditions mean each exposure took approximately one minute; any drift during this period would create false movement in the captured images that would then create artefacts in DIC analysis.

An additional benefit of the gold coating is that it produces an extremely fine surface texture on the sample. The gold is not laid down uniformly, but instead forms a slightly wrinkled surface on top of the oxide layer. These extremely small scale surface features show up well due to the very high resolution of the NVision SEM and gold's high atomic number, aiding DIC recognition of the surface and increase tracking accuracy.

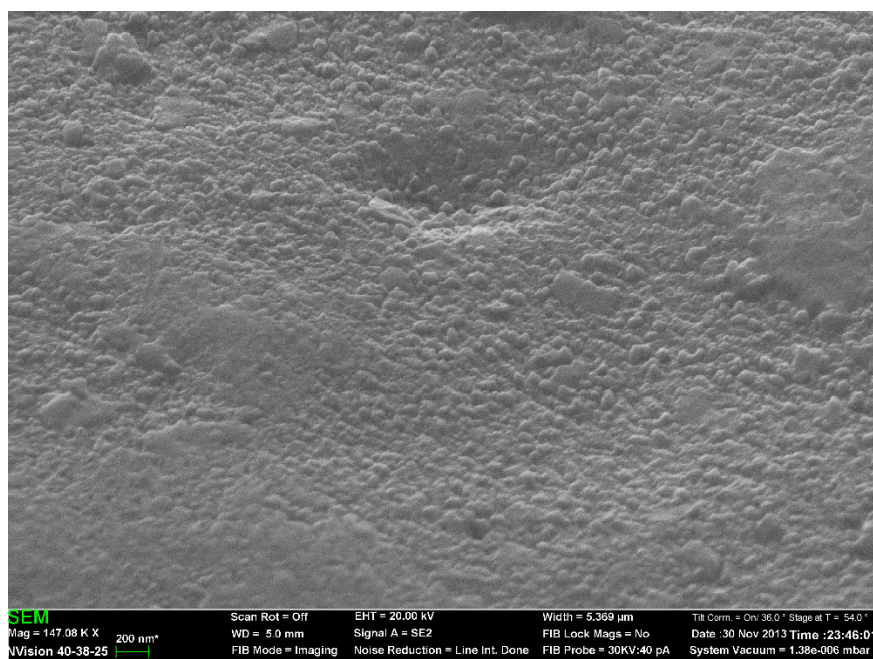


Figure 37 SEM Secondary electron micrograph of a ZIRLO oxidised sample surface after gold coating. The fine texture of the gold coating is a natural result of the gold coating. Larger features in the ZrO_2 surface are visible beneath the gold coating.

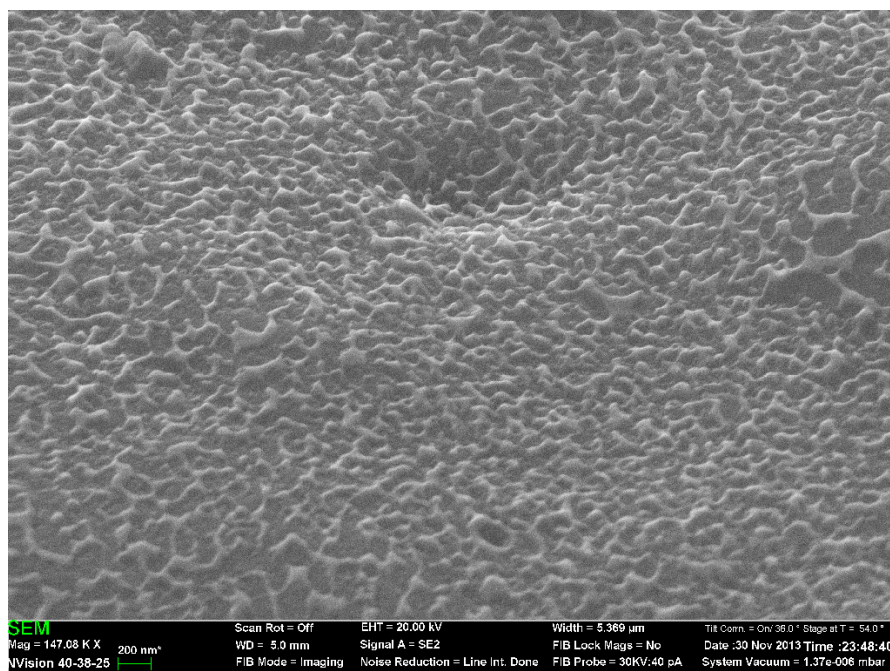


Figure 38 SEM Secondary electron micrograph of a ZIRLO oxidised sample surface after gold coating and one 20 pA imaging pass with the NVision FIB. The single scan of the

gallium beam appears to cause the gold to agglomerate into a larger scale and higher contrast surface configuration. The same larger features are visible below the coarser pattern.

Imaging the gold coated surface with the gallium beam of the FIB created a more coarsely textured surface where gold particles seem to have agglomerated. This new surface has larger, higher contrast features that are more resistant to obscuration by redeposited material, and provide better markers to be used throughout the whole milling procedure.

FIB Procedure

Samples were loaded into the Nvision and alignment of both the FIB and SEM columns was performed on a corner of the sample. Due to the extreme accuracy required for image capture, the FIB was allowed to settle for approximately thirty minutes. During this time the vacuum in the chamber reached a steady state. Additionally, the temperature of the stage, mounting stub and specimen equalised, and the SEM beam optics came up to operating temperature.

A site of interest was identified using the SEM image. Sites were selected having a relatively flat surface and a good coating of gold. The FIB beam was then given a final alignment without imaging the chosen site. A single, 20pA, 1024x768 pixel image (which produced the desired surface texture) of the site was collected, and used to layout the milling annulus.

After this point, no further FIB imaging occurred so as to protect delicate surface features; all further use of the gallium beam was strictly for milling in the annular region.

Milling a ring was achieved by using the FeatureMill package in the Zeiss Software. An initial light milling pass at 20pA in the shape of the annulus was used to define the core or island of interest. Once this island was defined, the SEM was precisely aligned. Using the 10 μm aperture and a scan speed of approximately 1 minute, five 3072x2304 pixel images were captured to act as the initial reference point for DIC analysis. The five images were checked against themselves for drift or other artefacts. By checking the cross correlation of these images (which were taken without any milling occurring between them), any movement picked up by DIC analysis must be a result of either image distortions or movement of the sample.

Once initial images had been saved milling was started. A 20pA beam was used to mill a ring shaped trench around the island of interest. Unfortunately, automatic control of the depth of this trench was not possible due to milling conditions changing with depth. Therefore, milling was performed in stages of approximately 0.5 μm depth. For most samples the viewing angle, trench width and trench depth allowed direct measurement of the depth by viewing the rear wall of the trench.

After each 0.5 μm step was milled, a new series of five high fidelity images of the island was captured using the SEM beam. Again, capturing five images allowed cross correlation of the sample in the same state to check for drift between images.

Milling of the annulus continued until full depth was reached, when the oxide had been penetrated and the underlying metal substrate was visible. At this point more milling would have revealed the stresses present in the metal and not the oxide, however the increasing depth of the trench hinders efficient milling and redeposition of material on the patterned surface impairs DIC. A final set of five images was captured using the same imaging conditions as before to act as a final data point in the analysis.

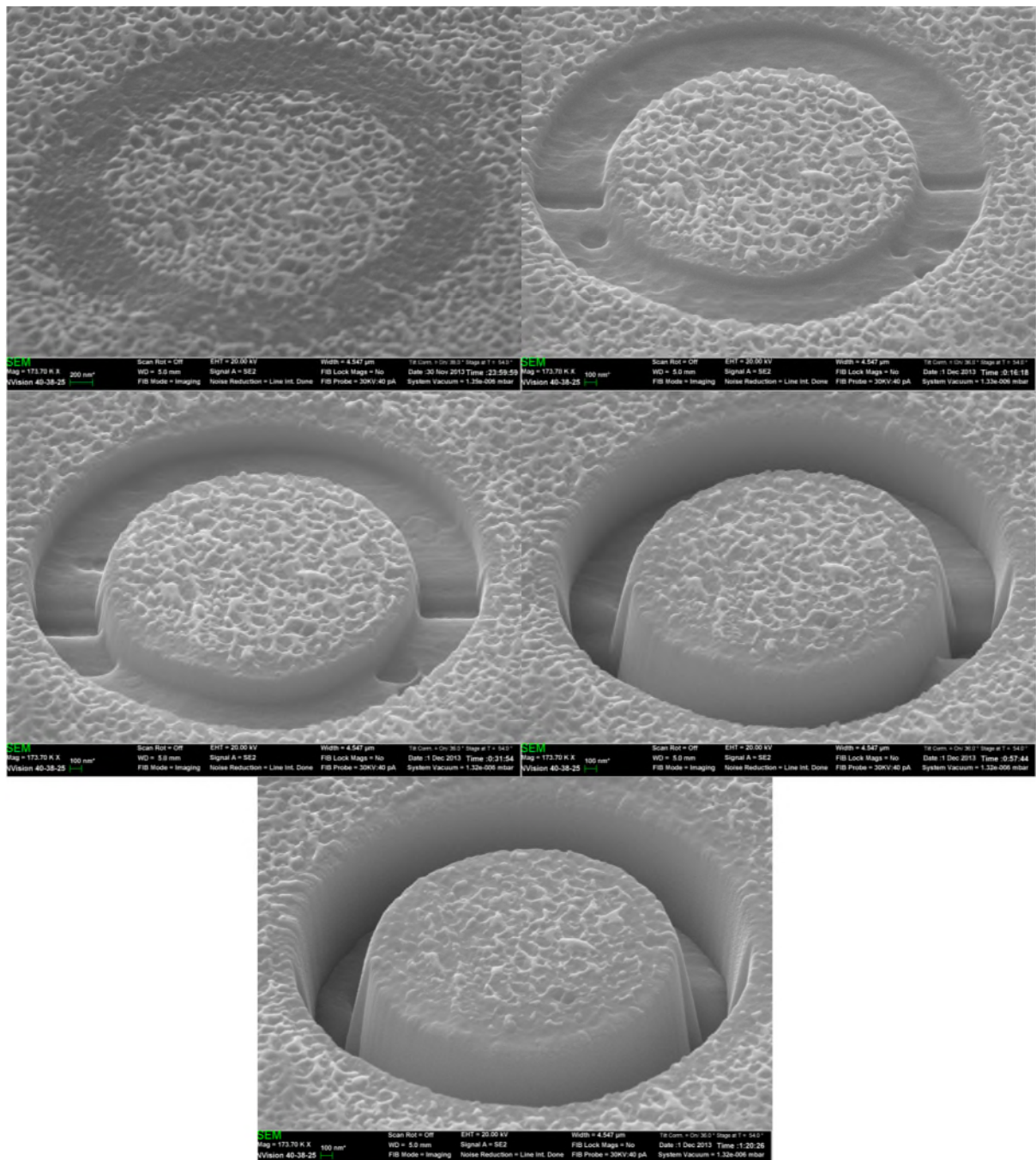


Figure 39 Showing the milling stages for a 54 day ZIRLO specimen. As the trench deepens the same features can be picked out on the island's top surface. Some slight obscuration of the gold coating pattern is evident but most of the features are still trackable. The minute movements caused by relaxation are not apparent to casual observation but can be measured using DIC.

Data Analysis

The images, stored as 32 bit, 3072 x 2304 pixel .tif files, were analysed using a digital image correlation package for MatLab written by Chris Eberl, Robert Thompson, Daniel Gianola, and Sven Bundschuh at Karlsruhe Institute of Technology and Johns Hopkins University[107]. This package uses digital image correlation techniques previously used to analyse the movements of stars in astronomical images executed using Matlab's proprietary language.

The program operates by defining many small windows over the image, finding peaks within the small windows and then matching these windows in subsequent images to determine the movement of features between the two image captures. From this movement the software can determine a two dimensional strain map of the sample. The software is also able to filter effects of strain (i.e. peaks moving in relation to one another) from the effects of translation and rotation (peaks moving together), which significantly simplifies data processing and accounts for small translational errors in image acquisition.

In order to compensate for large image displacements, first a coarse grid is defined from which the rough displacement is calculated. This step is shown in Figure 40.

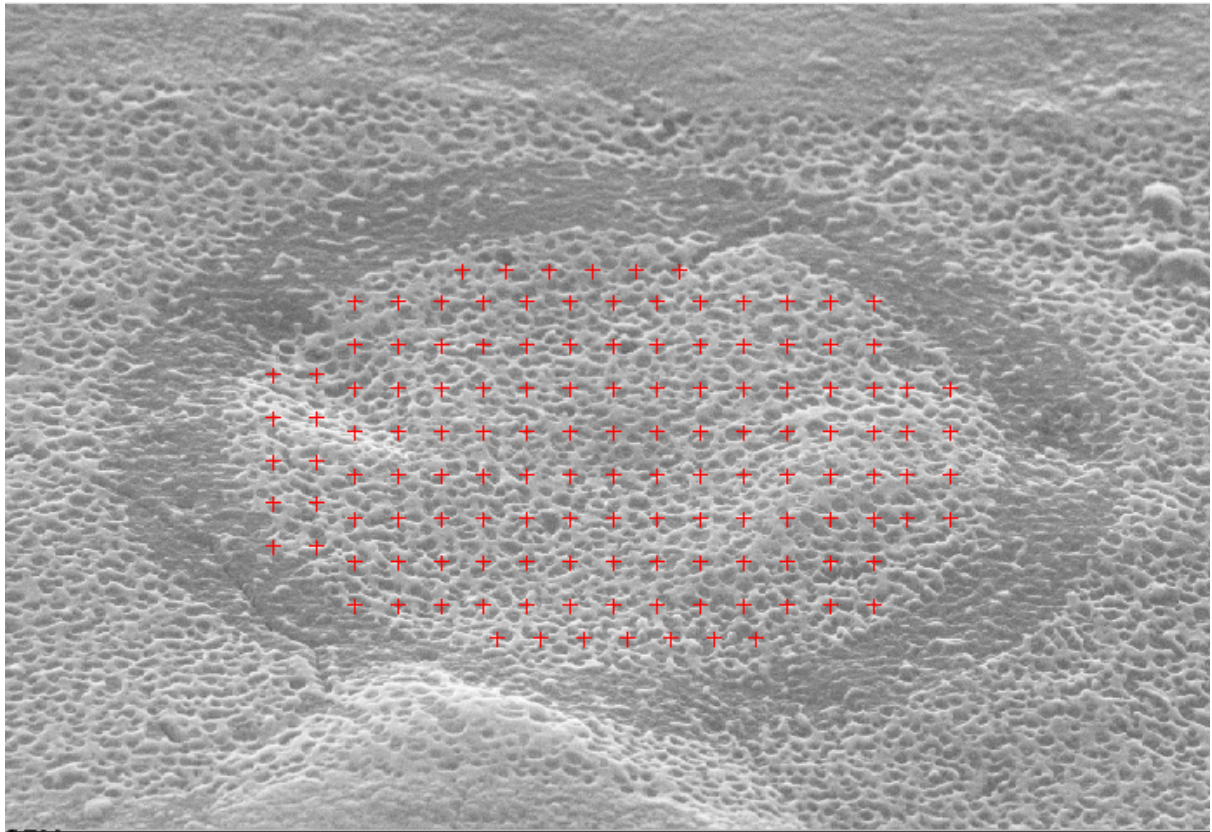


Figure 40 Using the initial image after defining the milling annulus, a rough grid of 150 widely spaced markers (red crosses) is defined in the region of interest in order to pick up and compensate for large sample displacements. The larger spacing and larger windows allows the software to detect movements beyond the size of the smaller windows used for fine measurement and to compensate accordingly. Also visible is the contrast between the gold surface imaged with the FIB beam, and the undisturbed surface at top.

A coarse grid is necessary as small windows may match a different peak from the expected one, and as such produce an erroneous result. The results of this approximate measurement are used to inform a second more detailed correlation.

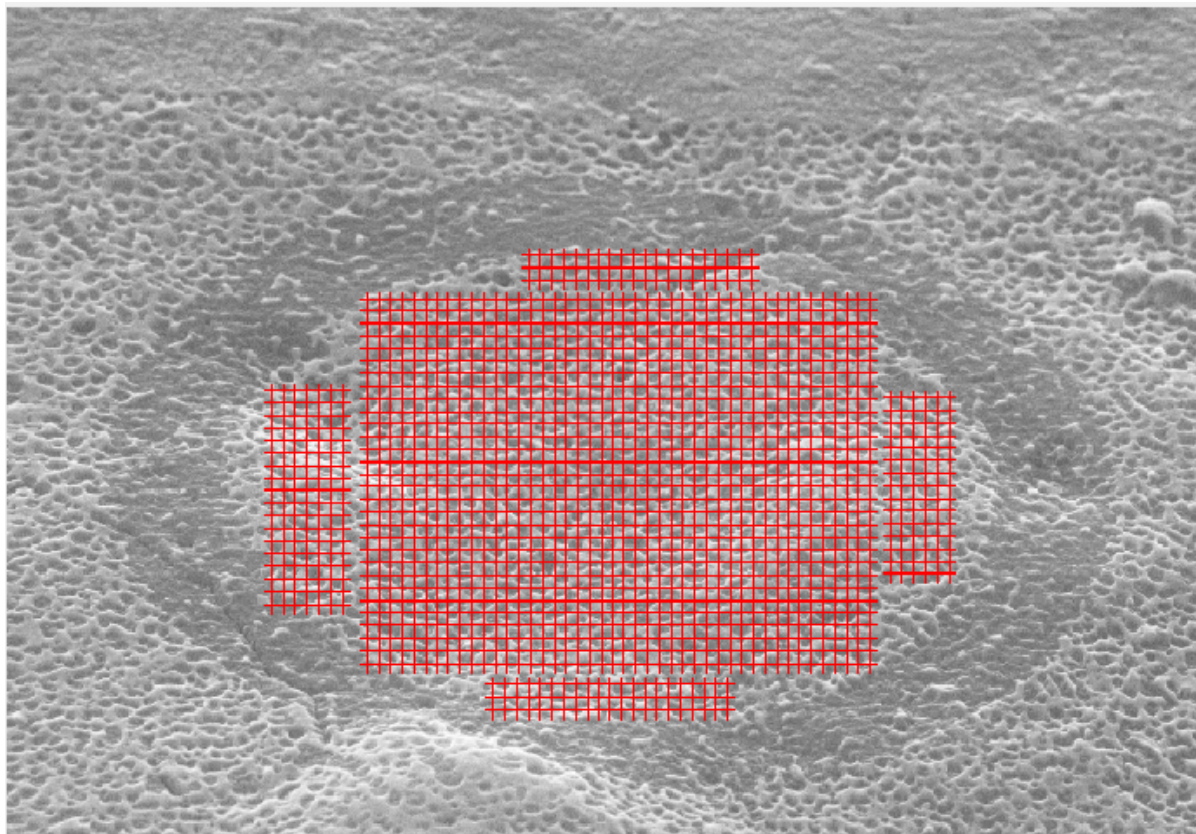


Figure 41 Once pre correlation is complete a new grid of 1500 markers is defined for detailed analysis of the same images. Since the position of each marker is tracked individually, the precise distribution of markers is unimportant.

The markers in the detailed grid are spaced at 30 pixel intervals, each centred on a 30 pixel window, providing maximum registration of the sample surface.

Calculation of strain proceeds by the program first tracking the rough markers through the series of images in order to calculate any large displacements. This list of large displacement between images is used when the final correlation of the fine markers is performed, in order to roughly position the markers before peak fitting, increasing the likelihood of the correct peak being used for tracking.

These markers are then tracked through the series of images to be processed and the movements of markers between images stored in a list of displacements.

With the images used in this experiment, processing time was not a limiting factor; the correlation of each set of thirty to forty images could be completed in approximately 20 minutes. It is possible to analyse thousands of images with thousands of markers in each but this would significantly slow calculation of displacements.

Noise reduction

Some noise in the image capture and tracking is unavoidable, and removing as much as this noise as possible improves the accuracy of the final calculations. Care must be taken when removing noise as data is inevitably lost; removing too much noise from the raw data can change the value of final strain measured for samples, as shown below.

The DIC package used for this analysis has a number of ways to filter marker displacement data, used to remove markers that have failed to track correctly. The method used in this analysis functions by calculating the relative movement of a marker from its 20 nearest neighbours for each image. Large shifts in marker position indicate a point has not tracked correctly (most likely a different peak has been selected in the sub image window and has correspondingly registered a large shift in position) and these points are removed before strain calculations are performed.

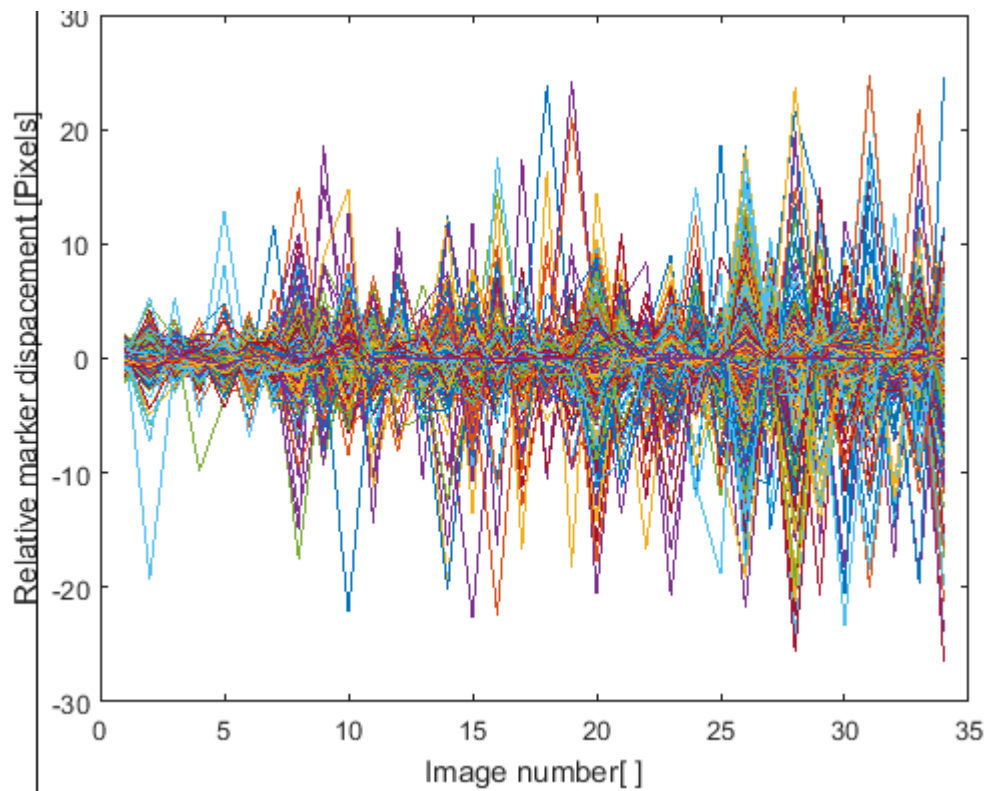


Figure 42 This graph shows the displacements of every individual marker through the correlation. Displacement is calculated relative to the marker's 20 nearest neighbours. Large displacements (for example, in excess of 10 pixels) are likely the result of mistaken tracking and this graph can be used to eliminate such points from the correlation.

Noise reduction has the potential to lose or discard information from the correlation, so the correct amount of noise to remove, the best way to do this and the effect of removing noise on the data must be considered.

A simple approach to removing noise would be to define a threshold of relative pixel movement, above which one could define a marker as badly tracked and this information discarded. The way a relative displacement between markers is calculated, however, means that markers with large relative movements due to misrecognition of markers will also affect

the relative movement of their neighbours, either creating or hiding large displacements in their neighbours.

The simple approach to noise reduction was tested by running a correlation and imposing various cut-offs of relative motion to act as noise filters. The results are summarised in Figure 43, showing the effect of drastic noise reduction. The raw data and the resulting strain calculation show noise up to thirty pixel relative movement, though the strain graph still shows a clear trend despite the noise. A ten pixel relative motion threshold smooths out the strain considerably in the latter half (i.e. where most movement has actually occurred) though does not perform well in the early part of the curve, introducing several large spikes.

Thresholding the data to a 5 pixel movement eliminates almost all noise in the late part of the graph, though again performs poorly in the early part of the curve. Both applied thresholds significantly reduce the measured strain calculated from the images. The maximum strain achieved by using the raw data is 3.5×10^{-3} , whilst imposing a severe threshold which removes all points moving more than five pixels reduces this strain by almost an order of magnitude.

A more sensitive approach to noise reduction is to successively apply filters to the relative movement of points rather than one large filter that captures many points. This involves only removing points that are clearly very badly tracked, rather than all points with higher than average movement. This approach allows badly tracked markers to be removed, and then the relative movements of the other markers can be recalculated without the effect of these badly tracked markers affecting them.

This approach is shown in Figure 45, where the effect of removing noise by subsequently applying thresholds of 25, 20, 15, 10 and 5 pixel movement as noise cut-offs on the calculated strain is demonstrated. Strain graphs A, C and E show ultimate strain values of approximately 3×10^{-3} whereas strain graphs G and I show that the calculated strain is

beginning to reduce, suggesting significant data is being lost from the calculation at these thresholds. Between graphs E and G there is also an apparent change in the shape of the strain graph, where the latter part becomes noticeably flatter. The noise graphs H and J (corresponding to thresholds of 10 and 5 pixel movement) show that noise is drastically reduced in the later part of these graphs. This could suggest that either data is being lost in the latter half of the graph, or the continuing upward slope of the graphs with lower noise reduction is in part an artefact.

A systematic approach to applying the filters reduces the chance to introduce bias into results, as could happen by subjectively judging the correct value of filters to apply.

Comparing the data where noise has been reduced with one large pass or sequential passes as shown in Figure 44 reveals some of the benefits of this approach. Graphs C and D (which employed multi pass filtering) show less noise in the strain graph and relative motion graph, whilst also preserving more of the calculated strain, as the single 15 pixel filter shows a significant reduction in calculated strain. In fact strain graph D shows a final strain very close to the value attained from the raw data of 3.5×10^{-3} .

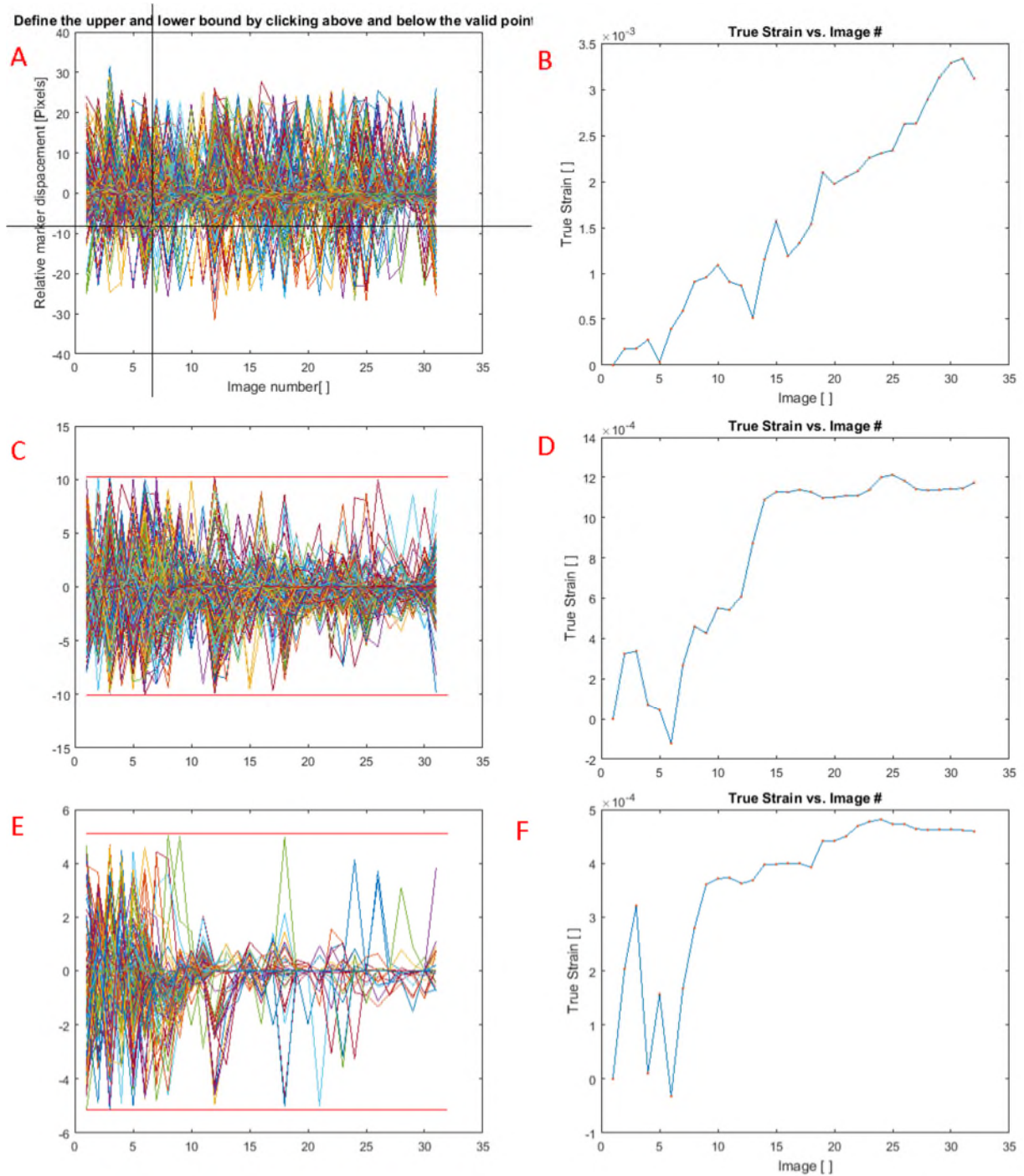


Figure 43 A shows the relative pixel movements (noise) from a correlation performed on a series of images from a 34 day ZIRLO sample; this data has not had the noise reduced and shows the full raw data. B shows the average strain calculated from this data without any noise reduction. C shows the same correlation noise thresholded to remove any points which have moved a distance greater than 10 pixels compared to their neighbours. D shows the

resulting strain calculation. E Shows data from the same correlation thresholdled to 5 pixels movement, and F, the resulting strain calculation.

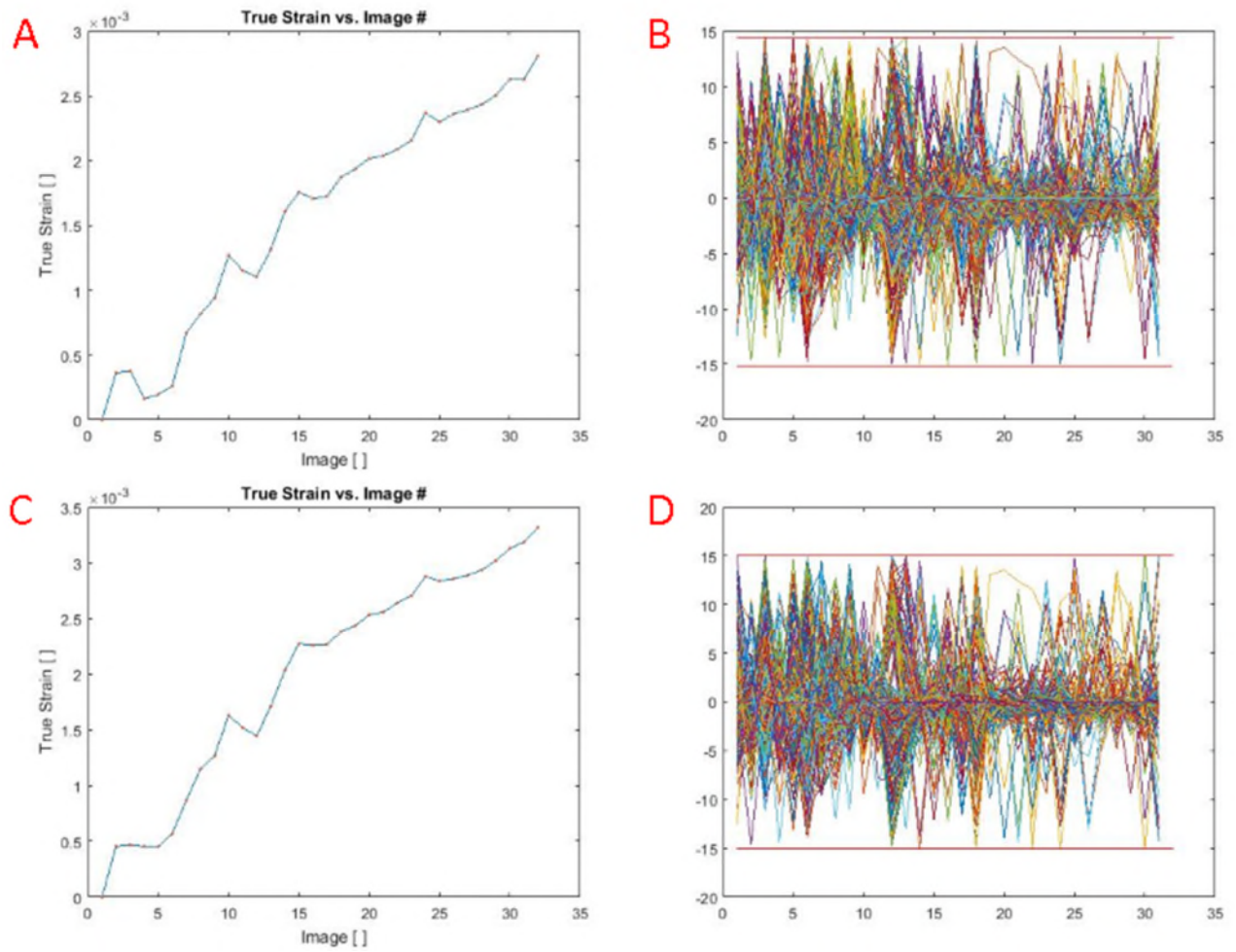


Figure 44 Showing the results of different approaches to noise reduction, Strain graph A and noise graph B show the results of applying a single 15 pixel filter, whilst graphs C and D show the results of progressively applying 25, 20 and 15 pixel filters.

Whenever noise thresholds were used to delete badly tracked markers they were applied at exactly the same threshold above and below the zero line so as not to introduce a bias towards expansion or contraction in the results. The large numbers of markers used in these

correlations should mean approximately equal numbers of markers are badly tracked in “compressive” and “tensile” directions (i.e. towards and away from the centre of the island)

Reviewing the different approaches to noise removal from correlation data, the process which gave the best data fidelity, maximum noise reduction and repeatability was determined to be the subsequent application of thresholds of 25, 20 and 15 pixel relative movement. Removing more noise than this significantly reduced the measured peak strain and altered the shape of the strain graph.

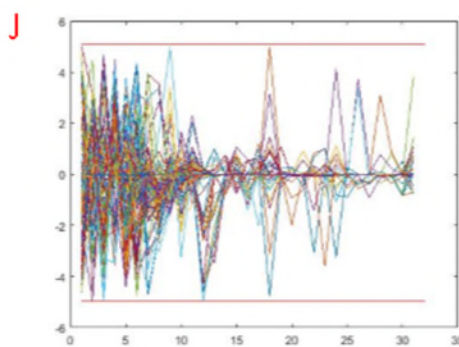
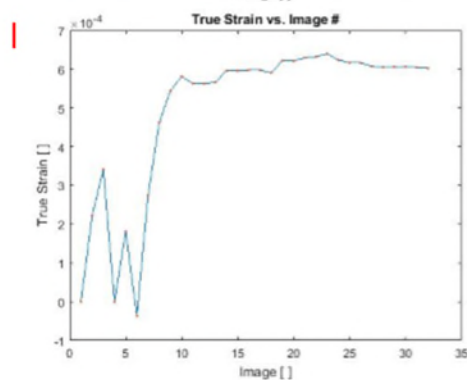
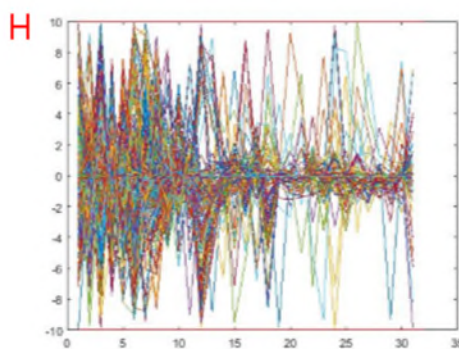
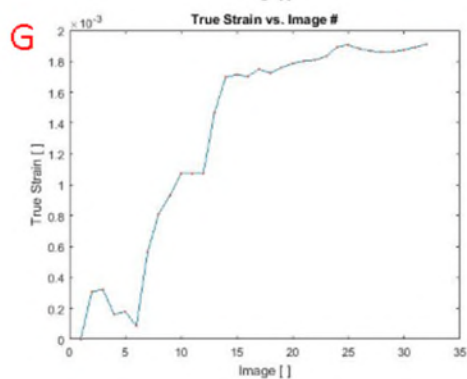
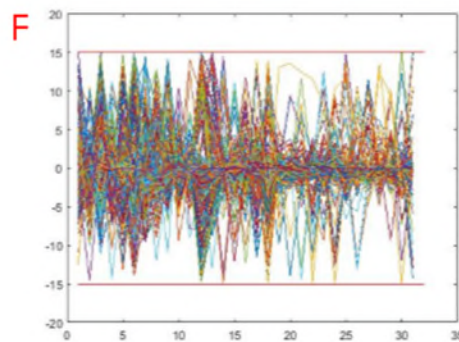
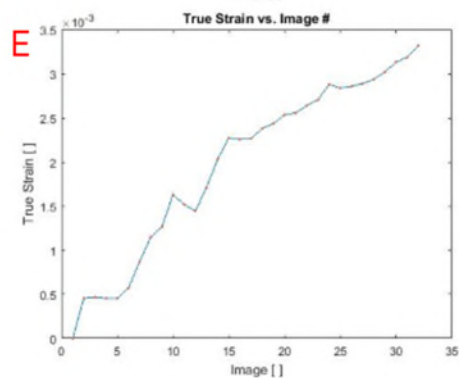
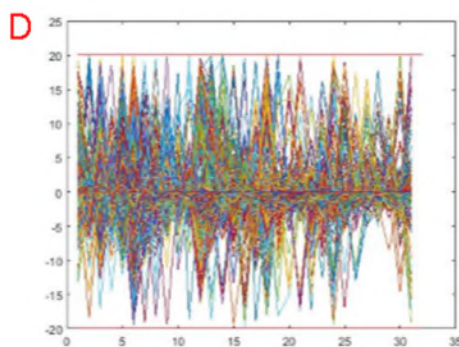
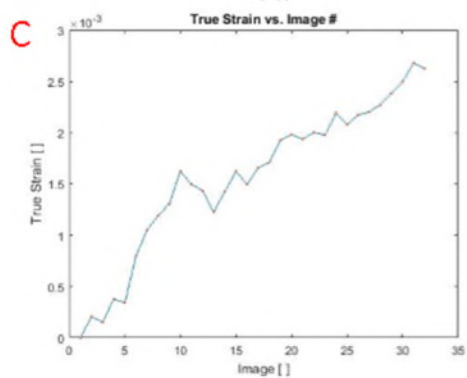
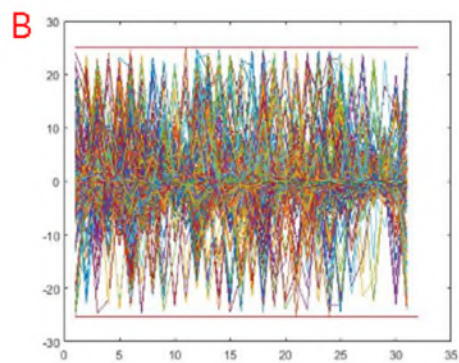
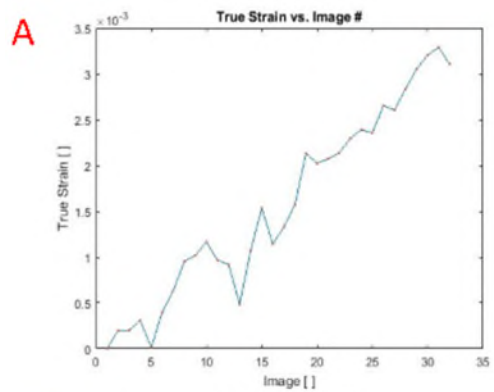


Figure 45 A set of true strain and associated noise graphs showing the progressive removal of noise and the effect on the calculated true strain. A and B show noise removal of all points moving more than 25 pixels, C and D show the subsequent removal of all points moving more than 20 pixels, E and F show removal of points moving more than 15 pixels, G and H show a cut-off of 10 pixels and I and J show the removal of points moving more than 5 pixels. As can be seen, early passes reduce noise whilst maintaining the value of peak stress, whilst the later filters of 5 or 10 pixels begin to significantly alter these results.

Strain calculation

After the grid of points is defined on the starting image, a 30 pixel by 30 pixel window around that point is examined to find a peak. This peak then serves as a datum to calculate the displacement of different parts of the image. The positions of the peaks are tracked through each subsequent image using the previously measured shifts to update positions and account for large movements.

The final position of the peak can be compared to the starting positions, and from this the displacement calculated. Figure 46 shows the calculated displacements from a typical correlation.

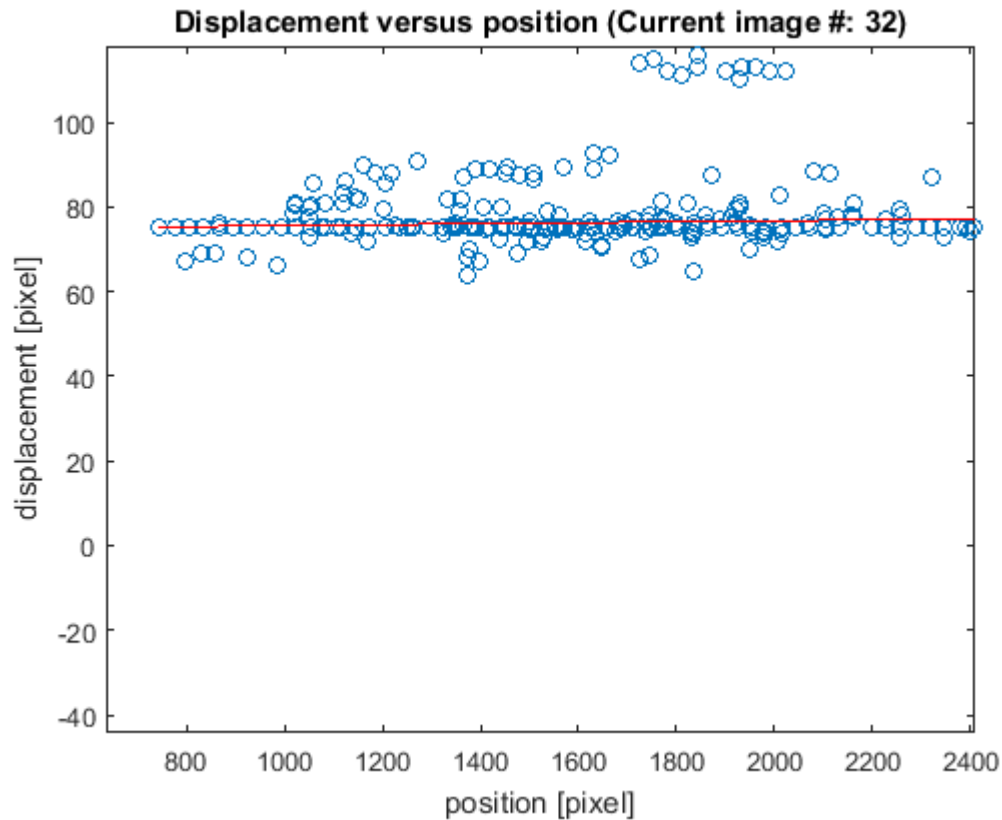


Figure 46 a graph showing the total displacements of markers between the initial and final images of a 32 image correlation. The X-axis is the position of a marker within the image and so starts above 0. The y-axis represents total displacement and includes total image displacement due to sample movement, etc. The red line indicates the gradient used to calculate the displacement divided by marker displacement.

Since each marker is individually recorded, the starting and final separations can be calculated for every pair of markers across the image. This change in marker separation, as well as the initial marker positions, can be used to calculate the average strain over the whole image. The averaged result, using every combination of markers possible, produced a much more reliable measure of strain compared to measuring the strain between any two points, as

it partially averaged out many of the effects of noise due to badly tracked markers and used many more markers as data points.



Figure 47 A strain graph calculated from the correlation shown in the previous figure. This is raw data without the removal of badly tracked markers. The positive strain shows an expansion of distance between markers. The final strain of 3.5×10^{-3} is reached progressively as the trench is deepened and more stress is relieved.

Calibration

In order to test the reliability and sensitivity of the DIC package and the suitability of these images a single image was selected and then modified with image processing software to

produce a set of standard images that have known scaling constants. This set of images was then analysed to find the measured strain and checked against the known scaling constants.

The image selected was an initial image of a 54 day ZIRLO sample, which was then edited using GIMP (GNU Image Manipulation Program, a free, open source image processor) to produce a series of 6 images, each one having been scaled up by 0.1 percent in the milled island of interest, corresponding to an enlargement of approximately 1 pixel in the 1000 pixel wide island. This set of images could then serve as a standard against which the accuracy of the correlation could be checked. GIMP was used to edit images because it retains the same bit depth of the image (necessary for accurate numerical comparison of brightness values), uses cubic interpolation for scaling images (which reduces errors compared to other methods) and allows saving images in an uncompressed .tif format.

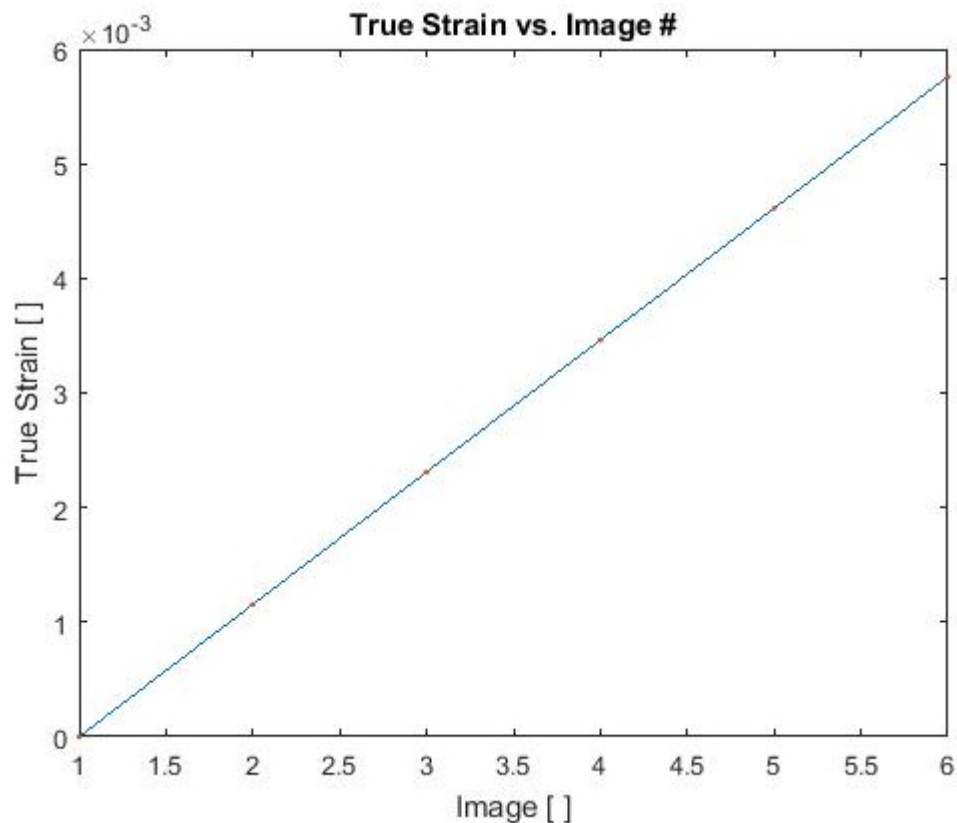


Figure 48 The strain graph produced by performing DIC tracking on the set of artificially scaled images. The straight line matches the consistent scaling of the calibration images. The

fact that the points all lie directly on the line shows that the random error associated with tracking is very low. The final strain value (0.575%) is slightly lower than the expected 0.6%.

Figure 48 shows the strain graph calculated from the correlation of these set images. The images were manipulated to have an enlargement of 0.1 percent in 6 steps. The total enlargement of 0.6 percent is well measured by the correlation software, with the final measurement being 0.575 percent. This small error is likely caused by effects on the pixel level, as a cubic interpolation of a signal on a pixel scale cannot produce a perfectly smooth result.

Figure 49 shows the low noise levels produced by this correlation. The largest relative movements of markers is approximately 0.5 pixels, which indicated extremely high tracking fidelity. This ideal scenario in which the same image (eliminating errors due to noise, or sample movement) is rescaled, leaving behind only the error caused by the correlation process itself. This error appears to be less than 0.5 pixels over a 1000 pixel island. Rescaling the same image eliminates errors caused by redeposition on the surface of the sample obscuring features. The error also includes any error introduced by a cubic interpolation caused by the image manipulation.

Repeatability of the images is another possible source of error in correlating them. As each sample was imaged multiple times between milling steps, this set of images of the same surface present an opportunity to test the noise inherent in the images and quantify this source of error.

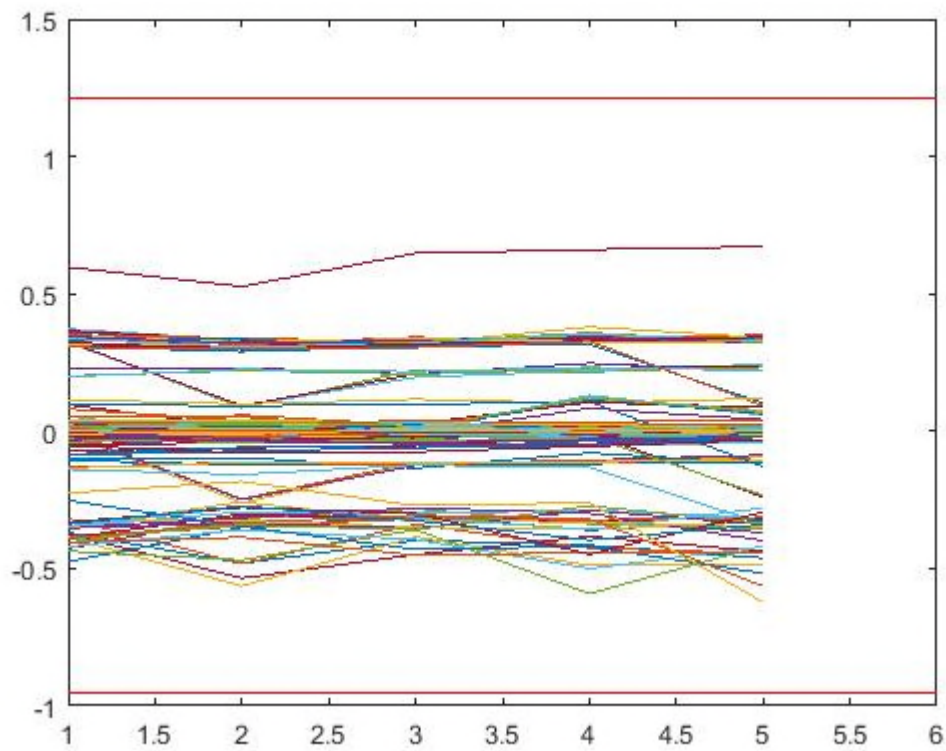


Figure 49 This graph shows the relative motion between nearest neighbour markers for the DIC performed on the artificially scaled images. The noise level does not exceed 0.5pixels, implying an extremely low tracking error for this process.

A 34 day ZIRLO sample was imaged 6 times and a correlation performed to pick up any apparent strain between these images. Any enlargement detected would indicate a systematic error in the imaging conditions, such as thermal drift, electrostatic charging effects or other artefacts.

Figure 50 shows the strain calculated from this imaging procedure. The extremely small values (on the order of 10^{-5}) show that imaging is not a significant source of error in this procedure. Additionally, graphing relative displacements of the points as a proxy for noise in the images (Figure 51) shows very small values of relative marker displacement compared to those found in a correlation of real data.

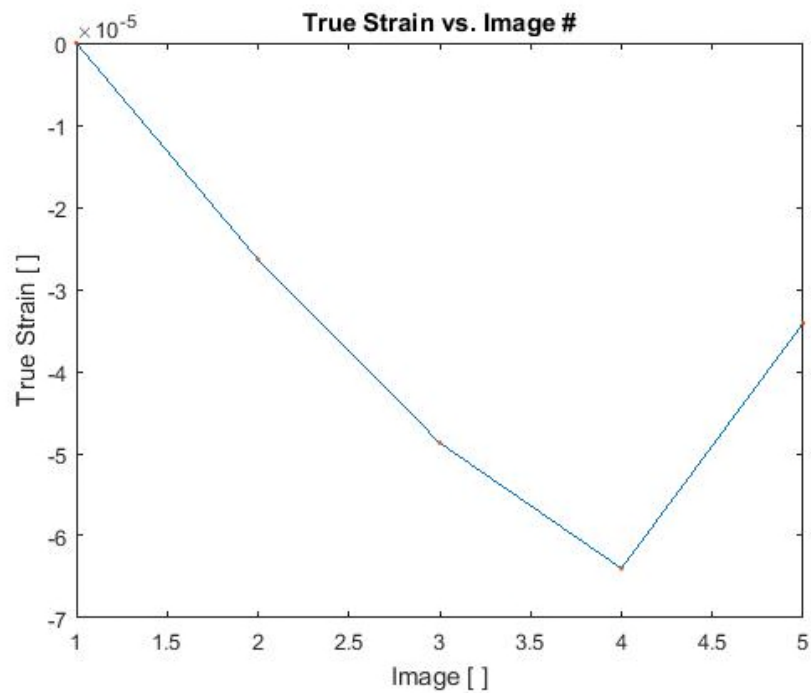


Figure 50 Strain graph showing the result of correlating multiple images of the same sample without milling between steps. The extremely small strain values (order 10^{-5}) indicate a negligible effect of imaging artefacts in the final result.

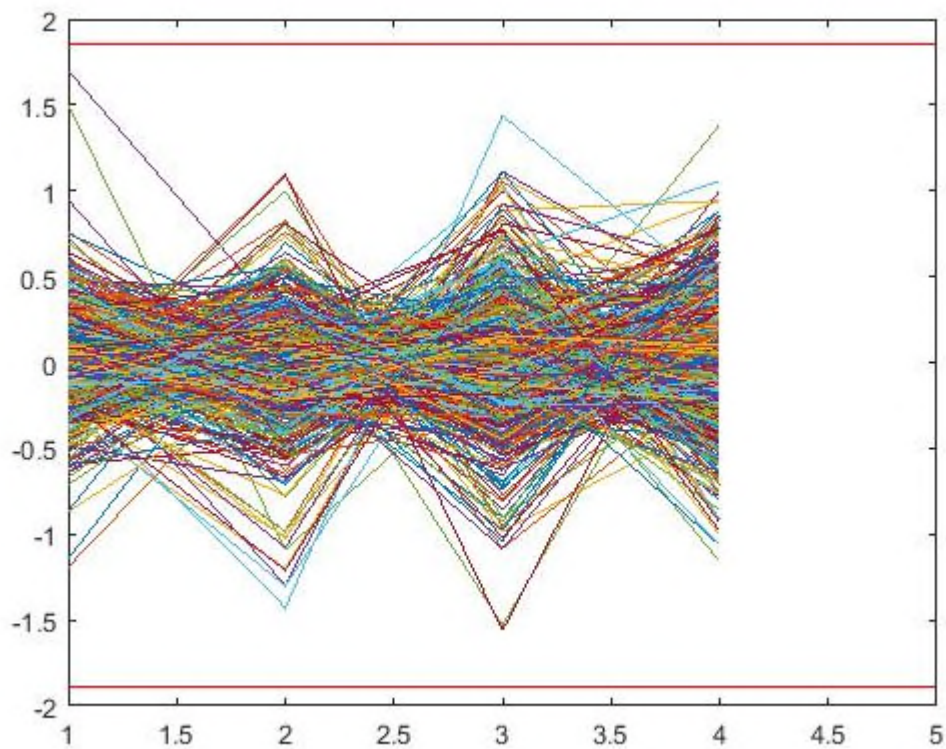


Figure 51 A graph of relative displacements of markers used in the imaging conditions test. Most values are less than one pixel. The homogeneous distribution of noise (above and below the 0 line) shows that this noise, whilst larger than the actual values of apparent strain picked up in the images, is mostly self-cancelling, thus not affecting the results.

Results

Having established a consistent procedure for distributing markers, running the correlation and reducing noise and calculating strain, results can now be processed in a consistent way.

Samples were produced with ZIRLO coupons having undergone 54 and 100 days of total oxidation in conditions closely matching those of a PWR to gather results from material that is both pre transition and post-transition. By using the same samples studied elsewhere in this

research it also allows a comparison to be made between techniques to gain the fullest possible understanding of the sample conditions at each stage of oxidation.

Table 5 shows the final strain measured from each area measured on 54 and 100 day ZIRLO samples.

Table 5 This table summarises the samples used and the final strain measured by DIC after the last milling step.

Site	Final Strain	
	54 Days Oxidation	100 Days Oxidation
α	5.8×10^{-3}	
β	8.4×10^{-3}	
γ	6×10^{-3}	
δ		7.5×10^{-4}
ϵ		2×10^{-3}

The measured strain figures for the two classes of samples show that the 54 day samples have consistently higher final strains than the 100 day samples. The 54 day results are also clustered quite tightly together. The 100 day samples show lower final strains, but of particular note is the site δ result showing a much lower strain than any other (an order of magnitude lower than the 54 day samples). The large disparity between the two 100 day samples is certainly a result worthy of investigation in the context of the transition expected at around this oxidation time.

These results are presented in more detail in Figure 52 through to Figure 56. The figures include the first and last images of the milling run (omitting intermediate steps), a graph of the displacements of all markers from their initial positions, a graph of relative marker

movement representing noise and the averaged one-dimensional strain for all intermediate image steps.

The start and end images (A and B) show the overall process and the graph of displacements (C) shows the total displacement of every marker based on its position in the image. A graph of noise is included (D) based on movement relative to immediate neighbours to give an idea of the point in the process at which most noise occurs. The final graph of one-dimensional average strain (E) is the most important result, and shows the strain in the oxide relieved by the milling procedure.

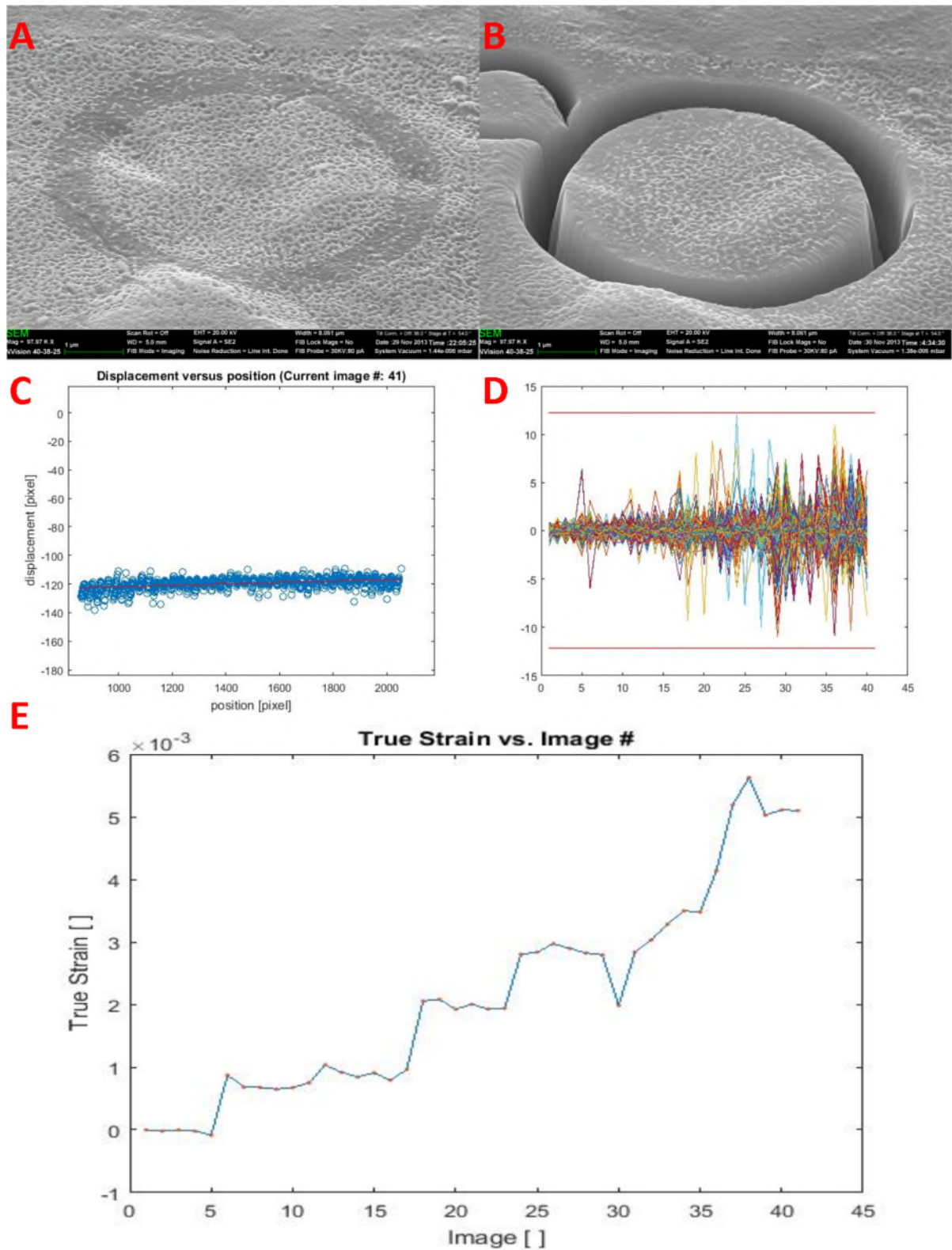


Figure 52 A site on a 54 day ZIRLO sample. A shows the region of interest before milling, B shows the same region after milling has been completed, some slight obscuring of the surface pattern can be observed. C is a graph of the displacements of all markers from their initial

positions, and as can be seen there is only a small scatter. D is a graph of the noise, which increased in later steps. The strain graph E shows the relaxation of stress as the material is freed from the larger sample. Additionally, the individual milling steps and series of five images can be seen between steps as plateaus and sudden increases in the strain.

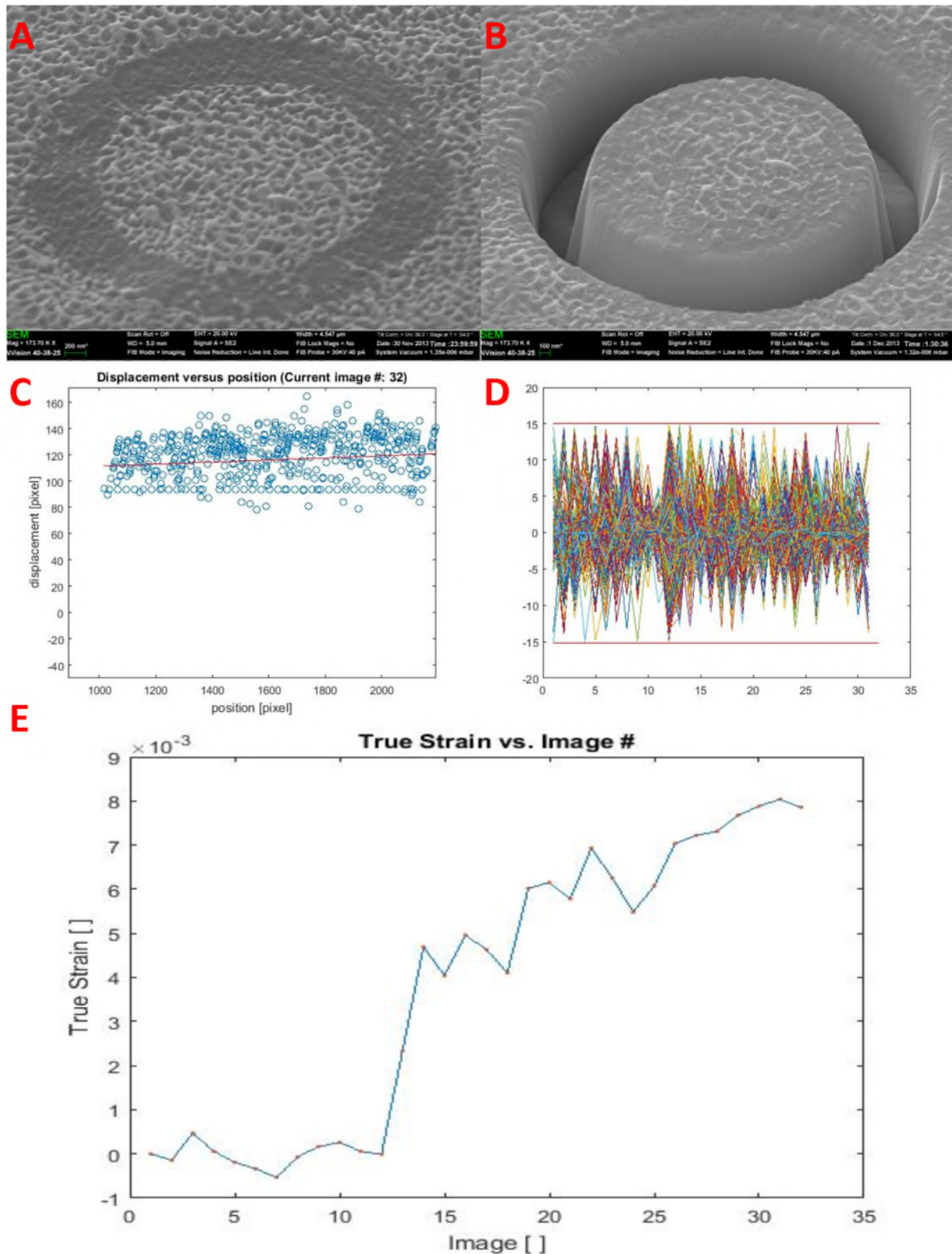


Figure 53 β site on a 54 day ZIRLO sample. A shows the region of interest before milling, B shows the same region after milling has been completed, some slight obscuring of the surface pattern can be observed. C is a graph of the displacements of all markers from their initial

positions; some of the displacements lie away from the main distribution indicating a degree of noise remains in the tracking. D is a graph of the noise, which remained almost constant throughout the process. The strain graph E shows the relaxation of stress as the material is freed from the larger sample. Initially, little stress is relieved but around image twelve a much larger jump in the measured strain occurs.

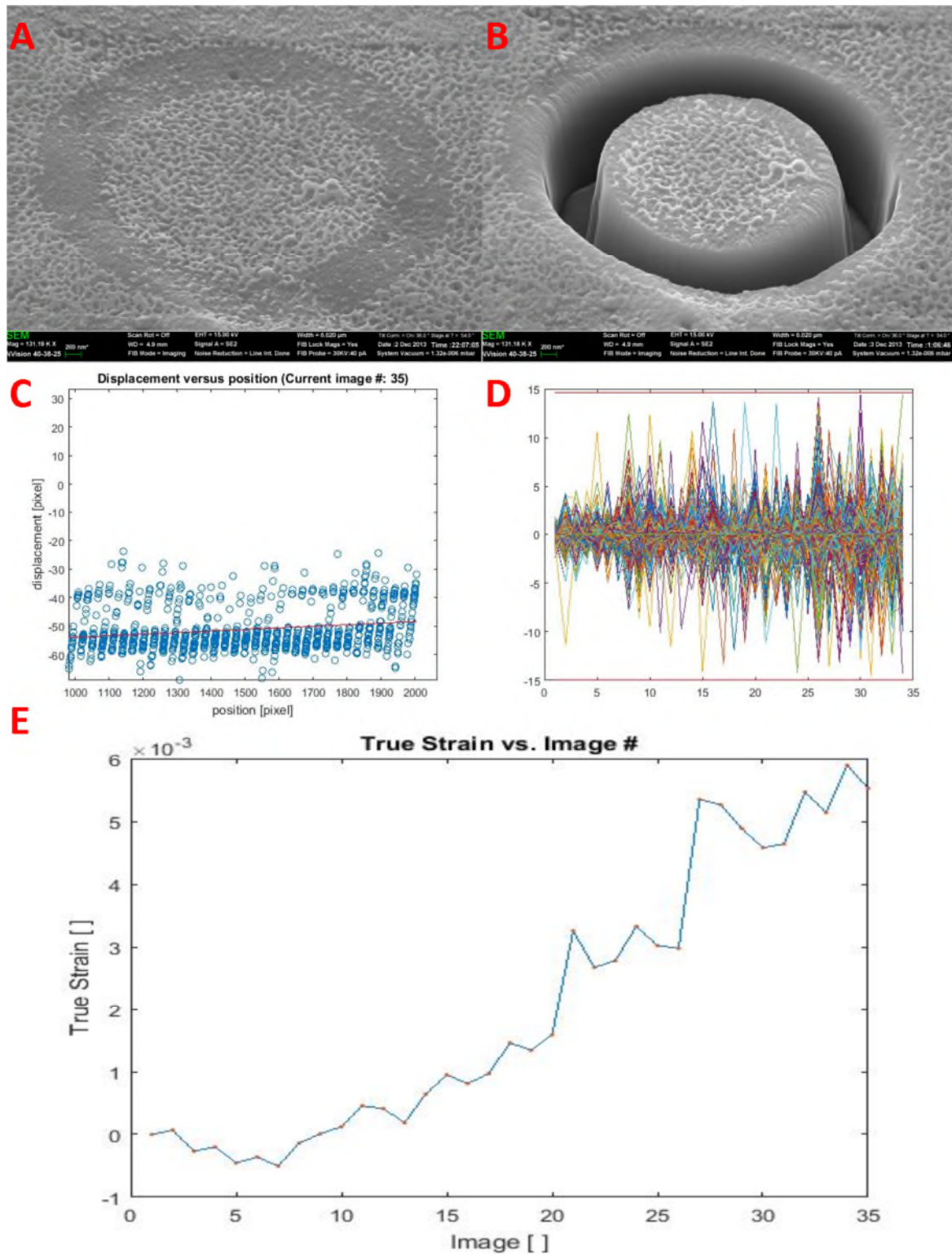


Figure 54 γ site on a 54 day ZIRLO sample. A shows the region of interest before milling, B shows the same region after milling has been completed, some slight obscuring of the surface pattern can be observed. C is a graph of the displacements of all markers from their initial positions; some of the displacements lie away from the main distribution indicating a degree

of noise remains in the tracking. D is a graph of the noise, which increased in later steps. The strain graph E shows the relaxation of stress as the material is freed from the larger sample. Additionally, the individual milling steps and series of five images can be seen between steps as plateaus and sudden increases in the strain.

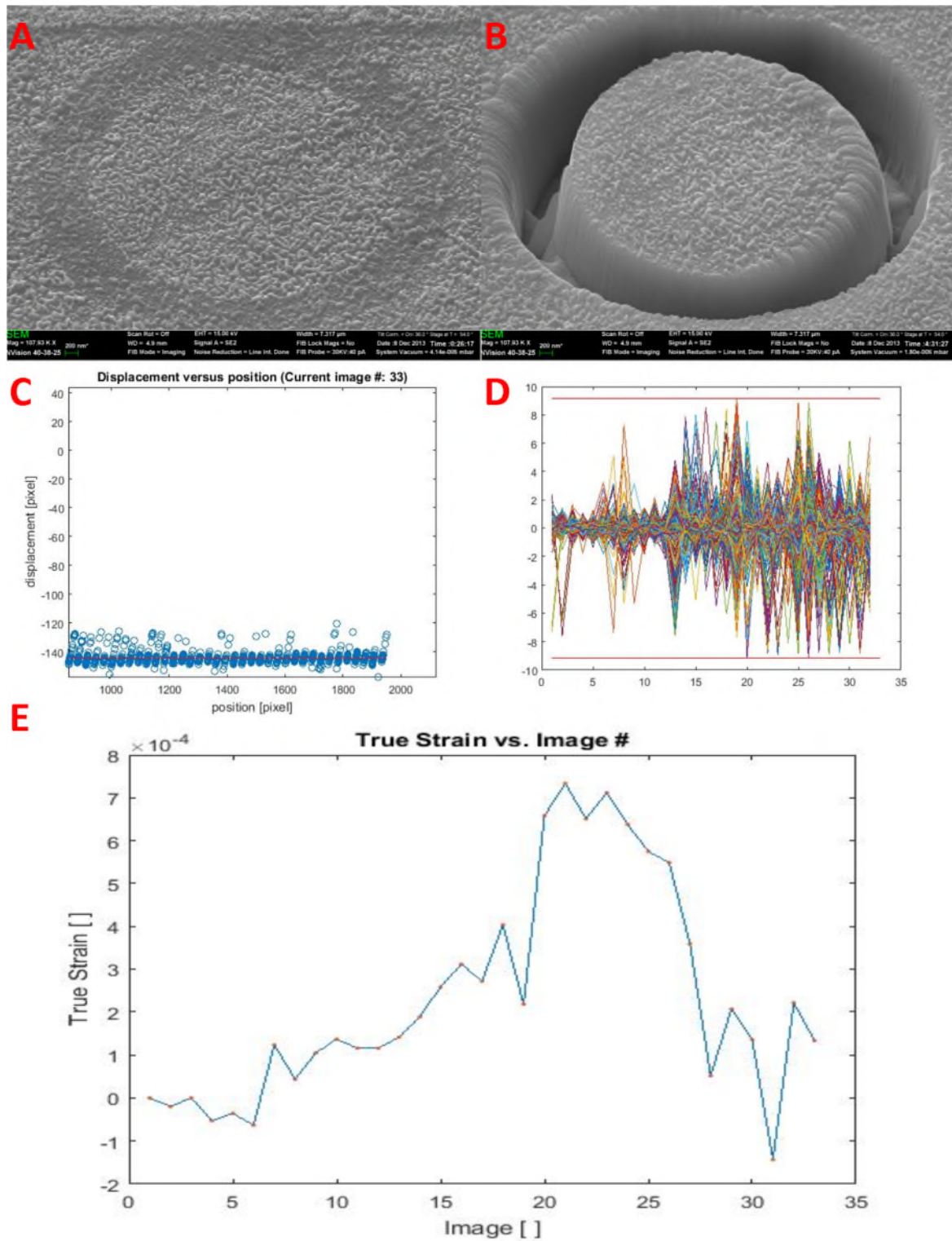


Figure 55 δ site on a 100 day ZIRLO sample. A shows the region of interest before milling, B shows the same region after milling has been completed, some slight obscuring of the surface pattern can be observed. C is a graph of the displacements of all markers from their initial positions; there is little scatter. D is a graph of the noise, which increased in later steps. The

strain graph E shows the relaxation of stress as the material is freed from the larger sample.

This strain graph shows a different behaviour, where strain reaches a maximum, value before declining. This may be the result of milling into the metal at the end of the milling run

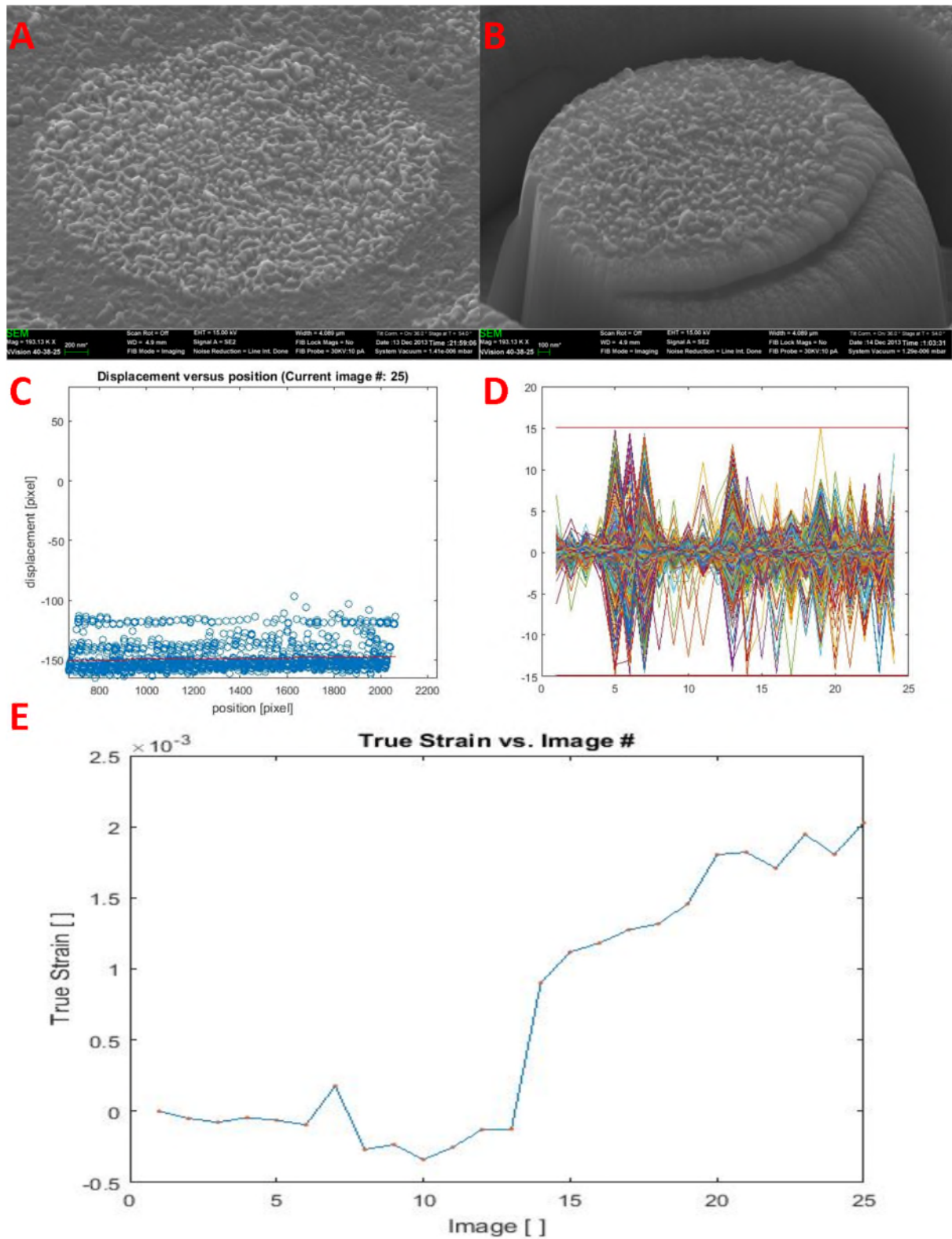


Figure 56 ϵ site on a 100 day ZIRLO sample. A shows the region of interest before milling, B shows the same region after milling has been completed, some slight obscuring of the surface pattern can be observed. C is a graph of the displacements of all markers from their initial

positions; some of the displacements lie away from the main distribution indicating a degree of noise remains in the tracking. D is a graph of the noise, which remained almost constant throughout the process. The strain graph E shows the relaxation of stress as the material is freed from the larger sample. Initially, little stress is relieved but around image twelve a much larger jump in the measured strain occurs.

One-dimensional strain graphs

All the one dimensional strain graphs show similar behaviour as the depth of milling increases. Initially very little strain is relieved over the first few images with the line staying mostly level. As milling proceeds the amount of strain relieved increases, in some samples (such as ϵ and β) this jump is quite abrupt, whilst other samples show a slower release of strain (α , for example). Towards the end of the milling procedure the rate of strain relief again slows, although no samples show a perfect plateau and as such it is likely that not all strain was relieved.

All 54 day samples (α , β and γ) showed similar final values of strain relief, although the profiles of strain relief did show a difference, with α and γ showing a relatively constant rate of strain relief and β showing a large jump in strain between images 12 and 13. This large jump (when a strain of 5×10^{-3} was released) seems not to be noise as the value of released strain is maintained in subsequent images. This may indicate the presence of a highly stressed region in the oxide at a depth passed through in the previous milling step.

Looking at the noise graphs for the three 54 day samples shows that α and γ both had low noise in the early stages of milling (particularly in the case of α where relative motion was as low as 1 pixel in the early images and milling steps), whereas β showed a relatively constant level of noise throughout. Interestingly, the lowest noise region of the β milling process was around image 12, exactly where the high jump in strain released occurred. This may indicate

that the true value of the strain was being hidden by noise in the early images before suddenly being picked up around image 12, although there is no obvious reason this should be the case as all samples followed the same milling and noise reduction procedures.

The 100 day samples showed two distinct profiles in the calculated one-dimensional strain graphs. Sample ϵ showed a similar profile to the 34 day samples, although the ultimate strain was much lower (2×10^{-3} compared to an average of 6.7×10^{-3}), in which strain was released mainly in one large event around image 14 and then more slowly until the end of the milling process. Again this large release in strain does not seem to be an artefact as the strain value is maintained in subsequent images, and is also accompanied by a reduction in the amount of noise (Figure 56 panel D), which also suggests this result is reliable. Sample δ initially showed the familiar pattern but differed in two aspects, firstly the total released strain was an order of magnitude lower (7.5×10^{-4}) and secondly it shows a sharp drop in the released strain around image 25. This reduction in strain is accompanied by quite a large amount of noise (Figure 55 panel D), which when examined closely appears to be skewed below the zero line with many peaks reaching all the way down to the lower noise bound. A pronounced skew in the noise when taken in the context of the much smaller strain released may account for this apparent “re-straining” after image 25.

All the one-dimensional average strain graphs are plotted with the image number as the dependent variable, as opposed to depth of milling. Additionally, the images are taken in batches of 5 after a milling increment; this can be seen particularly well in site α where the strain graph shows individual flat plateaus for groups of five images and then a step to the next plateau. Ideally, the released strain would be plotted against depth for all strain graphs. However, the milling steps are not necessarily of constant depth because as the milled trench becomes deeper, redepositing of material increases and slows the rate of milling because

material must be removed twice. This complicates the correlation between released strain and depth.

Some depths at important points in the milling process can be obtained, however, as all images are stored and many images can be directly measured to ascertain depth. For example, the ϵ site showed a distinct jump in released strain between images 13 and 14. The direct measurement of the image is shown in Figure 57, and from this it can be seen that a much larger depth has been milled, accounting for the larger than average release in residual stain. The total depth milled between these images is 520 nm.

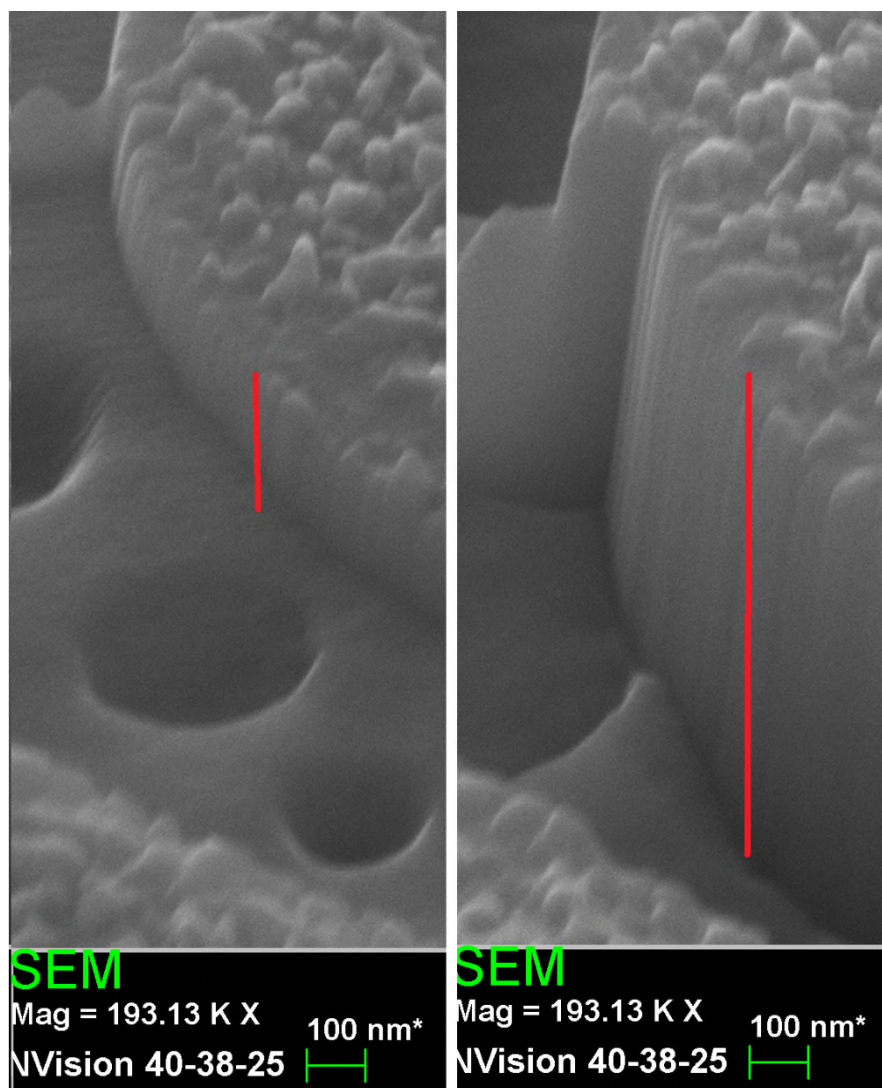


Figure 57 Depth measurement of ϵ site coinciding with the large jump in relieved stress between images 13 and 14, the trench depth of in image 13 is 250 nm and the trench depth in image 14 is 770. The change in depth being 520 nm

Site β exhibited a similar jump in released strain between images 12 and 13, as examined in Figure 58. Here, the total change in depth (from 200 nm to 410 nm) was much lower, but correlated with a 3×10^{-3} release of strain. This indicated that this layer was more stressed than that exhibited in the ϵ sample, which showed a 1×10^{-3} release of strain over 520.

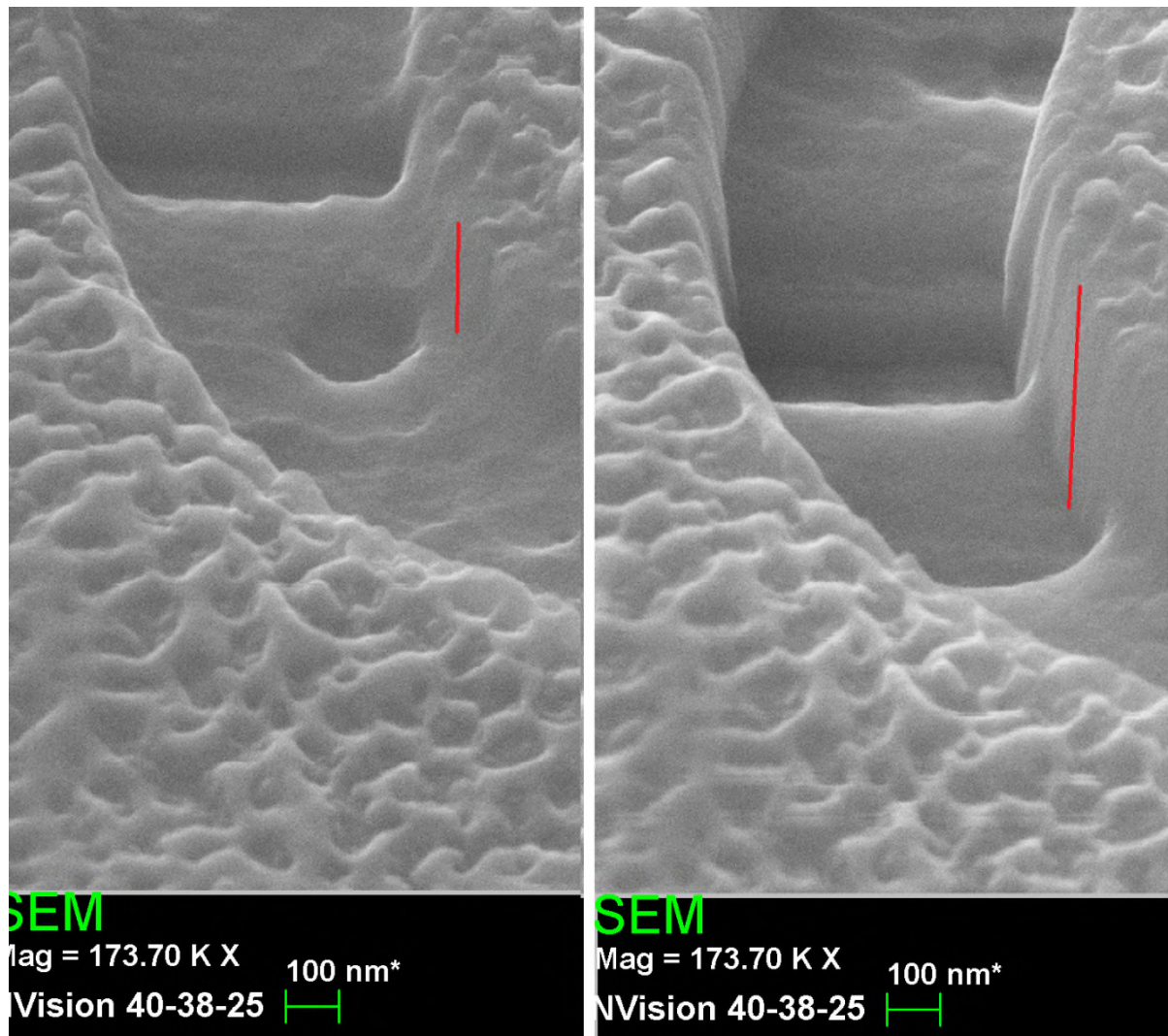


Figure 58 Referring back to the change in depth between image 13 and 14 on the β site sample. The depth in image 13 is 200 nm and the depth in image 14 is 410 nm. The total change in depth is 210 nm.

For some samples it was possible to plot the strain against depth for all steps in the milling process as the trench could be directly measured even in the later stages. This is shown in Figure 59 where data for the α site is replotted with depth as the controlled variable. Comparing it to the unnormalised strain graph shows a slightly different shape where the

release of stress in the latter half of the milling process is slower than portrayed in the raw data. Unfortunately it was not possible to do this for all samples.

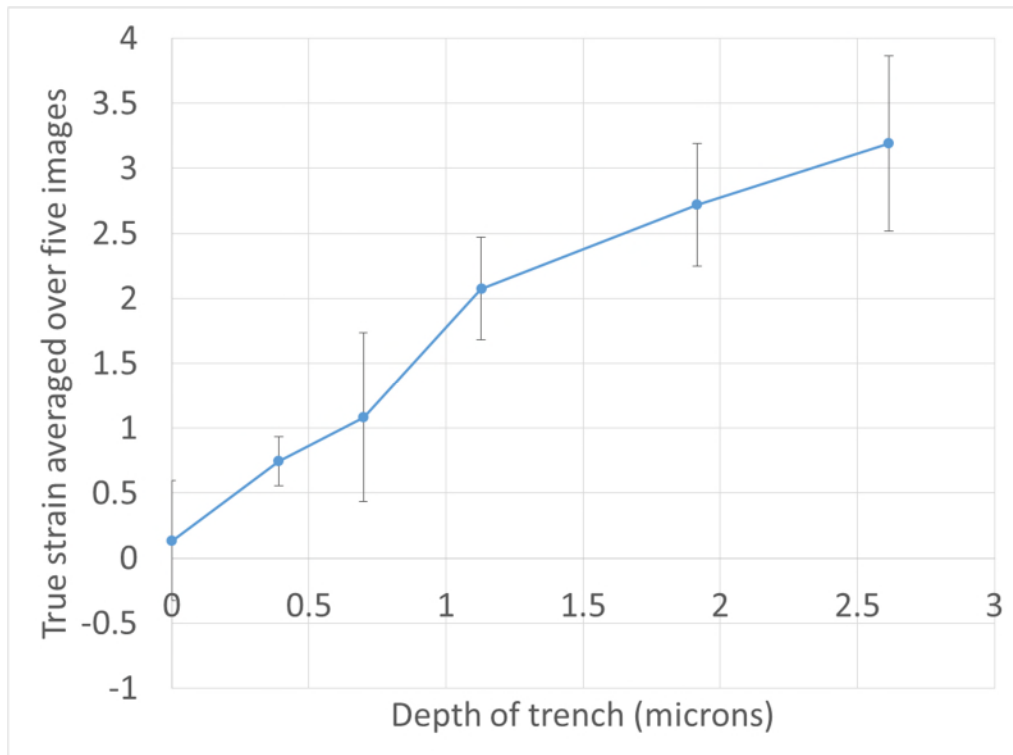


Figure 59 A graph of strain ($\times 10^{-3}$) against milled depth for the α site images. Milled depth determined by direct measurement of the back face of the trench. Compared to the graph which was not normalised against milling depth, it can be seen less stress is released in the latter stages of the milling process.

Stress evaluation

The one-dimensional plane strains can be recovered from measurements of images, but extracting the stress that causes these strains requires further calculation. The particular case of determining the stress in zirconium oxides is somewhat complicated by a number of factors such as the coating/substrate arrangement of material, the nanocrystalline oxide, the possible presence of large horizontal cracks in the oxide, differing stress at different depths in the oxide and anisotropy of the oxide crystal shape (columnar, oriented normal to the metal-oxide interface).

The stress state in the material can be assumed to be equal in both in-plane directions, with a near zero component of stress normal to the plane due to the free surface of the exterior oxide. The grain size of the oxide is small compared to the size of the milling island, and the stress in the oxide is entirely compressive (as it arises from a volumetric expansion), and so the assumption of continuum mechanics (i.e. the whole island can be considered as one homogenous solid, rather than considering individual grains and boundaries) is not unreasonable.

The ring core milling work undertaken by Korsunsky et al [103] has considered the stress states of annular milling trenches for continuum based systems using both classical elasticity equations and finite element based analysis. The annular trenches are designed to relieve all stress in the oxide layer, and assuming sufficient depth of milling this condition should hold true [103, 104]. In this case the final milling depth of most trenches was between 1.5 μm and 2.0 μm , which is of the same order as the diameter of the island (approximately 3 μm). Ideally milling would have continued deeper, but this presented problems. As the trench became

deeper, milling slowed and the redeposited material on the sample surface became more of a problem. Reducing the size of the island would reduce the surface area of the top and therefore the number of marker tracking locations, and increase the relative errors associated with imaging. The strain graphs show a distinct reduction in strain release towards the end of the milling procedure, which suggests that the strain relief is either complete or nearly complete.

Considering the oxide as a continuous media that deforms elastically one can use Hooke's law to estimate the stresses relaxed between the initial undisturbed state and the fully milled island. Considering only the in-plane stresses and assuming the out-of-plane stress is negligible

$$\sigma_3 = 0$$

and assuming the stress is equibiaxial sets

$$\sigma_1 = \sigma_2$$

then if the strain change between the milled and unmilled states is $\Delta\epsilon$ then Hooke's Law shows

$$\Delta\epsilon = \frac{1}{E} (\sigma_1 - \nu\sigma_2 - \nu\sigma_3)$$

which for in-plane, equibiaxial stress simplifies to

$$\Delta\epsilon = \frac{\sigma(1 - \nu)}{E}$$

And solved for the residual stress

$$\sigma = \frac{E\Delta\epsilon}{(1 - \nu)}$$

This equation is also assumed to be true for all increments of relieved strain at intermediate milling steps [104].

An appropriate value of the Young's modulus of zirconium dioxide to use in these calculations will necessarily be a simplification of the full picture where the oxide texture and anisotropy of the compliance tensor will affect the amount of strain relieved for a given residual stress. Similarly, the value of Poisson's ratio will have to be selected taking these factors into account.

Parise et al [100] determined by Brillouin scattering and ultrasonic wave speed measurements that the possible values of E vary from 144 to 324 GPa and the Poisson's ratio can vary from 0.13 to 0.43 based on the anisotropy of the elastic properties of monoclinic ZrO₂ [108].

The anisotropy of the compliance tensor necessitates taking into account the texture of the oxide. Studies of the oxide microstructure using automated TEM indexing and Transmission EBSD [81] show the most likely monoclinic grain orientation has (10 $\bar{3}$) planes parallel to the metal-oxide interface. Additionally, it was found more than 50% of grains were within 10° of this orientation. As a simplification it will be assumed here that all grains share this orientation.

Using Voigt notation for a compliance tensor, the stress and strain can be related in matrix form

$$\varepsilon = \mathbf{S}\sigma$$

Where $\mathbf{S}$ is the compliance tensor, and we can estimate the value of the Young's modulus for the in-plane directions.

The compliance tensor presented by Parise [100] is oriented with the [001] direction normal to the sample surface, which is also assumed to be the predominant fibre direction in that

work. The justification for this decision was not explained and so the direction assumed for this work will be that demonstrated by Garner et al, $[10\bar{3}]$ [81].

Some work in this field makes use of Young's modulus data from indentation tests but this does not appear to take into account the fibre texture of the oxide. Additionally, a complete presentation and justification of a process to arrive at a representative value of Young's modulus is not easily found in the literature, and so has been carried out for the monoclinic ZrO_2 system.

Starting with the compliance tensor presented by Parise, we note a rotation to the $[10\bar{3}]$ direction is required. Since both the $[10\bar{3}]$ and the $[001]$ directions are on the x-z plane, the β angle lies between the x and z axes and the y-axis remains normal to the x-z plane, a single rotation around the y-axis is sufficient to achieve this transformation.

Finding the required angle of rotation in a non-orthonormal geometry requires a metric tensor consisting of the dot products of the unit cell vectors.

$$g_{ij} = \begin{bmatrix} \underline{a} \cdot \underline{a} & \underline{a} \cdot \underline{b} & \underline{a} \cdot \underline{c} \\ \underline{b} \cdot \underline{a} & \underline{b} \cdot \underline{b} & \underline{b} \cdot \underline{c} \\ \underline{c} \cdot \underline{a} & \underline{c} \cdot \underline{b} & \underline{c} \cdot \underline{c} \end{bmatrix} = \begin{bmatrix} a^2 & ab \cos \gamma & ac \cos \beta \\ ba \cos \gamma & b^2 & bc \cos \alpha \\ ca \cos \beta & cb \cos \alpha & c^2 \end{bmatrix}$$

For a monoclinic geometry with $\alpha = \beta = 90^\circ$ this reduces to

$$g_{ij} = \begin{bmatrix} a^2 & 0 & ac \cos \beta \\ 0 & b^2 & 0 \\ ca \cos \beta & 0 & c^2 \end{bmatrix}$$

The angle between $[001]$ and $[10\bar{3}]$ is calculated using the cosine rule

$$\cos \theta = \frac{[001] \cdot [10\bar{3}]}{||001|| ||10\bar{3}||}$$

with appropriate inclusion of the metric tensor

$$\begin{aligned}
[001] \cdot [10\bar{3}] &= [001] g_{ij} \begin{bmatrix} 1 \\ 0 \\ \bar{3} \end{bmatrix} = [001] \begin{bmatrix} a^2 & 0 & ac \cos \beta \\ 0 & b^2 & 0 \\ ca \cos \beta & 0 & c^2 \end{bmatrix} \begin{bmatrix} 1 \\ 0 \\ \bar{3} \end{bmatrix} \\
&= [001] \begin{bmatrix} a^2 - 3ac \cos \beta \\ 0 \\ ac \cos \beta - 3c^2 \end{bmatrix} = ac \cos \beta - 3c^2
\end{aligned}$$

The metric tensor corrects for the monoclinic frame of reference where the x and z axes are not orthogonal and thus x and z components are not independent of each other.

The magnitudes of the two vectors are calculated as self dot products also using the metric tensor

$$|001| = [001] g_{ij} \begin{bmatrix} 0 \\ 0 \\ 1 \end{bmatrix} = [001] \begin{bmatrix} ac \cos \beta \\ 0 \\ c^2 \end{bmatrix} = \sqrt{c^2}$$

$$|10\bar{3}| = [10\bar{3}] g_{ij} \begin{bmatrix} 1 \\ 0 \\ \bar{3} \end{bmatrix} = [10\bar{3}] \begin{bmatrix} a^2 - 3ac \cos \beta \\ 0 \\ ac \cos \beta - 3c^2 \end{bmatrix} = \sqrt{a^2 - 3ac \cos \beta - 3ac \cos \beta + 9c^2}$$

Calculating the cosine of the angle can now proceed as laid out previously

$$\begin{aligned}
\cos \theta &= \frac{[001] \cdot [10\bar{3}]}{|[001]| |10\bar{3}|} \\
\cos \theta &= \frac{ac \cos \beta - 3c^2}{(\sqrt{c^2})(\sqrt{a^2 - 3ac \cos \beta - 3ac \cos \beta + 9c^2})}
\end{aligned}$$

The values used in this calculation are taken from the same source as the compliance tensor for consistency [100]

Table 6 lattice parameters of Monoclinic ZrO₂

Parameter	Value
A	0.51463 nm
B	0.52135 nm
C	0.5311 nm
A	90°
B	99.2°
Γ	90°

$$\cos \theta = \frac{-0.8899}{\sqrt{(0.28067)(3.065641)}}$$

$$\theta = 163.13^\circ$$

Having ascertained the correct rotation angle between the [001] and [10 $\bar{3}$] directions, the compliance tensor can be rotated to the correct orientation.

The rotation matrix for a single rotation around the y-axis is presented below

$$K = \begin{pmatrix} \cos^2\theta & 0 & \sin^2\theta & 0 & 2\cos\theta\sin\theta & 0 \\ 0 & 1 & 0 & 0 & 0 & 0 \\ \sin^2\theta & 0 & \cos^2\theta & 0 & 2\cos\theta\sin\theta & 0 \\ 0 & 0 & 0 & \cos\theta & 0 & \sin\theta \\ -\cos\theta\sin\theta & 0 & \cos\theta\sin\theta & 0 & \cos^2\theta - \sin^2\theta & 0 \\ 0 & 0 & 0 & \sin\theta & 0 & \cos\theta \end{pmatrix}$$

Rotation is achieved by the following matrix multiplication to find the compliance matrix oriented with the [10 $\bar{3}$] direction oriented normal to the sample surface.

$$\mathbf{S}_{[10\bar{3}]} = \mathbf{K}\mathbf{S}\mathbf{K}^T$$

The following values are used for $\mathbf{S}$ in GPa^{-1} [100]

$$\mathbf{S} = \begin{pmatrix} 0.00345 & -0.00128 & -0.00116 & 0 & 0.00173 & 0 \\ -0.00128 & 0.00355 & -0.00178 & 0 & -0.00268 & 0 \\ -0.00116 & -0.00178 & 0.00537 & 0 & 0.00242 & 0 \\ 0 & 0 & 0 & 0.0114 & 0 & 0.00342 \\ 0.00173 & -0.00268 & 0.00242 & 0 & 0.00153 & 0 \\ 0 & 0 & 0 & 0.00342 & 0 & 0.00873 \end{pmatrix}$$

Omitting the multiplication for brevity, the result is the compliance tensor rotated to the predominant fibre direction of the monoclinic crystals in the oxide, presented below (to three significant figures)

$$\mathbf{S}_{[10\bar{3}]} = \begin{pmatrix} 0.00124 & 0.00017 & -0.00109 & 0 & 0.00191 & 0 \\ -0.00017 & 0.00355 & -0.00323 & 0 & -0.00209 & 0 \\ -0.00109 & -0.00323 & 0.00744 & 0 & 0.00101 & 0 \\ 0 & 0 & 0 & 0.01307 & 0 & 0.00210 \\ 0.00191 & -0.00209 & 0.00101 & 0 & 0.00160 & 0 \\ 0 & 0 & 0 & 0.00210 & 0 & 0.00706 \end{pmatrix}$$

Examining the rotated compliance tensor we can see the value 0.00355 (second row, second column) is unchanged as would be expected from a rotation around the y-axis.

With the rotated compliance tensor and the measured values of strain, the residual stress can now be calculated from the relationship between stress and strain

$$\boldsymbol{\varepsilon} = \mathbf{S}_{[10\bar{3}]}\boldsymbol{\sigma}$$

$$\begin{pmatrix} \varepsilon_1 \\ \varepsilon_2 \\ \varepsilon_3 \\ \varepsilon_4 \\ \varepsilon_5 \\ \varepsilon_6 \end{pmatrix} = \begin{pmatrix} 0.00124 & 0.00017 & -0.00109 & 0 & 0.00191 & 0 \\ -0.00017 & 0.00355 & -0.00323 & 0 & -0.00209 & 0 \\ -0.00109 & -0.00323 & 0.00744 & 0 & 0.00101 & 0 \\ 0 & 0 & 0 & 0.01307 & 0 & 0.00210 \\ 0.00191 & -0.00209 & 0.00101 & 0 & 0.00160 & 0 \\ 0 & 0 & 0 & 0.00210 & 0 & 0.00706 \end{pmatrix} \begin{pmatrix} \sigma_1 \\ \sigma_2 \\ \sigma_3 \\ \sigma_4 \\ \sigma_5 \\ \sigma_6 \end{pmatrix}$$

Looking specifically at the in-plane strains (ε_1 and ε_2) and the in-plane stresses (σ_1 and σ_2) we can derive equations for calculating the in-plane stresses. Additionally, an out-of-plane strain (ε_3) is generated by the relaxation of these in-plane stresses, which was not measured but can be calculated.

$$\varepsilon_1 = 0.00124\sigma_1 + 0.00017\sigma_2$$

$$\varepsilon_2 = -0.00017\sigma_1 + 0.00355\sigma_2$$

$$\varepsilon_3 = -0.00109\sigma_1 + 0.00323\sigma_2$$

The DIC procedure measured an average one dimensional strain which can be expressed as

$$\varepsilon = \frac{\varepsilon_1 + \varepsilon_2}{2}$$

Substituting the individual stress-strain equations into the expression for average strain allows the calculation of stress assuming the two in-plane stresses are equal.

$$\sigma = \sigma_1 = \sigma_2$$

$$\varepsilon = \frac{(0.00124\sigma + 0.00017\sigma - 0.00017\sigma + 0.00355\sigma)}{2}$$

$$\sigma = 417.5 \varepsilon$$

Stress here is calculated in GPa as the compliance tensor was expressed in GPa^{-1} . Once stress has been calculated the value of ε_3 can also be calculated.

Table 7 Calculated stress and out of plane strain ε_3 values for sample sites. These values do not account for possible phase change in the oxide.

Site	Final Strain		Final Stress GPa	Out of plane strain ϵ_3
	54 Days Oxidation	100 Days Oxidation		
α	5.8×10^{-3}		2.4	-1.0×10^{-2}
β	8.4×10^{-3}		3.5	-1.5×10^{-2}
γ	6×10^{-3}		2.5	-1.1×10^{-2}
δ		7.5×10^{-4}	0.3	-1.3×10^{-3}
ϵ		2×10^{-3}	0.8	-3.5×10^{-3}

The calculated stress values for these samples show good evidence for a difference in the residual stresses in the 54 and 100 day samples, with all 54 day samples releasing stresses in excess of 2 GPa whilst the 100 samples released less than 1 GPa. A standard T test (designed to evaluate the statistical significance of differences between sets of values based on their means, standard deviations and number of samples) reveals significance better than $p=0.05$.

These experiments appear to be the first use of semi-destructive milling techniques applied to measure residual stress in zirconium alloy oxides. In contrast to diffraction techniques relying on measuring the difference in atomic spacing to measure strain and infer stress, this technique picks up any expansion in the sample surface that may be caused by other phenomena such as a phase changes. Particularly in the 54 day samples showing large strains, a phase change from tetragonal to monoclinic may be expected, which would contribute to some of the apparent strain measured by the image correlation.

The tetragonal phase of ZrO_2 is not stable either at the temperatures of corrosion or investigation and is commonly thought to be stabilised by small grain size [109] and by compressive stress [110]. Estimating the amount of tetragonal phase that converted to monoclinic during these experiments is not simple as the transition will happen gradually as

stress is relieved and as such is hard to distinguish from movement due to elastic relaxation. Experimental techniques that measure only the elastic portion of the relaxation by directly measuring the bond length of specific bonds can provide an estimate of the amount of movement caused by elastic relaxation, under the assumption that milling released all elastic stress from the material. Work using synchrotron XRD has shown elastic stresses in the range 1.8-2.1 GPa[102, 111], which in the case of the 54 day samples would leave 0.1 to 1.5 GPa of apparent stress as the result of a phase change.

The 100 day samples did not show stresses high enough to suggest they were undergoing a significant phase change, which is consistent with other work indicating that the fraction of tetragonal oxide is at its lowest after transition [109]. It is likely that any tetragonal grains present before milling were stabilised by the small grain size and as such remained stable throughout the process.

In theory it may be possible to estimate the amount of tetragonal-to-monoclinic conversion occurring during these milling operations by considering the excess strain (above that which would be expected from purely elastic relaxation from 2 GPa) and assuming it is caused by a phase change. However, the 3% volume increase associated with phase change would unlikely be distributed uniformly and so this calculation would require a more complex understanding of the phase change. Specifically, how much of the volumetric expansion associated with the phase change is accommodated by the exterior free surface, and how much oriented to increase in plane compressive stress.

This estimate of phase fraction could be cross checked by performing XRD on specimens before milling, which would also allow a measurement of elastic stress. In this way both techniques allow two ways to check their measurements of a sample.

Error estimations

The grain morphology of zirconium oxide films is well known to vary widely over local and larger scales, with many different features ranging in size between those of oxide grains (~ 50 nm) and those of the underlying metal grains ($\sim 4\mu\text{m}$)[27, 112]. The differing metal grain orientations, metal-oxide interface features, SPP distributions and oxide voids are all likely to have an effect on both the build-up and release of residual stress, and as such a degree of variability in the stress values obtained should be expected even using a process with high intrinsic accuracy.

Testing the DIC protocol on sample images of known distortions produced results that closely matched the expected values, producing a calculated strain within 4% of the true value. When considering the size of the strains involved this represents an error less than the size of a pixel. The averaging of many measurements allows sub pixel accuracy using this technique. This is the dominant component of the error in the strain measurement (errors associated with the imaging process were an order of magnitude smaller).

The random error associated with noise in the DIC program is relatively small and does not seem to alter the interpretation of these results. The fact that the variation in derived strain values is much larger than the measurement error suggests the technique is picking up variation in behaviour caused by intrinsic (local) characteristics of the sample. Studies which mention variability of sample morphology and crystallography[34] suggest local variations in the character of the metal/oxide interface are to be expected, and may be of the correct scale to cause the variability seen in these results.

Discussion

The importance of residual stress in the oxide film arising from the expansion of metal to oxide has been an increasingly studied area over the last decade. With the greater understanding of oxide behaviour near transitions and the possible importance of creep in the metal substrate, this area of research is likely to increase in importance for further investigations into transition effects and the development of alloys that delay transition and so provide superior corrosion resistance.

Most measurements of stress in zirconium oxide films have been made with either XRD techniques or use of partial oxidation in order to induce sample bending. The semi-destructive technique demonstrated here represents a third way to measure residual stress in oxidised samples.

The most obvious result of this work shows the difference in behaviour between samples with pre- and post-transition oxides. Pre-transition samples showed higher strains and higher residual stresses and/or tetragonal to monoclinic phase change. This is consistent with results obtained by other techniques such as XRD measurements. The difference between the two sample sets appears to be statistically significant although the limited number of samples is less than ideal.

The much reduced relaxation of post-transition samples is strong evidence that transition is associated with a reduction in residual stress. The increase in oxidation rate also associated with transition is likely linked to this reduction in stress although the data collected in this experiment cannot determine the link between these two phenomena.

The fact that no samples showed residual tensile stresses is a demonstration that whilst the oxide can exhibit a gradient of residual compressive stress, at no point does this gradient

result in tensile stresses. This is likely due to the friable nature of the nanocrystalline oxide with many stress concentrating features that would promote cracking immediately after the creation of tensile stresses, such as the large number of voids present in the outer layers of oxides studied under TEM (for which samples are necessarily completely stress relieved due to sample preparation).

It should be noted that whilst some strain graphs may show slight negative strains (indicating contraction and thus a residual tensile stress), this value occurs near the beginning of the test and is always less than the value of the error so can be deemed insignificant)

The sequential depthing of ring core milling allows more confidence in measuring the strain at the surface of samples. The initial milling stages are able to interrogate much shallower depths than would be possible via XRD.

Even though no samples exhibited tensile stress at the surface, all samples showed a clear gradient of stress, with the highest stresses found near the metal-oxide interfaces. This is consistent with mechanisms involving creep, where creep in the metal substrate means the compressive stress is lessened for oxide material produced earlier. As new oxide is produced under this material and the metal continues to creep, a gradient is formed.

Several samples showed a tailing off of released stress towards the end of the milling procedure (for example the δ site and β site). This suggests that the entire oxide scale was milled through and the metal substrate had been reached.

Most samples did not show any indication of measuring tensile stress once the metal had been reached. This is likely because the metal mills more slowly than oxide, in addition to the already compromised milling conditions of a deep narrow trench. The compressive stress of the oxide must be balanced by a corresponding tensile stress in the metal although this may

be distributed over a much larger depth and so the shallow milling at the end of these procedures would be unlikely to release large amounts of compressive stress.

The strain graph for the δ site measurements do show a significant drop in the compressive stress, although no significant tensile stresses are discovered. The drop in compressive stress may indicate layers of material holding a tensile stress are being discovered, which may be the metal.

The gold coating also appears not to have influenced the results as there is no significant change in relieved stress during the early stages of milling, as might be expected if the coating layer built up large residual stresses.

Further work

The main limitation of this work is the labour and time intensive nature of gathering data. This results in a small number of measurements, necessarily limiting the number of variables that can be investigated (for example, it would not have been practicable to investigate the full suite of samples prepared for the NanoSIMS work, and so only comparisons between two oxidation times for the same alloy were made. A fuller investigation would include comparisons between alloy compositions, multiple oxidation times and possibly heat treatments. This work was primarily intended to provide the community with another measure (based on a different physical principle) of residual stress in the oxide, and to demonstrate the technique for further work. The reduced sample size still allowed demonstration of this concept.

Execution of the technique could be improved in various ways. The milling procedure could feasibly be automated as has been done with the production of microcantilevers [113]. The limiting factor in this instance would likely be the need to refocus and stigmatize the SEM as milling proceeds to obtain the best possible images. Automation of the milling would also allow for the use of even smaller milling currents, which would reduce the problem of redeposition obscuring markers. Another technique that would aid in reducing redeposition is the deposition of a deliberate barrier on the perimeter of the island, or possibly milling small purpose-designed markers.

The semi-destructive nature of this technique allows numerous options for complementary work on the same samples. For example, the milled island readily presents itself for the creation of a TEM foil as is commonly performed in the FIB. The analysis of the foil could then be performed with the context of knowing the residual stress that it maintained during sample production.

EBSD could also be performed on a cross-sectioned island after stress relief to study how the grain orientations affect the build-up of stress. Three dimensional FIB sectioning and EBSD measurements could build a complete picture of a sample. With known grain orientations (particularly of the underlying metal grains) a more reliable value of Young's Modulus which would vary locally and directionally could be used, thus allowing correlation of features (such as humps in the metal/oxide interface or cracks in the oxide) with local stress conditions.

The non-destructive nature of XRD measurements would allow both techniques to be performed on the same sample, giving a fuller characterisation of the material and also comparing the results of the two techniques.

Porosity Analysis by Cathodic Polarisation

The oxide transition effect exhibited by zirconium oxides is characterised by a sudden increase in the oxidation rate along with several other changes. There exists evidence that the sudden increase in oxidation rate is associated with penetration of the oxidising media to the metal/oxide interface and thus causing a rapid oxidation reaction as the highly reactive metal is exposed to a source of free oxygen. The presence of the oxidising media under the oxide implies the oxide is no longer protective (i.e. forming a barrier to the ingress of water or oxygen), and because the chemical makeup of the oxide is unchanged during transition, porosity in the oxide layer is a probable cause of this phenomenon.

Understanding of this porosity is important for any full understanding of the zirconium corrosion picture. Investigating the initiation of porosity (the conditions that cause porosity to commence); the direction (porosity may initiate at the outside or the inside of the oxide scale); the location and extent (it may be localised or part of a larger interconnected network), and the size of pores created are all possible routes of enquiry.

Unfortunately, answering these questions using traditional electron microscopy techniques is extremely challenging. Porosity can be imaged using a TEM (using Fresnel contrast), but preparation of foils is difficult and the likely relief of all stress during sample creation will cast doubt on any result. Directly imaging the porosity of a bulk cross-sectional sample is not suited to SEM techniques due to the nature of imaging using secondary electrons from an interaction volume of the sample. The presence of many grain boundaries makes the porosity (which itself will likely manifest along grain boundaries) extremely difficult to discern using these techniques.

A technique to highlight the porosity is required in order to allow imaging with either TEM or SEM. The assumed nature of porosity (if present) to hold liquid provides a possible solution for decorating this pores and thus making them visible to electron microscopy techniques.

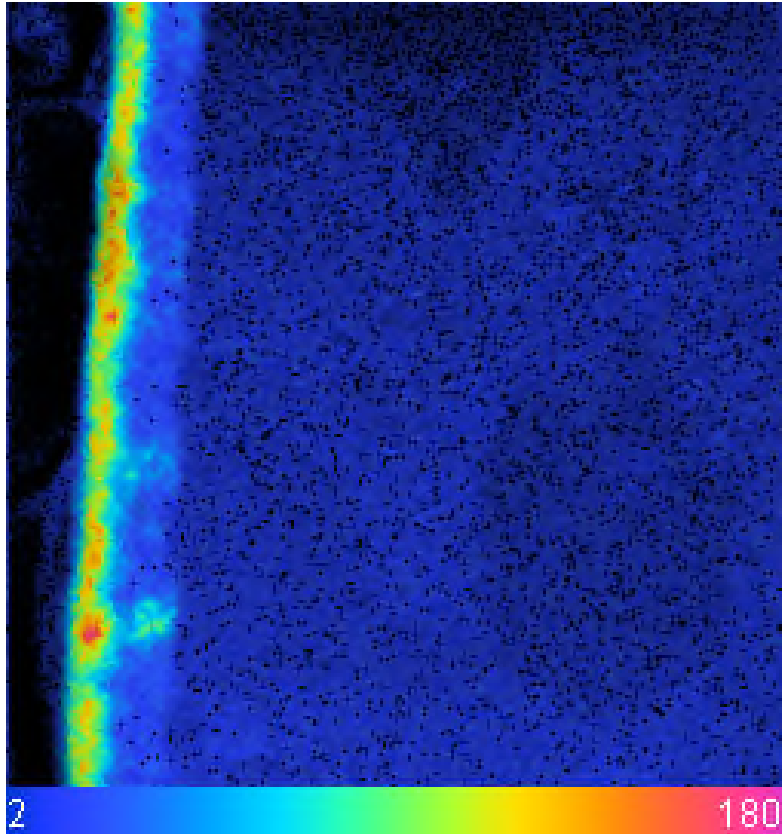


Figure 60 An image captured with the NanoSIMS showing thin penetrations of enriched oxygen through the oxide. These features are suggestive of pores.

A technique employed by Cox [114-116] involves applying an electrolytic solution to an oxide surface and constructing a circuit to try and induce a current to flow through the oxide (carried by any assumed porosity). Using a solution of copper sulphate and biasing the zirconium substrate positively with respect to the electrode in the electrolyte will cause the reduction of copper ions (and hence deposition of metallic copper) at any site where solution

and metal are in contact. The very high electrical resistance of zirconium oxides would cause current to only flow through a pore filled with electrolytic solution. Sustaining the flow of current continues to deposit copper until copper is visible on the surface of a specimen.

This technique has several potential benefits for the study of zirconium oxides. Firstly, it highlights porosity with a visible marker that can later be analysed using EM techniques. The technique also provides information about the bulk or aggregate porosity of an oxide film; measurement of the current and time of deposition can be directly related to the amount of porosity in a sample, which can be compared between samples.

The technique outlined by Cox [114-116] requires samples that have been prepared by soldering a wire to one corner (after removal of the oxide in this location) and the edges or any other unoxidised portions being masked with a nonconductive epoxy.

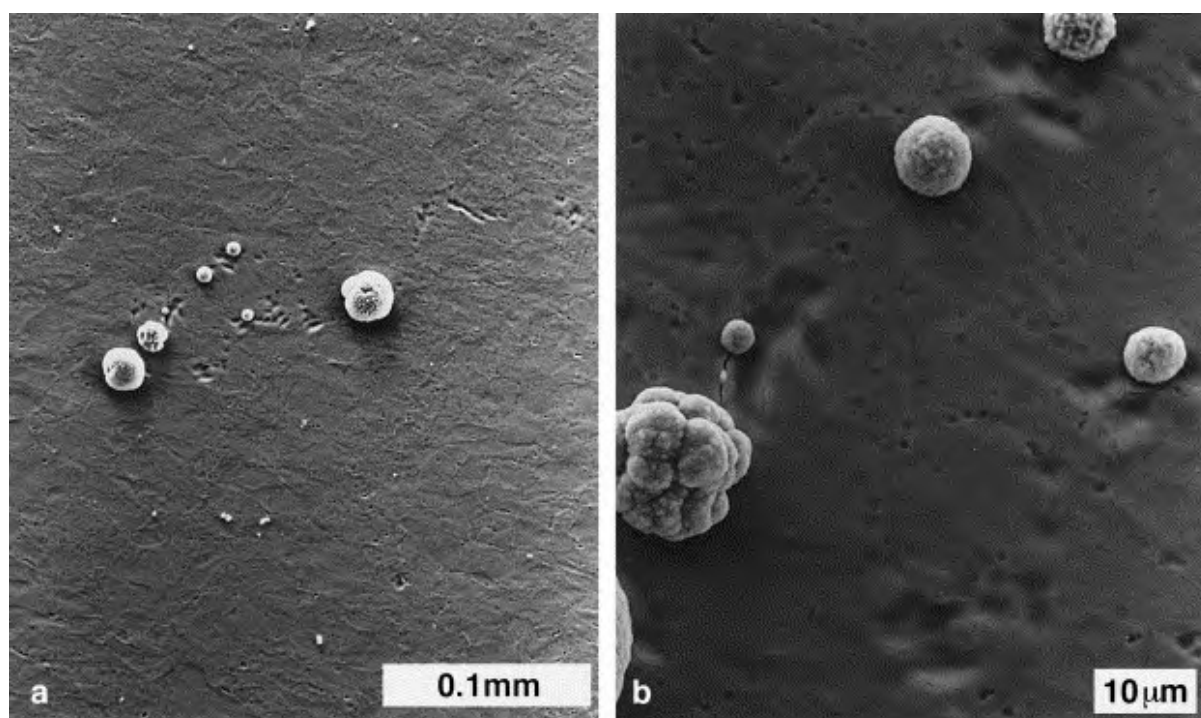


Figure 61 Two SEM micrographs showing the nodules of copper formed on the exterior surface of the oxide, presumably once a pore has been filled with copper and a conductive path has formed. Image a shows a larger scale view of copper nodules associated with small

flaws or pits in the oxide. Image b shows tiny crack-like features are visible beneath some of the nodules, as well as the rough texture on their surface. Reproduced from [114]

The prepared samples were then immersed in a 0.1 molar CuSO_4 solution and connected to a power supply limited to a maximum voltage of 1 V and maximum current of 1 mA/m². The current was switched on for periods of up to several minutes in order to deposit small copper balls.

The results reported by Cox [116] indicate small nodules of copper were deposited at sites in the oxide associated with cracks, pits or similar features that may indicate porosity. This was accomplished by first mapping the copper balls in an SEM, dissolving these deposits using nitric acid and then imaging the same sites to identify features that may be responsible for porosity.

The copper deposition was repeated after dissolving the previous copper markers and it was found that the same sites were decorated. After dissolution of the second set of nodules, the samples were oxidised for a further 24 hours in a steam autoclave and once again tested via copper deposition. Previous sites of copper decoration were subsequently found to have “de-activated” and new sites appeared. Cox concluded that previously active sites had re-passivated and any potential conduction path of porosity had been sealed.

This series of papers received citation but the technique apparently was never repeated. Access to modern instruments and techniques presented the opportunity to extend this line of work with the ability to image features within oxides, where a thin trace of copper would display prominently against a background of zirconium dioxide.

Two techniques were selected to image the oxide features associated with copper decoration: 3D FIB sectioning and TEM liftout. Both of these techniques allow high resolution images to be taken of any region in the oxide. Deploying these techniques on sites where copper nodules formed provides a previously unavailable picture of the phenomenon associated with porosity in oxide scales.

The copper decoration was initially carried out on Zircaloy 4 samples oxidised in a 600°C air environment. This produced oxides of approximately 1µm thickness.

The experimental procedure differed slightly from that employed by Cox. Instead of soldering a wire to the corner of the sample and immersing in a CuSO₄ solution, a specialised apparatus was constructed in order to ease specimen preparation and retain consistency between exposures. Machining of the apparatus was undertaken in the Oxford University Material Science Department Machine Workshop by Laurie Walton.

The apparatus consisted of a PTFE vessel 80mm in diameter with a small hole (3mm) bored in the centre of the base. A 6mm rubber O ring was inserted into a groove in the underside of the vessel to provide a seal between sample and solution. A clamping arrangement consisting of a copper plate and four PTFE screws pressed the oxide side of a sample coupon against the O ring. The rear side of the sample was abraded to remove oxide and a power supply connected to form a circuit with electron current flowing from the copper anode suspended in solution through the power supply to the rear side of the sample. The circuit was closed by positive copper ions dissolving at the anode and redepositing through porosity in the oxide.

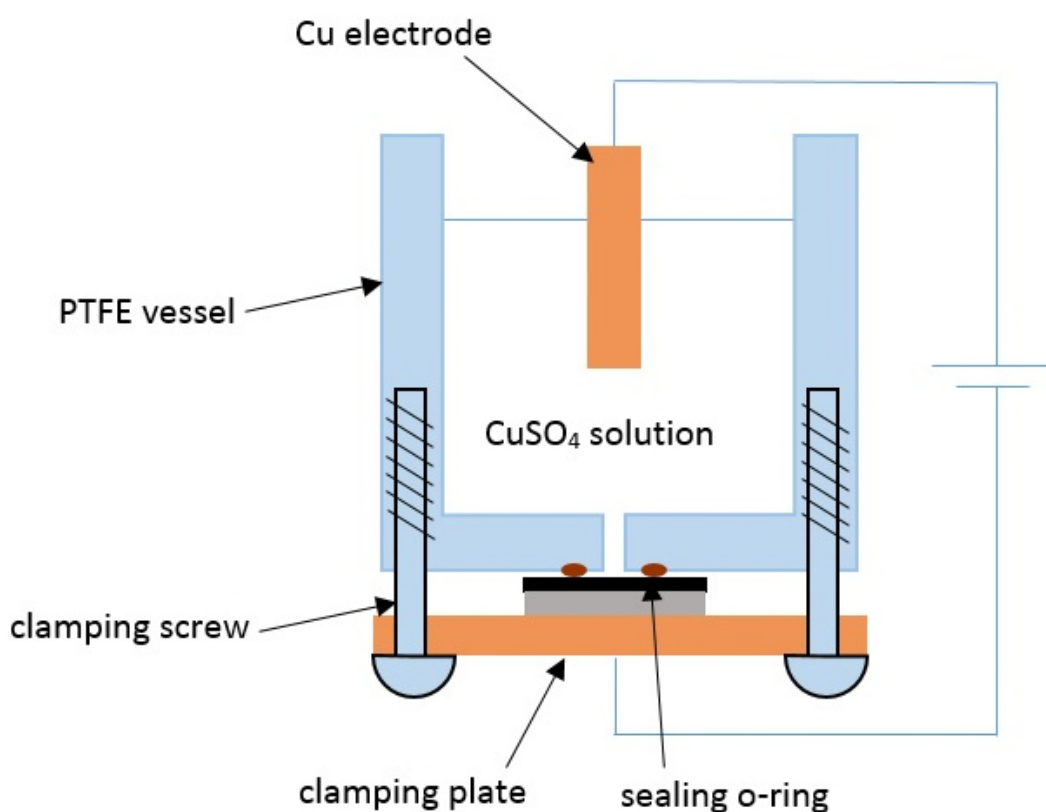


Figure 62A diagram of the PTFE plating apparatus used to deposit copper on oxidised specimens. The sealing O-ring forms a barrier around a small area of the sample to be exposed. A current path is formed from the rear, unoxidised portion of the zirconium sample, through the copper clamping plate and through the power supply to the copper electrode.

Initial experiments were conducted with bare Zircaloy4 samples to ensure the electrochemistry was suitable. It was found that additions of one drop of sulphuric acid was required to achieve plating of the metallic copper onto the bare Zircaloy4. This behaviour can be observed in the Pourbaix diagram of copper, as shown in figure Figure 63.

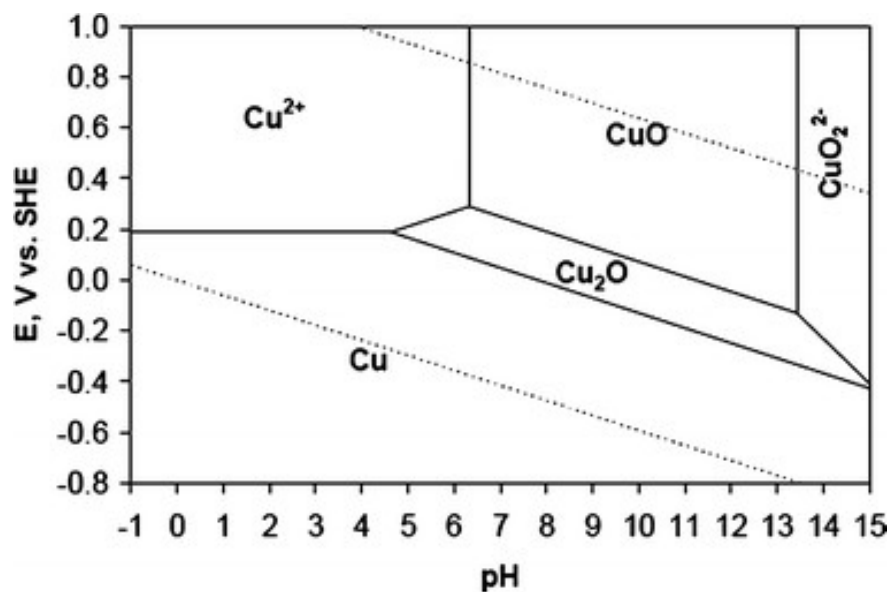


Figure 63 (reproduced from [4]) The Pourbaix diagram for copper.

Once plating of bare samples had been achieved, tests continued with oxidised samples.

Initially, it was extremely difficult to create a circuit in which current flowed through the solution. Limiting the voltage to one volt as per the original experiment produced a current of less than 1 nA, measured with the ammeter wired in series. Increasing the voltage to two volts still did not induce plating to occur.

The difference between the technique employed here and the work described by Cox is the differing sample preparation. The samples used in the PTFE apparatus had no need for a wire soldered to one corner. The method of oxidation also differed; Cox used samples prepared in a steam autoclave whilst for expediency the samples used here were prepared quickly in an atmospheric furnace.

The fact that the samples without oxide readily produced deposits of copper on the surface matching the shape of the ring suggests that the basic experimental setup was workable but that some particular of the oxide prevented the formation of conductive paths in the oxide.

In two instances samples were induced to produce plating. In one incident the sample was exposed to high voltage (10 volts) for less than one second. This voltage produced multiple small copper nodules on the sample surface. Additionally, once the voltage had been reduced, this sample could then be plated at 1 volt as would be expected.

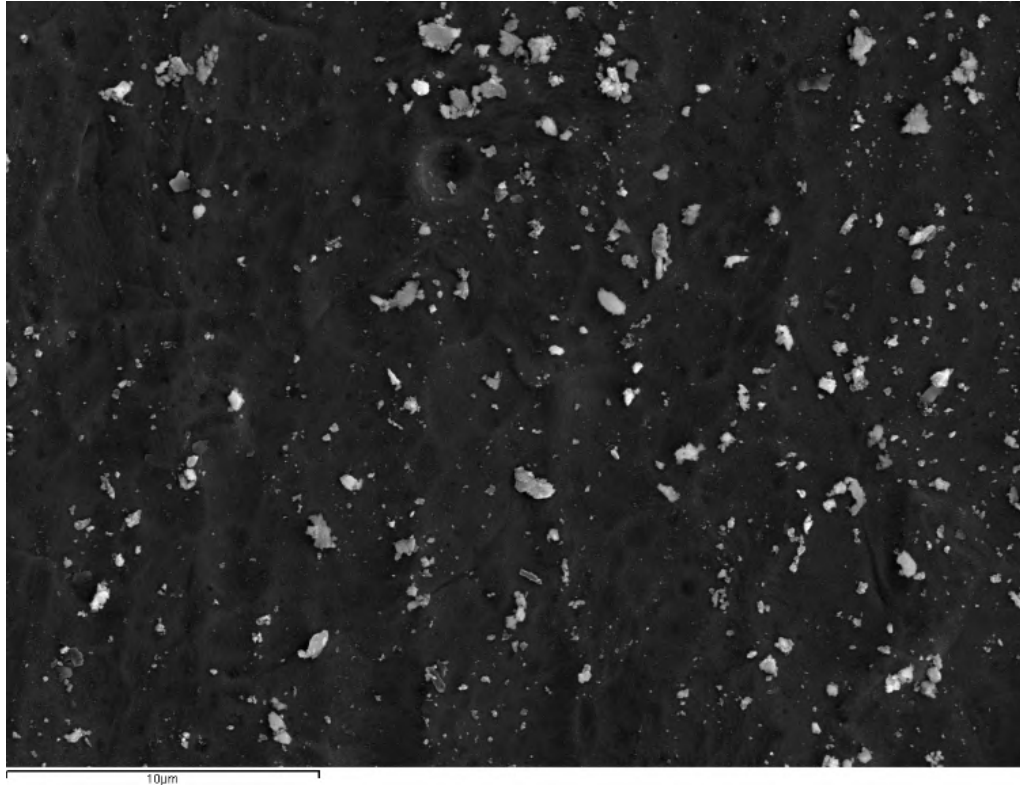


Figure 64 SEM micrograph of copper nodules (bright white) deposited on the exterior of a zirconium oxide film. This sample was briefly exposed to 10 V to start the plating process. The nodules were up to 1µm in length and appear evenly distributed over the surface, no feature appears to be required to form the deposits.

The formation of small copper nodules on the surface of the specimen matched those imaged by Cox remarkably closely. Multiple deposits formed of varying sizes, showing approximately 50 in a 10 µm by 10 µm area.

The second intervention that achieved plating was mechanical damage to the oxide surface. A nonconductive oxide sample in the PTFE apparatus was scratched with the tip of a diamond scribe to penetrate the oxide layer and reveal metal underneath. This immediately produced a plating current at 1 V. Additionally, copper nodules were observed over the whole exposure surface, not just in the region of the scratch.

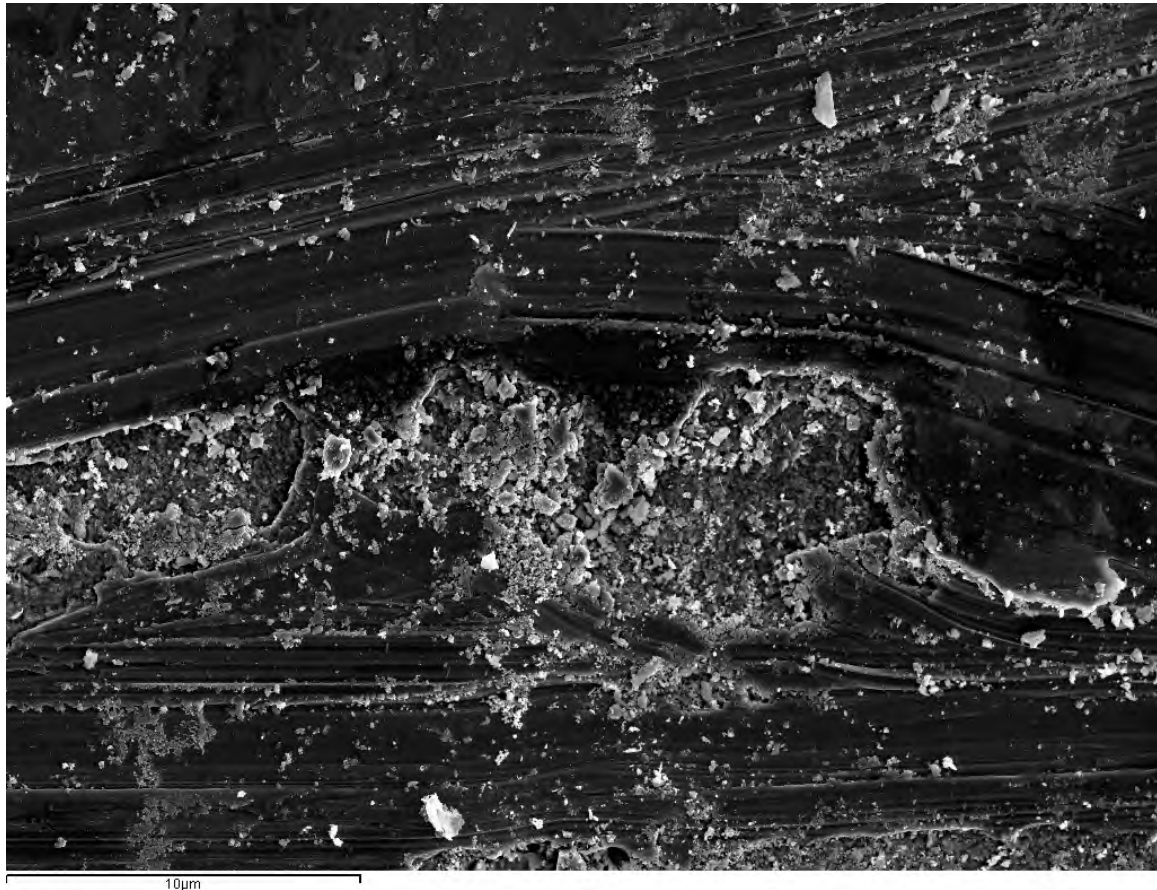


Figure 65 Copper deposition on the exterior oxide of a sample that had been scratched in order to start the plating process. The copper is distributed widely on the surface and does not only form on the scratch.

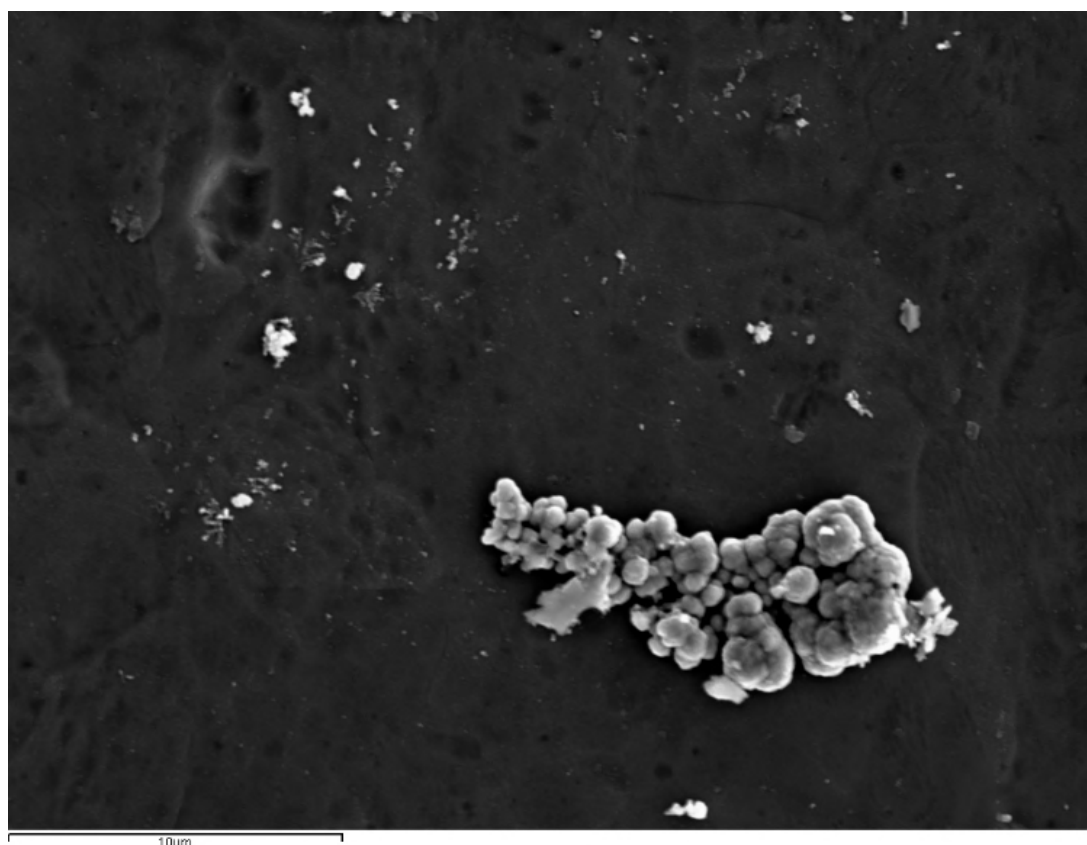


Figure 66 SEM micrograph of a particularly large deposit formed on the surface of a zirconium oxide

Despite a large number of attempts, deposition of copper nodules on an undamaged zirconium oxide did not seem to occur under these conditions. The fact that copper was readily deposited on bare specimens and specimens that had been damaged in some way suggests that the electrochemistry of the experiment was functional, and that some other detail differed between this work and the earlier work performed by Cox.

The main difference between the two techniques was the sample preparation, in which Cox soldered a wire and masked unoxidised portions of the site with epoxy. These steps were omitted in this work in favour of a more specialised apparatus.

Further investigation was undertaken on the copper deposits that had been created through exposure to high voltage. For this, samples were mounted on 12.5 mm stubs, gold coated and examined in one of two FIBs (FEI FIB200 or ZEISS NVision). Sectioning of the oxide under deposits allows the discovery of any features that may have led to the deposition of copper at these locations.

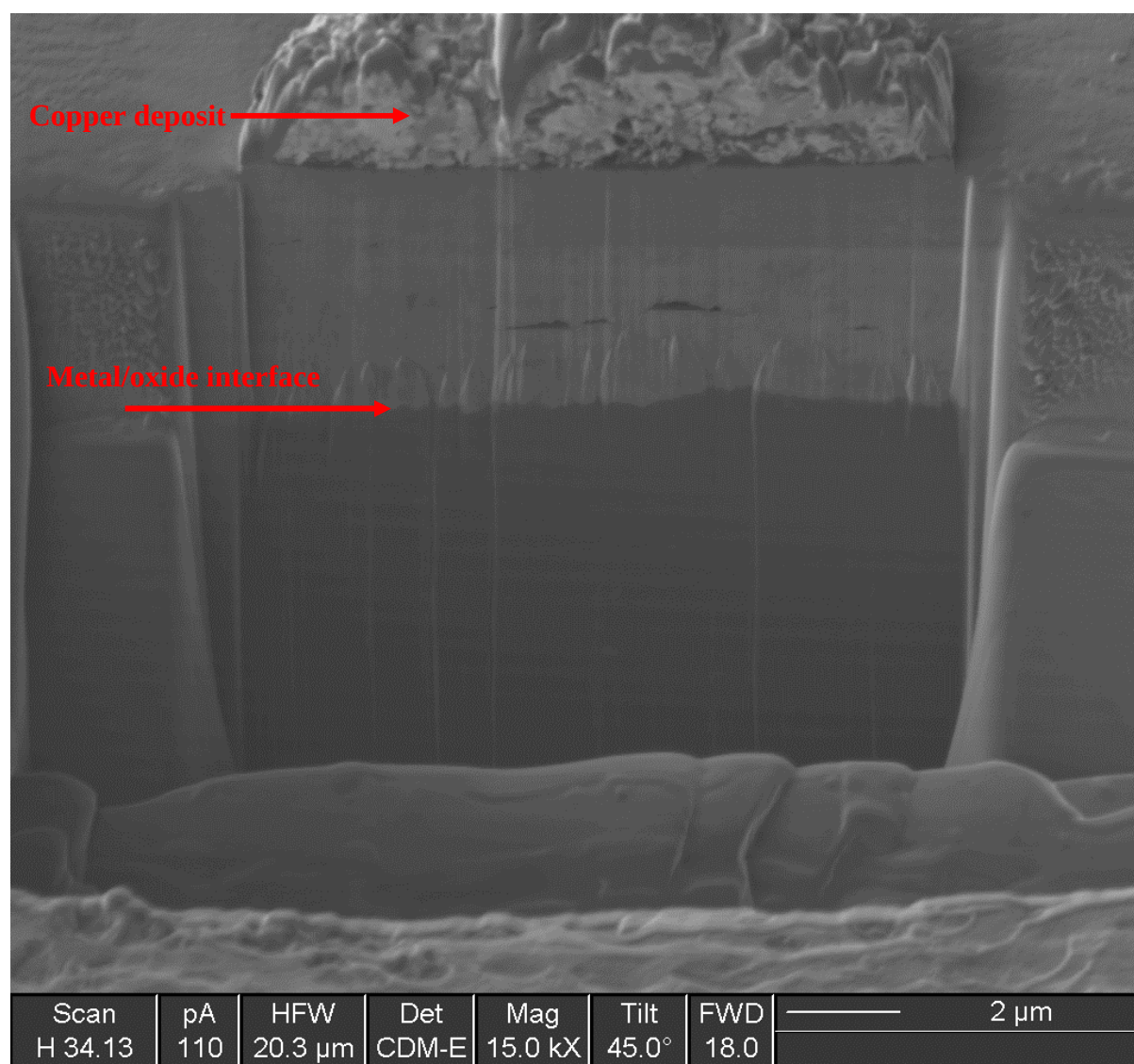


Figure 67 FIB image of sectioned oxide under a copper deposit. No obvious trace of copper is apparent through the oxide. The horizontal cracks in the oxide remain empty. Vertical lines on the section surface are caused by curtaining, i.e. imperfect scanning of the milling beam, and do not represent vertical features present in the oxide.

FIB sections of a large deposit did not show a highlighting of porosity as was originally intended. The oxide immediately under the deposit did not differ in appearance from many other non-treated oxides examined in a similar manner. The lateral cracks frequently present in these oxides were apparent but were clearly not filled with copper, which would have shown high contrast due to its atomic number. This suggests that no porosity network reached these cracks, and whichever current flowed from the metal to the exterior of the oxide was mediated entirely by the outward flow of electrons rather than the inward flow of positive copper ions.

More detailed sectioning and imaging were possible using the Zeiss NVision, which possess superior resolution due to its SEM column.

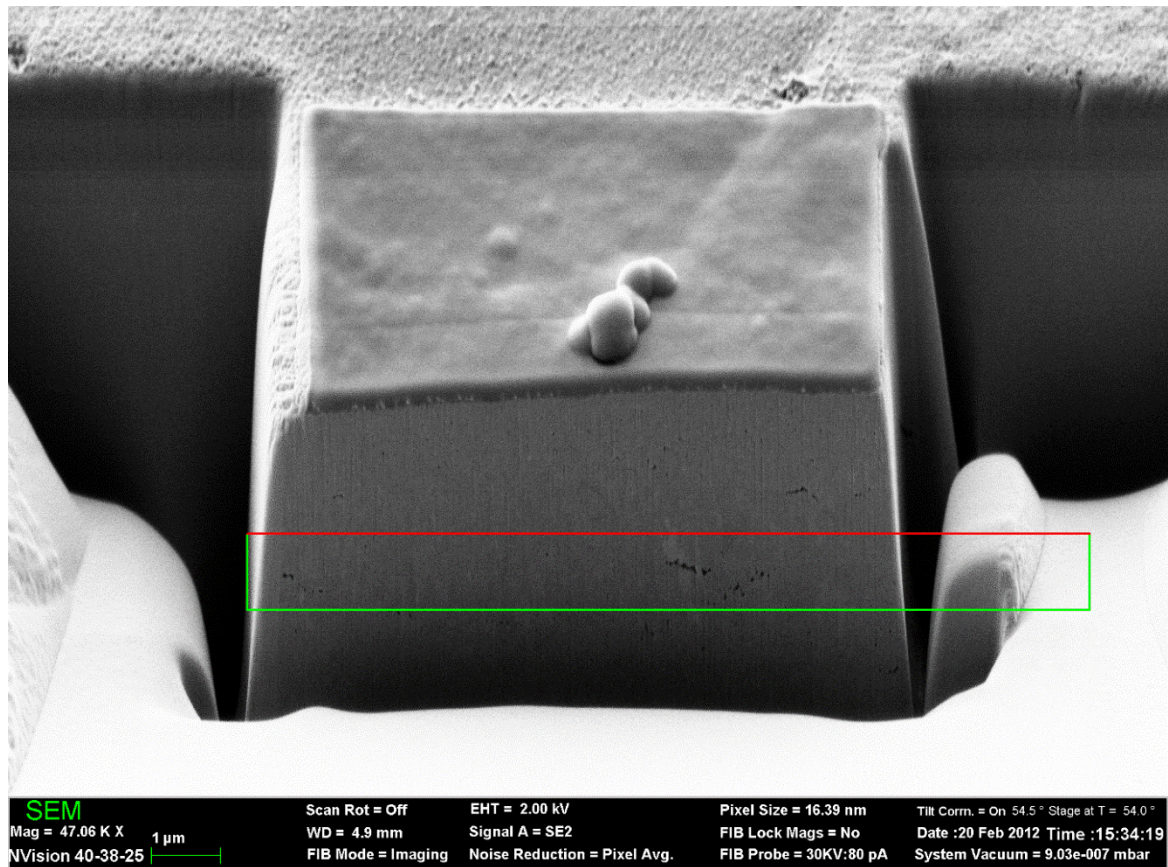


Figure 68 The setup for 3D FIB sectioning of a copper nodule. The copper nodule and surrounding area have been coated in a layer of deposited carbon protect surface features.

The trenches to either side aid in evacuation of the milled material resulting in cleaner cross sections.

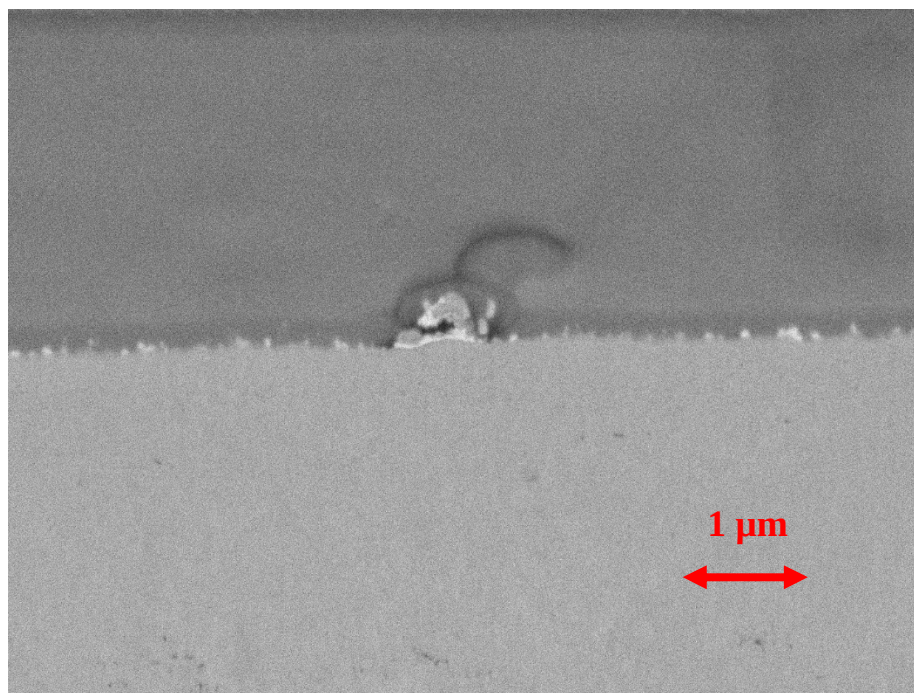


Figure 69 A sample image of the 3D cross section. As can be seen the copper nodule does not extend into the oxide beneath. The small bright spots on the surface are due to the effect of gold coating.

Similar results were obtained from 3D FIB sectioning using the NVision. No traces of copper extended into the oxide below nodules, and again, horizontal cracks in the oxide remained clear of copper. This can be seen in Figure 68 and Figure 69.

The original intent of this work was to build on the experiments of Cox. Firstly, by the use of new techniques to explore this porosity. Secondly, to use this technique on the same corpus of samples used for other experiments, to gain an insight into the presence of porosity in these samples. Unfortunately, it appears that the technique is perhaps not as reliable as might

be expected, and proved unsuitable for the analysis of porosity in these specimens in the way originally intended.

A possible conclusion might be that these oxide films do not contain pores that are accessible to CuSO_4 electrolyte. Examining the oxide under copper nodules showed no trace of copper in these locations, further suggesting that pores did not exist even after activation by either high voltage or mechanical damage, and that nodule formation occurred only due the outward flow of electrons reducing copper ions at the surface. In this circumstance it would appear that some variable differed in the work of Cox that allowed the deposition of copper.

The traces of copper may simply be too small to detect in the instruments used for this exploratory work, which would explain the absence of evidence in FIB sectioning, but not in the inability to plate copper in the first place.

This technique seemed promising initially, but did not provide any satisfactory results. There is very little literature available as no other researchers have taken up the technique for work on zirconium oxides. Cox remains the only author to publish results measured using this method.

Conclusions

The study of one set of samples by multiple techniques has provided an increased understanding of the oxide characteristics around transition. Isotopic doping and subsequent NanoSIMS analysis provides insight into the nature of protective nature of pre transition oxides and how that character breaks down at transition. Ring core milling has provided a new measure of residual stress in zirconium oxides, in particular the stress states of pre and post transition oxides. The same samples were used for both sets of experiment, allowing correlation of one set of results with the other.

NanoSIMS analysis showed pre-transition oxides (samples with oxide thickness below 3 μm) incorporate oxygen on the outer surface of the oxide, in a manner consistent with the outward diffusion of oxygen vacancies to the exterior and oxidation of new metal atoms at the metal/oxide interface (sometimes termed vacancy hopping). The pre-transition oxide being wholly protective fits well with the observation of slowing oxidation rate with increasing oxide thickness.

Ring core milling of the same pre-transition oxides showed the presence of a residual compressive stress, this compressive stress is greatest towards the metal/oxide interface, and it likely above 2GPa. Relief of this stress through milling produced strains in excess of the elastic stress reported by other researchers, suggesting an amount of phase transformation was also taking place in the unconstrained oxide.

Post transition oxides showed a markedly different ^{18}O distribution, exhibiting penetration of the oxidising specie through the outer oxide, to the metal/oxide interface where a new band of oxide rapidly formed. Not only did some regions of the 80+20 day sample show complete

transition and others pre-transition, but in certain pre-transition regions, extremely local penetrations of ^{18}O could be seen, suggesting transition is a very local phenomenon.

In several images the transition point itself was captured, as ^{18}O was detected on both the exterior (pre-transition) and underneath (post transition) the oxide scale in the same location. This is of particular interest as it demonstrates that the entire thickness of the oxide film is protective, right up until transition, where it rapidly changes to completely non protective, with very little ^{18}O found in the oxide between these two points.

Analysis of the stress contained in (presumed) post transition oxides showed a statistically significant lower compressive stress compared to pre-transition oxides. This reduction in compressive stress, and reduction in retained tetragonal phase may be what allows the development of porosity in oxides losing their protective character.

Oxide thickness was determined to be main criteria for oxides to undergo transition, rather than time of oxidation. Samples which had been exposed to autoclave conditions for longer did not necessarily undergo transition, whilst samples exposed for shorter times showed multiple transition events in regions where the oxide had reached the critical thickness.

The appearance of ^{18}O on either the exterior of the oxide or at the metal/oxide interface only, and very rarely in between suggests that the transit time for oxygen through post transition oxide is extremely low, consistent with a porosity based model of oxide transition.

Porosity is further implied by elemental analysis of boron location on oxide scales (where boron had been added to the oxidising environment, as would be found in a reactor), where boron was found to co-locate with ^{18}O , either on the outside of pre-transition, or underneath post transition oxides. Porosity would explain the passage of boron (as a solute) to these areas of the oxide once protectivity had broken down.

Porosity reaching the metal/oxide interface is a good candidate for the rapid increase in oxidation rate experienced at transition as the close proximity of oxidising media and highly reactive zirconium can rapidly produce new oxide once they are no longer separated.

As pure characterisations of the oxide before and after transition, neither of these techniques is best suited to explain the root cause of porosity development, or of it reaching the metal/oxide interface.

Demonstration of the “all or nothing” protective nature of pre-transition oxides, combined with residual stress results suggesting the pre-transition oxide tries to relieve both elastic and (phase transformation based) martensitic, does allow a tentative suggestion of a possible cause of porosity generation which explains some of the behaviours presented here and in other work.

Freshly exposed zirconium metal will oxidise rapidly, forming a coating of zirconium dioxide. This coating will be under compressive stress due to the high Pilling Bedworth ratio, and the metal under a corresponding tensile stress. The stress allows formation of tetragonal oxide under temperature conditions which would normally not allow it. As the oxide thickens, the protective nature of the oxide slows further oxidation as the diffusion of oxygen vacancies become more difficult. The high stress at the metal/oxide interface induces the metal substrate to creep. This creep will reduce the compressive elastic stress in the oxide. The rate of oxidation decreases until the creation of new oxide is extremely slow (the whole oxide remains protective).

At some point the relaxation of elastic stress in the oxide brings the compressive stress below the critical value to retain tetragonal oxide. Initially the tetragonal grains which are not stabilised (either by small grain size or an advantageous orientation) will transform to monoclinic. This transformation is accompanied by a volumetric expansion which will the

increase the compressive stress, stabilising the remaining tetragonal phase. In this way the oxide is maintained at the critical stress for tetragonal stabilisation, each time creep lowers the stress, more tetragonal oxide is transformed.

During this phase of oxidation, the oxide is still entirely protective, thus replacement of consumed tetragonal oxide is very low. The creep process continues until almost all tetragonal oxide is consumed (any remaining tetragonal oxide will instead be stabilised by small grain size or perhaps some interaction with an SPP). At this point the stress in the oxide cannot be maintained and compressive stress begins to drop well below that required for tetragonal stabilisation. The compressive stress in the oxide can now drop to the point where porosity can form through the entire oxide, rendering the oxide non protective and admitting water to the metal/oxide interface and thus occasioning a transition.

This speculative model accounts for some observations made of zirconium alloy oxidation. For example, the oxide remains wholly protective until transition occurs. The rapid generation of porosity throughout the entire oxide scale better matches with ^{18}O observations than models predicting a gradual approach of porosity towards the metal. Any porosity sufficiently developed to admit water would not produce the rapid change in oxidation rate if it approached the metal gradually, as the short distance between metal and water would create a negative feedback loop, increasing the speed of growth as porosity approaches.

Future Work

The experimental work presented in this Thesis presents several opportunities for further investigation into the mechanisms of oxide transition.

The NanoSIMS work mostly presents a neat package, which has demonstrated amongst other things the fact that the full layer thickness of the current oxide scale acts as a barrier to oxygen ingress, the penetration of boron through porous oxides and the localised nature of transition.

Further questions were raised about the difference in penetration profile between Zircaloy 4 and ZIRLO oxides, the former showing a more diffuse gradient of oxygen ingress and the latter a more concentrated thin line of oxygen incorporation. No immediate mechanism suggests itself to explain this difference, although as the suite of samples contained more ZIRLO specimens, a full comparison was not possible. Answers may lie in a close examination of the grain structure of the oxide, which is largely below the resolution limit of the NanoSIMS. Preparation of TEM samples or other thin film techniques would allow use of AOM or TKD which could then be correlated with the O¹⁸ maps of the same areas acquired previously. Some artifacts may be introduced in the production of thin film specimens due to release of stress and subsequent phase change, although grain size and morphology should be largely preserved.

Several small features were also seen in the ZIRLO films indicating an ingress of oxygen but without substantial oxide thickening in these areas (see Figure 30) which are currently unexplained and previously unreported. Further investigation of these features using the previous techniques may be fruitful.

The incidence of finding boron under porous oxide layers provides scope for performing similar experiments more cheaply (without the need to isotopically dope the corroding media). Boron should be added to any corrosion experiment in order to simulate reactor conditions, boron analysis of samples corroded in such environments could act as a convenient way to test oxide transition state in a wide range of experiments where the oxide

is cross sectioned. The major difficulty is in employing instruments which are sensitive enough to pick up very low concentrations of boron.

The liftout of TEM specimens from a flat cross section, allows use of imaging techniques on an oxide cross section whilst still retaining much of the stress state before subsequent analysis in a TEM. This allows imaging of samples in both stressed and stress relieved conditions in addition to using various techniques (such as NanoSIMS) on a bulk cross section.

Comparison of images before and after liftout may provide information about the extent of phase transformation and stress stabilisation present in bulk oxides.

The differences in oxidation rate between grains of differing orientation would be a relatively simple phenomenon to explore more fully using differing instruments. If a large (long) oxide cross section could be polished, and then mapped with conventional EBSD, the oxide thickness could be compared with the underlying metal grain orientation. A better understanding of how grain orientation affects oxidation rate would be most useful in future work. The main difficulty may lie in producing samples with sufficiently good polish to allow EBSD of the surfaces.

The exploratory work on ring core milling successfully proved a concept and demonstrated the applicability of this method to zirconium oxides. However the low number of results taken somewhat limit the confidence one can have in these observations. Extending this work by including more measurements on similar specimens would be an obvious first step. Automation of the procedure in a similar manner to that employed for cantilevers may be possible to facilitate this.

Expanding the pool of available specimens would also determine how the build up of stress and transformation strain differ between alloys.

Improvements in the technique (likely in imaging or methods to reduce redeposition) could allow the strain measurements to be examined on a local level (i.e. concentrated around features such as grain boundaries or similar).

The island produced in these experiments also provides an opportunity to perform a TEM liftout and examine the oxide in an unstressed condition, particularly if a local feature was found from spatially resolved milling.

Considering the implications of a possible creep based transition mechanism, a strong recommendation can be made to only conduct experiments at reactor temperatures and never at high temperatures to expedite sample production. The likely differing temperature dependence of creep and oxidation imply that significantly different transition behaviour may occur in these scenarios.

Further evaluation of creep based models is made difficult as frequently changes (in condition or alloying elements) which affect creep rates also affect the corrosion process in other ways (for example, tin will both reduce creep and stabilise the tetragonal phase, so may have complex or counterintuitive effects on transition behaviour).

A possible method to investigate creep dependence of transition without also affecting other critical factors is performing corrosion experiments with the imposition of an external stress to either accelerate or retard creep in the metal.

Experiments where oxidation is halted (for example, replacement of oxygen with inert argon) but temperature maintained may also allow investigation of the creep dependence of transition. By effectively switching off oxidation but maintaining the drivers of creep (high temperature and the stress already built up in the oxide), transition may occur if samples are held in these conditions. Subsequent reintroduction of oxygen would then allow oxidation to proceed at a high rate (post transition). If no transition occurs, it would suggest creep is not a

major factor in the transition of oxidation rate, or that creep alone cannot cause these transitions.

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