

THE ATOMIC SCALE STRUCTURE AND CHEMISTRY OF THE ZIRCALOY-4 METAL-OXIDE INTERFACE

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A great deal of careful experimentation has been carried out over the past 40 years on the critical mechanisms of oxidation in the zirconium alloys used for fuel cladding. However, there is still no consensus on how the nano-scale structure and chemistry of the metal/scale interface control the oxidation kinetics, although this information is vital for the accurate prediction of the performance of existing alloys and the design of new materials for higher burn-up regimes. Significant improvements in analytical instrumentation over the past few years now allow us to investigate this key interface with unprecedented spatial resolution and chemical sensitivity. This presentation will discuss sample preparation strategies for advanced TEM and 3-D atom probe analysis, and show that we have obtained new data on the nature of the sub-oxide adjacent to the interface.

I. INTRODUCTION

I.A. The corrosion of zirconium

Zirconium alloys have long been used for fuel cladding and other structural components in water-cooled power reactors due to their combination of low thermal neutron capture cross section, good corrosion resistance in high temperature water and adequate mechanical properties. However, for high fuel duties with high burn-up and extended fuel cycle operation, waterside corrosion of the material is becoming a primary limitation. The oxide grown on zirconium alloys typically exhibit a “breakaway” behavior in the prolonged corrosion process, which is characterized by loss of protectiveness at a thickness of a few micrometers, leading to a sharp increase in oxidation rate and rapid deterioration of the material.¹ The development of advanced zirconium alloys with improved corrosion resistance has been rather successful^{2,3,4,5,6} It is well known that even rather small changes in alloy chemistry and heat treatment can have dramatic effects on corrosion resistance, but the critical mechanisms by which local chemistry controls oxidation remain unclear.

Understanding of the processes that occur at the metal/oxide interface is crucial for a full mechanistic understanding of the oxidation process as this is where new zirconium oxide forms, and is likely to be crucial for the control of oxidation kinetics. Previous work employing in situ XRD,⁷ diffraction of synchrotron radiation^{8,9,10} and Raman spectroscopy^{11,12} has reported a higher fraction of the room temperature meta-stable tetragonal zirconium oxide (t-ZrO₂) close to the interface region. Investigations using surface analysis techniques such as x-ray photoelectron spectroscopy (XPS)^{13,14,15} and Auger electron spectroscopy (AES)^{14,16} have also indicated the

existence of a sub-stoichiometric oxide layer between metal and ZrO₂ during the initial oxidation of zirconium and its alloys in oxygen or water vapor, with varied compositions suggested by different authors.

I.B. Previous TEM Studies of Metal/Oxide interfaces in Zirconium Alloys

Transmission electron microscopy (TEM) has been frequently used for obtaining both microstructural and chemical information on zirconium alloys and their oxides, including at the metal/oxide interface. Compared to XPS and Raman spectroscopy, TEM studies often report much lower volume fractions of tetragonal oxide from analyzing electron diffraction patterns collected from the oxide near the interface.^{17,18,19} This is possibly due to transformation from the tetragonal phase to the equilibrium monoclinic phase induced by stress relaxation during sample preparation, because stress is well-known to stabilise the tetragonal phase.²⁰ Although the direct observation by TEM of tetragonal grains has been reported using dark field imaging with tetragonal reflections or high resolution imaging^{17,19,21,22}, the very similar plane spacings between monoclinic and tetragonal phases make the interpretation of these experiments very difficult.

A number of TEM studies have also been carried out on various zirconium alloys to investigate the nature of any sub-stoichiometric oxide layer at the metal/oxide interface.^{23,17,19,21,24} Several types of sub-oxide with different structures and compositions have been suggested. For example, ZrO with a cubic structure,^{23,25} Zr₃O_x with a rhombohedral structure²¹ or an ordered oxygen solid solution with approximately Zr₃O composition in ω-Zr hexagonal phase.²⁴ There is thus considerable disagreement in the TEM literature on the structure and composition of the oxide/metal interface.

Due to the limitations of conventional TEM sample preparation techniques such as mechanical polishing followed by ion milling or electrochemical polishing, most of the previous TEM work suffered from the quality of TEM samples in the sense of rather limited electron transparent area, usually in the order of several hundreds of nanometers in diameter, and also the inhomogeneity in foil thickness. Due to these problems, investigation of the oxide evolution at larger length scales becomes difficult, and thickness variations can significantly influence the quantitation of some analytical TEM techniques such as Energy Dispersive X-ray (EDX) microanalysis and Electron Energy Loss Spectroscopy (EELS).

More recently, focused ion beam (FIB) milling techniques have been very widely used for TEM specimen preparation and offer a number of major advantages over

more conventional methods.²⁶ The ability to precisely select the target area, the possibility of making large uniform, electron transparent areas with nearly parallel sides, and high throughput and reliability are all important factors for studying the evolution of oxide growth. In addition, by employing the *in-situ* lift-out FIB method, samples with optimum thickness for specific types of TEM characterization can be systematically prepared.²⁷ Very few TEM studies have yet employed these techniques for preparing thin foils to study zirconium oxidation.^{4,28}

I.C. Zirconium analysis in the 3-D Atom Probe

The 3-D atom probe (3DAP) is a microscope that allows the creation of 3-D “atom maps.” These reconstructions can be interrogated to determine properties of the nano-scale chemistry of the specimen material. The atom probe requires the fabrication of sharp, conductive needles so that the application of an electric potential generates a very high electric field at the needle apex. This potential is held just below that required to cause the ionization of atoms at the apex of the needle sample. A further pulse of energy can then be applied to allow the controlled ionization of atoms from the needle surface. Previous generations of atom probe instruments were limited in the delivery method of this pulse. Voltage pulsing allows the field at the apex to increase momentarily, increasing the probability of field evaporation exponentially. However, voltage pulsing is not effective for materials of low electrical conductivity, such as oxides. Also, the application of a voltage pulse is accompanied by a mechanical shock to the specimen, which may result in fracture. Alternatively, laser pulsing can be used. In this method the temperature of the tip is instantaneously heated by the incident radiation. The field evaporation process is dependant upon temperature, and so this momentary increase in thermal energy raises the probability of an ionization event. The ions liberated are subsequently projected from the surface towards a position-sensitive detector and identified by time-of-flight mass spectrometry and finally reconstructed into atom maps by tomography. The instrument benefits from high spatial resolution; around 0.5 nm lateral resolution and up to atomic resolution along the axis of the tip when analyzing a metal matrix. The 3DAP also has uniform chemical sensitivity across the whole mass-charge spectrum. These capabilities make it an interesting tool for studying the nano-chemistry of zirconium alloys.

The application of atom probe tomography to the oxidation of zirconium alloys has until recently been severely limited by the capability of the instrumentation. Kruger et al.²⁹ and Wadman et al.^{30, 31} used earlier, voltage pulsed, 1-D atom probe (1DAP) techniques to directly measure solute matrix concentration. Their interest lay in the detection and quantification of dilute solutes in the matrix in order to measure depletion after different heat treatments. Sano and Takeda³² used the 1DAP to analyze tin profiles in a range of Zr-Sn alloys. For Zircaloy-4 and Zr-0.6Sn binary alloy all of the tin was found to be in random solid solution over the length scale measured. For a higher tin Zr-1.39Sn binary alloy, small tin clusters composed of a few tens of atoms were reported in the matrix. 1DAP is a challenging technique, especially for

zirconium alloys; the tiny needles with end radii of the order of 50 nm analyzed by this process were frequently subject to fracture in these studies, partly because zirconium alloy materials were found to be sensitive to severe surface oxidation during atom probe specimen preparation.³³ Specimens were prepared using electrochemical etching in all three cases, using a solution consisting of varying proportions of acetic acid and perchloric acid.^{29,32} or perchloric acid, iso-butanol and methanol.¹⁸ These specimens typically allowed only 5-30 thousand ions to be collected for analysis, with the more heavily oxidized specimens failing more rapidly. In contrast, the smallest dataset presented below is 2.5 million ions, the largest being 25.6 million ions. This increase in the volume of data between the different generations of atom probe instrument allows much greater precision in the measurement of dilute solutes, and whereas specimen oxidation caused the fracture of atom probe specimens analyzed using 1DAP, it is now the surface oxide that we wish to analyze. Recently we have shown that atom probe tomography can be used to analyze insulating ceramic oxides, such as ZrO₂, grown on atom probe specimens.³⁴ Here we present data studying the interface between this oxide and the alloy substrate.

Despite the many interesting observations reported in previous publications, no consensus has yet been achieved on how the structure and chemistry of the metal/oxide interface control the oxidation kinetics, especially in the nano-scale range.. The purpose of this paper is to demonstrate that more detailed information can be obtained by employing the most up-to-date sample preparation and characterization techniques.

II. EXPERIMENTAL METHODS

II.A. Alloy Materials

Commercial Zircaloy-4 cladding tube was investigated in this study. The ingot chemistry for the material examined is given in Table 1. The tube was corrosion tested by EDF Energy in two metallurgical conditions, stress relief annealed (SRA) and recrystallised (RXA). The final anneal for the SRA material was at 486 °C for 3.5 hrs. The RXA heat treatment created an equiaxed microstructure by further annealing for 2 hrs at 620 °C in an Ar atmosphere. The tubes were subject to corrosion in a primary water autoclave at 360 °C for 2160 hrs (90 days). The water chemistry contained 2 ppm Li and 1000 ppm B as well as additional dissolved hydrogen. The weight gain data for the two states is comparable; (27.2 ± 0.3) mg.dm⁻² for RXA and (27.7 ± 0.3) mg.dm⁻² for the SRA material. The oxide formed after 90 days was found using optical microscopy to be pre-transition, around 1.8 µm in thickness.

	Sn*	Fe*	Cr*	Si ^	O^	C^
Top	1.28	0.22	0.11	99	1300	160
Middle	1.29	0.22	0.12	100	1260	150
Bottom	1.27	0.20	0.11	93	1320	160

Table 1: Chemical composition at three locations within the ingot. Values in *wt.% and ^ppm by weight.

II.B. Transmission Electron Microscopy

The *in situ* lift-out (INLO) FIB method was employed for the preparation of TEM foils from cut pieces of the tube material. A FEI FIB 200 instrument was used (30kV gallium incident beam with beam current of 50-5000 pA). Thin foil TEM sample preparation is described in detail elsewhere.^{26,27}

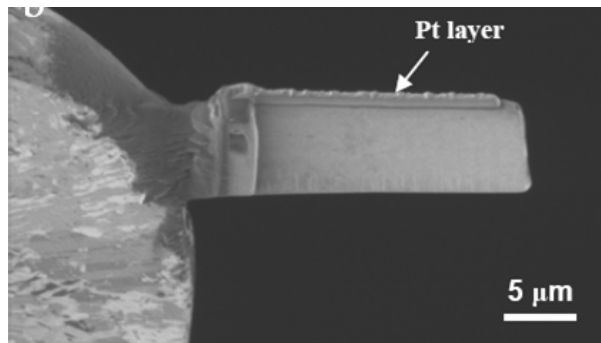


Figure 1: The lamella is welded to the TEM half-grid ready to be further thinned to electron transparency.

The main advantage of this FIB technique is the ability to produce TEM specimens with a large electron transparent area. For example, a TEM thin foil with an electron transparent area about 11 μm by 6.5 μm was achieved in the lamella shown in Figure 1. Another important advantage of the INLO method is that it allows further thinning of the specimen if it is found to be necessary. With care, the foil can be thinned to a thickness of 100 nm or even less, as required for EELS and HRTEM.

TEM analysis was carried out using a Philip CM20 microscope operated at 200 kV equipped with an Oxford Instruments ultra-thin window EDX detector, and a Jeol 3000F microscope, equipped with a Gatan GIF, operated at 297 kV. Several TEM specimens were investigated from the Zircaloy-4 tube material to ensure the reproducibility of observations.

II.C. 3-D Atom probe

Conventional atom probe specimen preparation techniques, where a conductive rod is electrochemically polished into a sharp needle, are not suitable for the fabrication of specimens containing an alloy-ceramic interface. A focused ion beam milling technique has been developed specifically for this kind of sample. A Zeiss NVision 40 was used for this method. The NVision is a dual beam FIB; a combined FIB and high resolution SEM fitted with a micromanipulator. In order to prevent specimen fracture at the metal-oxide interface, the tips were created with the interface running along the length of the tip, rather than across it. The disadvantage of this technique is that the interface is aligned along the direction of analysis which results in a reduced spatial resolution of 0.5 nm. Specimens are prepared by cutting out a wedge of the interface, similar to a TEM lift-out technique, as described elsewhere.³⁵ Once this has been performed, a micro-tip coupon (a silicon wafer with numerous posts on it) is then introduced into the FIB chamber. Each post can be transformed into a separate atom probe needle which can then be analyzed in the 3DAP. The prism is brought

into contact with the top of a post and welded on one side. The remainder of the prism is then cut free, creating a wedge welded to a post, as shown in Figure 2. The wedge is further secured by deposition of tungsten on to the opposite side. Channeling contrast enables easy identification of the position of the metal-oxide interface. Annular milling, similar to that performed in conventional atom probe FIB preparation³⁶, is used to create a tip from the block. High resolution SEM imaging is used to monitor the progression of the milling process, allowing the creation of specimens with the metal-oxide interface within the very narrow apex region. A low energy ion beam is then used to clean the surface of the specimen in a similar step to that for TEM foil preparation. A final image of a tip created using this method is shown in Figure 3.

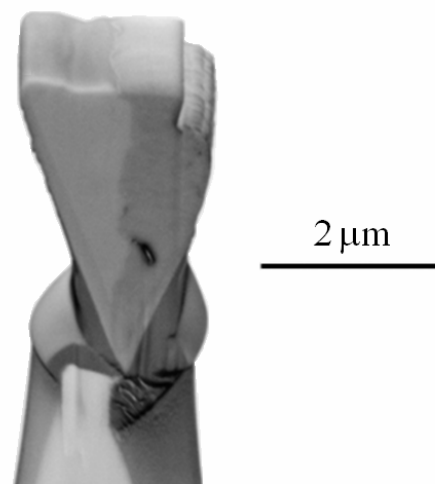


Figure 2: Inverted colour SEM image of the prism welded to the post, viewed side on. The welds are the dark regions between the wedge and the post surface. Channelling contrast allows the metal and oxide to be clearly distinguished, the metal region is on the left-hand side of the image, the oxide is on the right.

Atom probe analysis was conducted using an Imago Scientific Instruments LEAP[®] 3000 X HR, a 3D atom probe with enhanced field of view.³⁷ All the analysis was conducted at the OPAL facility at the University of Oxford, UK. Laser pulsing was used to remove ions, and the specimens were cooled to a temperature of 60 K. A 0.4 nJ, 10 ps laser pulse was used with a repetition rate of 200 kHz. The standing voltage on the tip was varied automatically in order to maintain an average evaporation rate of 5 ions for every 1000 laser pulses. This relatively high rate produces a low background signal.³⁸ Zirconium based atom probe tips have a tendency to fracture during analysis,³⁹ and the use of laser pulsing was necessary to minimize the incidence of fracture, and to deliver energy to the non-conductive region at the apex of the tip.

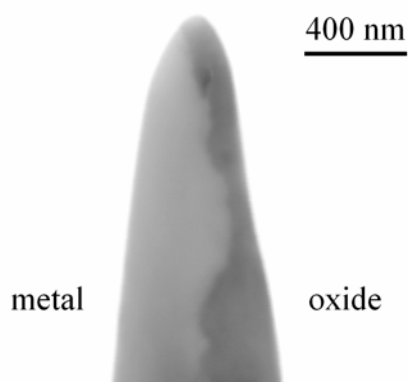


Figure 3: Inverted colour SEM image of the structure from Figure 2 after annular milling. About the top 300 nm of such a specimen can be analyzed by the atom probe.

III. RESULTS

III.A. Transmission Electron Microscopy

1. Overall structure of the oxide

An overview of the oxide grown on the alloy matrix is shown in Figure 4. Thanks to the large electron transparent area in the specimen, the whole oxide scale and metal substrate including the metal/oxide interface can be studied from the same sample. The thickness of the oxide is about 1.7 μm , indicating that the oxide is in the pre-transition (pre-breakaway) stage of the oxidation kinetics.

The oxide exhibits a columnar grain structure predominately at the innermost and middle part of the scale and a quasi-equiaxed structure mainly towards the outer surface, as can be seen clearly from the higher magnification image in Figure 5. The columnar grains are about 10-20 nm wide and 200-400 nm long, and the equiaxed grains are about 10-30 nm in diameter. The columnar grains near the metal/oxide interface appear to be better aligned and larger in size than those in the middle part of the oxide.

Cracks and pores were seen in the oxide, with an inhomogeneous distribution. They are much more common at the outer part of the oxide than in the inner. Those in the inner oxide seem isolated from the oxide surface. It was also found that the cracks and pores are often associated with equiaxed grains, as more clearly illustrated in Figure 6.

Analysis of a typical selected area diffraction pattern taken from the middle part of the oxide is shown in Figure 7. The diameter of the selected area aperture is about 830 nm. The diffraction pattern mainly contains reflections from monoclinic zirconium oxide. A variation of intensity along the diffraction arc was observed which indicates that the oxide is strongly textured. The strongest intensity of $(-111)_m$ poles was found at orientations about 25° and 65° away from the oxide surface normal, and the latter orientation is also the one for the strongest $(111)_m$ poles. Most of the reflections from the tetragonal oxide phase are very close to adjacent monoclinic reflections. When the sample thickness is reduced so that grain overlap in the foil is avoided, the presence of tetragonal oxide was

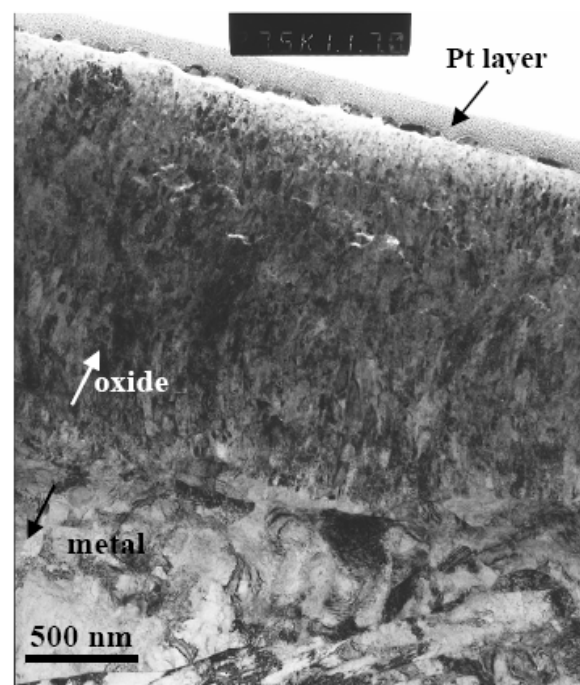


Figure 4: Bright field TEM image: An overview of the oxide grown on the Zircaloy-4 metal matrix.

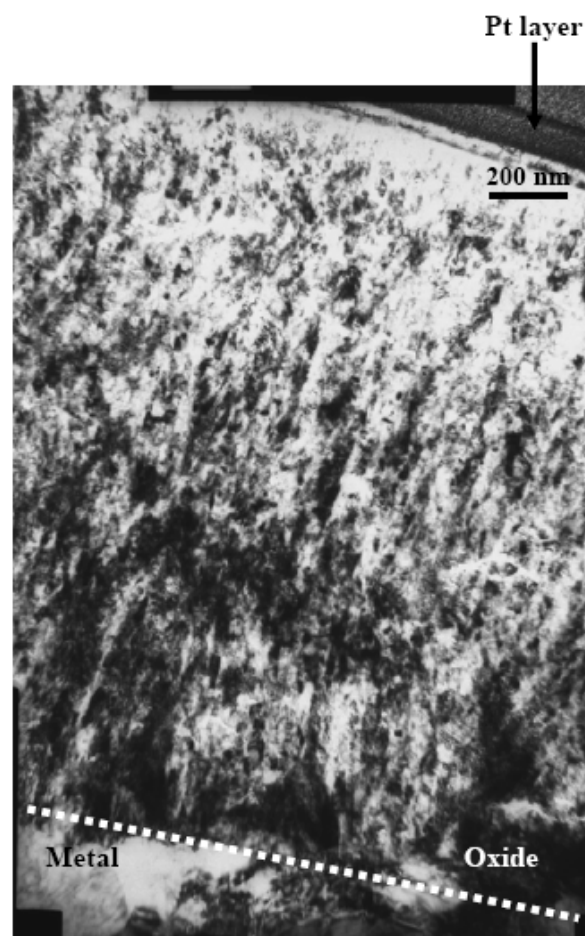


Figure 5: Bright field image: Oxide morphology consisting of columnar and quasi-equiaxed structure.

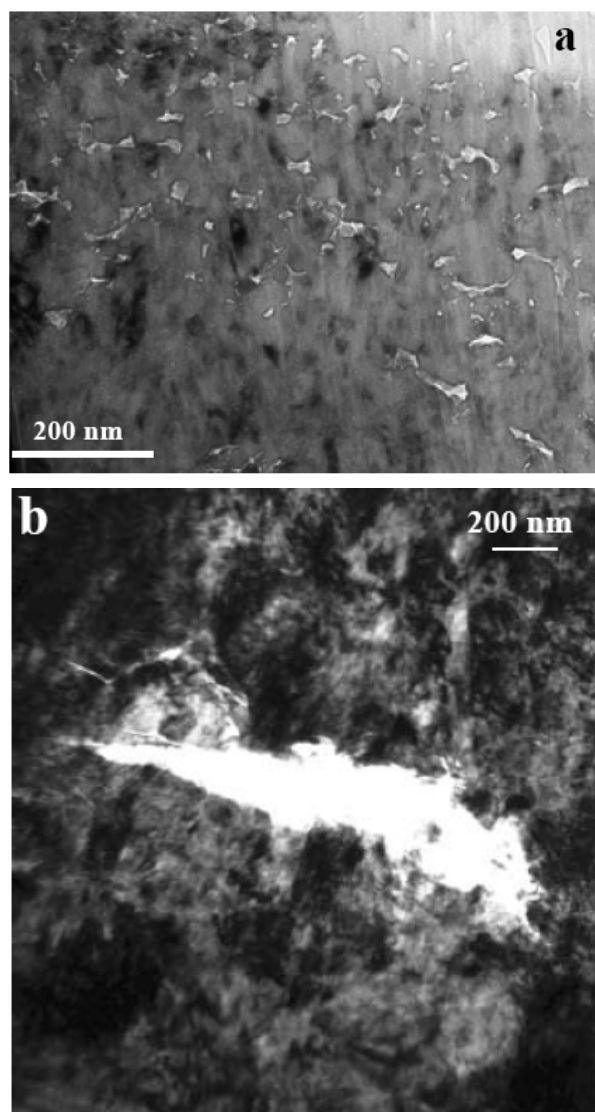


Figure 6 a) and b): Bright field TEM images of areas containing small cracks and pores, which are often associated with small equiaxed grains.

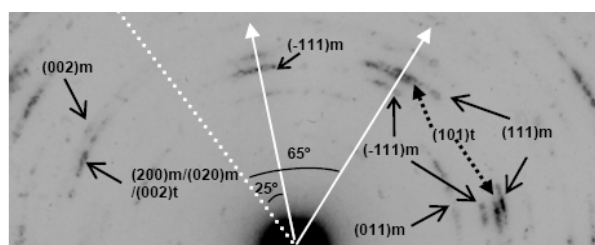


Figure 7: Selected area electron diffraction pattern of the middle part of the oxide. Dotted line shows the normal to the metal/oxide interface.

confirmed by the clear identification of $(101)_t$ reflections between $(-111)_m$ and $(111)_m$ reflections. The $(101)_t$ reflections appear to be strong at the orientations where $(-111)_m$ and $(111)_m$ are both strong, i.e. 65° away from the oxide surface normal. This kind of texture is qualitatively in agreement with previous TEM observation reported by Yilmazbayhan and co-workers,¹⁹ where the $(-111)_m$ poles

and the $(111)_m$ poles were found to be $30-45^\circ$ and $50-60^\circ$ away from the oxide surface normal respectively.

2. Metal/Oxide interface region

A metal/oxide interface that is well defined by the abrupt termination of columnar grains is apparent in Figure 8a. A particularly interesting feature is the existence of strongly diffracting grains between the columnar oxide grains and equiaxed metal substrate grains, forming a more or less continuous layer at the interface. These grains can be distinguished from the underlying metal and the columnar oxide by their blocky shape. Their size is about 50-100 nm along the oxide growth direction. More examples of this interfacial structure are given in Figure 8b, c and d, and small equiaxed grains of this type were always found along the metal/oxide interface.

In Figure 9a, a high angle annular dark field (HAADF) image of this metal/interface region is shown. The signal in HAADF images can be considered to be proportional to the average atomic number, assuming homogeneous thickness and density in the sample. Therefore, the metal matrix with a higher average atomic number appears brighter in the image and the oxide is darker. A distinct layer 80-100 nm thick with an intermediate contrast exists between the metal and the columnar oxide, indicating a different phase which seems to have an oxygen level in between those of the oxide and the metal, i.e. a sub-oxide.

In order to investigate the variation of the composition across the metal/oxide interface in more detail, we carried out EELS analysis in the form of point analyses and Energy-Filtered TEM (EFTEM). EFTEM thickness maps were acquired to ensure that the EELS spectra were free of multiple-scattering events. EELS analysis can provide reliable quantitative compositional data for light elements, and also has a spatial resolution high enough to study in detail the thin sub-oxide layer. Figure 9b shows the measured oxygen concentration profile across the interface region (see the line marked in Figure 9a). An intermediate layer with oxygen content of 44-52 % can be identified between the columnar oxide, ~60% oxygen, and the metal, ~37% oxygen. We note that the oxygen content in the bulk oxide is close to what would be expected for stoichiometric ZrO_2 , while the level of 37% oxygen in the alloy substrate is higher than expected compared to oxygen saturated Zr metal at 360°C in the equilibrium phase diagram.⁴⁰

Some interface grains, found by EDX analysis to contain a higher oxygen concentration than the metal matrix, were studied in more detail by micro-diffraction. It is often difficult to distinguish on the basis of a single pattern crystal structures that can be rather similar, and so the specimens were tilted to access as many low index zone axes as possible from individual interfacial grains. At this preliminary stage of our analysis we have strong indications that some interfacial grains can be identified as monoclinic ZrO_2 (presumably highly deficient in oxygen) or $\alpha\text{-Zr}$ (supersaturated with oxygen). For instance, the two interface grains in Figure 8d were identified as $\alpha\text{-Zr}$, and a typical micro-diffraction pattern is shown as an insert. More examples of this detailed study of grains at the metal/oxide interface are shown in Figure 10. However,

there were numerous examples where no unique interpretation of the diffraction evidence was possible. For instance some micro-diffraction patterns can be solved as a α -Zr phase at zone axis [110] or a rhombohedral phase with $a=5.5630$ and $c=15.5925$ at zone axis [210].⁴¹ This identification of a multiplicity of types of interfacial grain in the same sample may help explain the confusion in the literature on the nature of these phases.

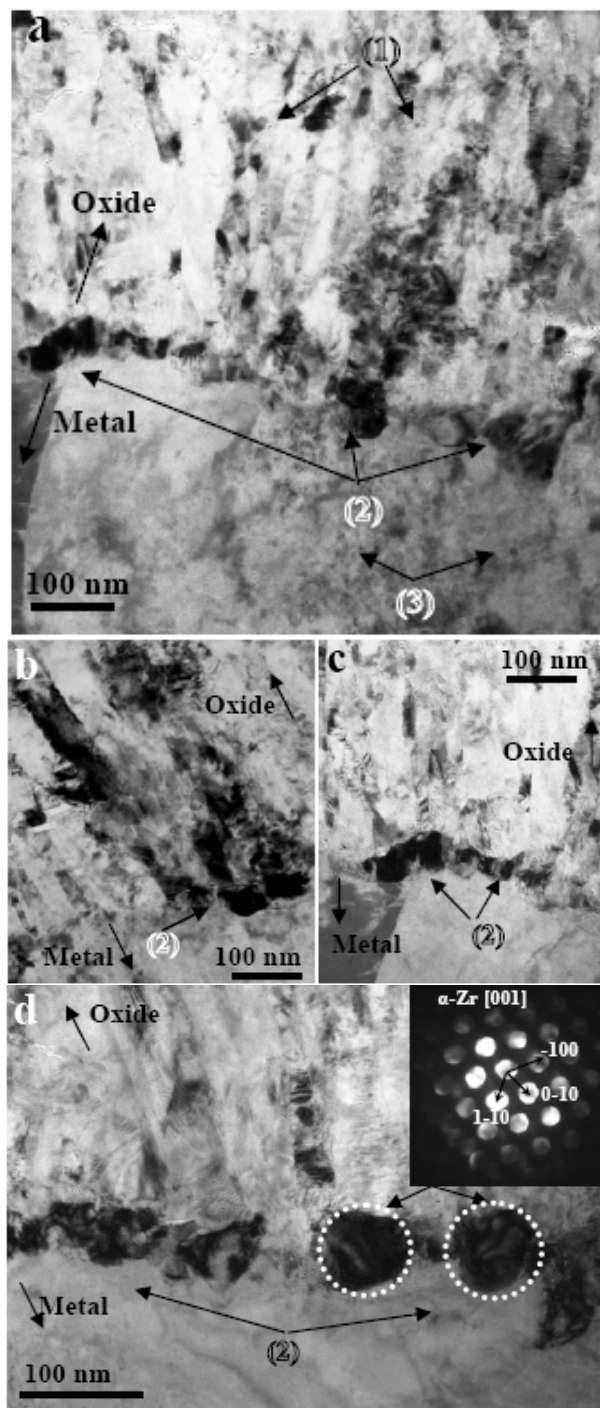


Figure 8: a) Metal/oxide interface defined by the front of columnar grains (1). An intermediate structure (2) may be seen between the columnar oxide and equiaxed metal grains (3). More examples of this intermediate structure are given in bright field TEM images b), c) and d).

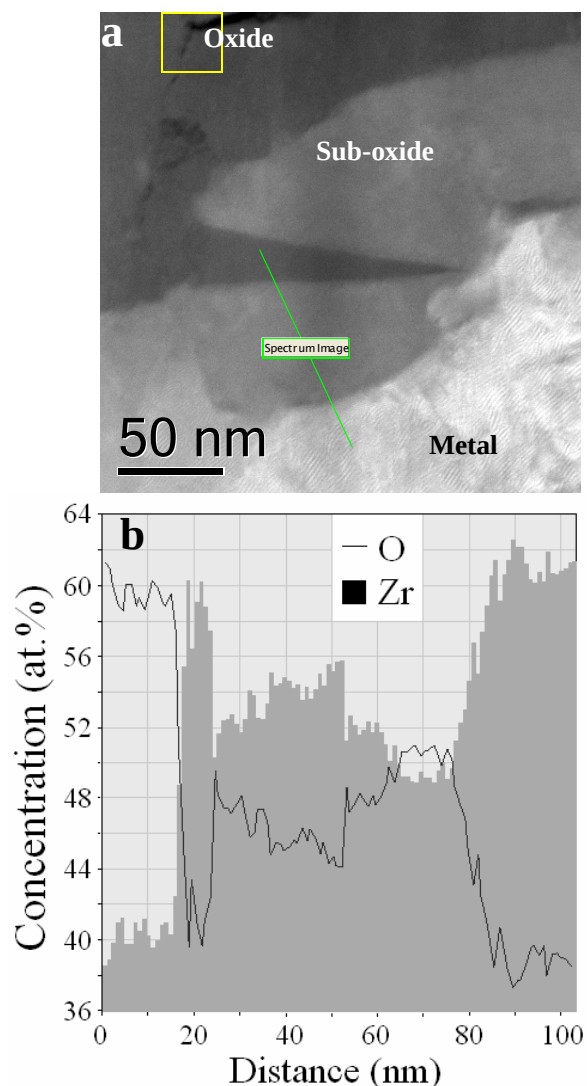


Figure 9: a) HAADF image of the metal/oxide interface; b) Profile of oxygen concentration across the metal/oxide interface measured by EELS along the line scan shown in a).

III.B. 3-D Atom Probe Analysis

Several specimens were successfully created that contained the metal-oxide interface in the apex region of the tip. A composition profile taken across the metal/oxide interface in such a sample is given in 11. It demonstrates a layer of intermediate composition between the alloy containing approximately 32% oxygen and the ceramic oxide containing the expected stoichiometry close to ZrO_2 . The composition of this intermediate region is ZrO . At the boundaries of this region there is a sharp transition to the alloy and ceramic oxide phases respectively. The oxygen content measured by the atom probe at the metal side of the metal/oxide interface is similar to that expected of a saturated solid solution⁴⁰. The difference between this result and that found with TEM will be discussed later.

Figure 12 shows the transition between the ZrO - ZrO_2 layers over a larger area of interface to improve the statistical significance of the data. Figures 12b and c demonstrate that there is segregation of both iron and tin to

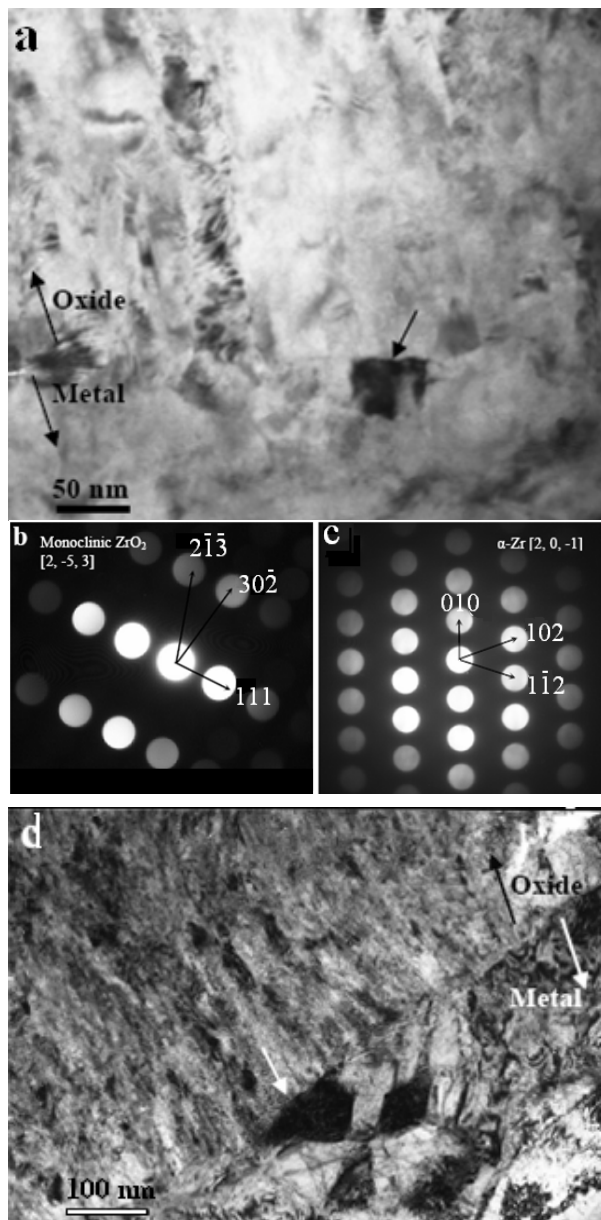


Figure 10: Examples of identified interface grains and their convergent beam diffraction patterns: a) a particle (arrowed) showing b) a monoclinic ZrO_2 structure and c) the $\alpha\text{-Zr}$ structure of d) a particle (arrowed).

this interface. The level of tin in the ZrO_2 region appears unusually high in Figure 12c as we would expect very little Sn in solution in the oxide. A possible reason for this can be understood from Figure 13 where Figures 13a and b show, from the metal and ZrO layers respectively, the mass-to-charge-state ratio in the region of the mass spectrum containing the characteristic peaks for tin. The resolution of the individual peaks is good and there is little background. Figure 13c shows the same region of the mass-to-charge spectrum in the ceramic oxide region. The poor thermal conductivity of the ZrO_2 causes ions to be emitted from the atom probe specimen for a period of time after a laser pulse is applied, as well as during the pulse. This distorts the mass-to-charge-state spectrum, causing 'thermal tails.' The delayed ions from the ZrO molecular

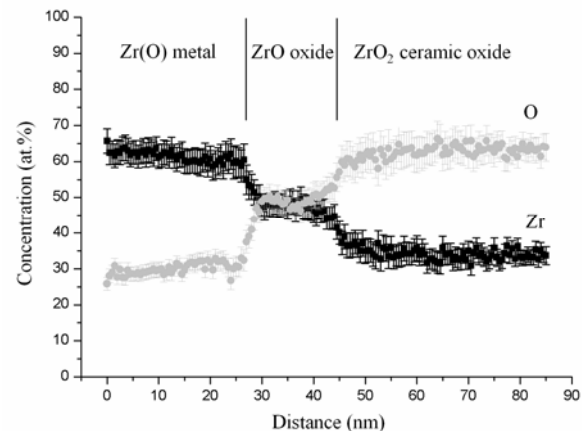


Figure 11: 3D atom probe composition profile taken across the metal/oxide interface of Zircaloy-4 (SRA) after 90 days in 360°C water.

ions detected at $u/e = 56$ spread over the region of the spectrum of Figure 13c containing the Sn peaks. It is not possible to distinguish the real signal from noise in this region, and causes an artificial increase in the apparent level of tin on the right hand side (the ZrO_2 region) of Figure c. The resolution of the peaks from each region can be related qualitatively with their electronic properties. The ZrO oxide layer displays properties much more similar to the metal substrate than the ZrO_2 ceramic.

The profiles shown in Figure 13 are taken over a large interface area, $30,000 \text{ nm}^2$. If we view the 3D atom map of such a region we notice that the tin appears to be clustered near the interface, rather than uniformly distributed at it, Figure 14. It is not possible to perform the same visual inspection for iron as the count is too low. However, we will have to undertake more analysis of possible focusing effects at the interface before we can come to a firm conclusion that Sn is localized in the grains at the metal/oxides interface.

IV. DISCUSSION

IV.A. The outer oxide

The oxidation of zirconium is known to occur by inward diffusion of oxygen ions through the oxide layer and the formation of new oxide at metal/oxide interface, therefore the observed oxide morphology in Figure 5 suggests the formation of an equiaxed structure first followed by columnar structures growing towards the metal to minimize the compressive stress resulting from the volume expansion on oxidation of the metal. This kind of morphology has been previously reported for pre-transition oxides on various zirconium alloys,^{22,42,43} but the development of a columnar-equiaxed structure towards the oxide surface can be seen much more clearly from the present study and other recent work⁴ using FIB specimen preparation techniques, where the TEM specimens have a large homogeneous electron transparent area encompassing the whole oxide layer.

The observation that the micro-cracks are primarily formed in regions containing higher fractions of equiaxed grains is in good agreement with previous studies.^{22,42,44}

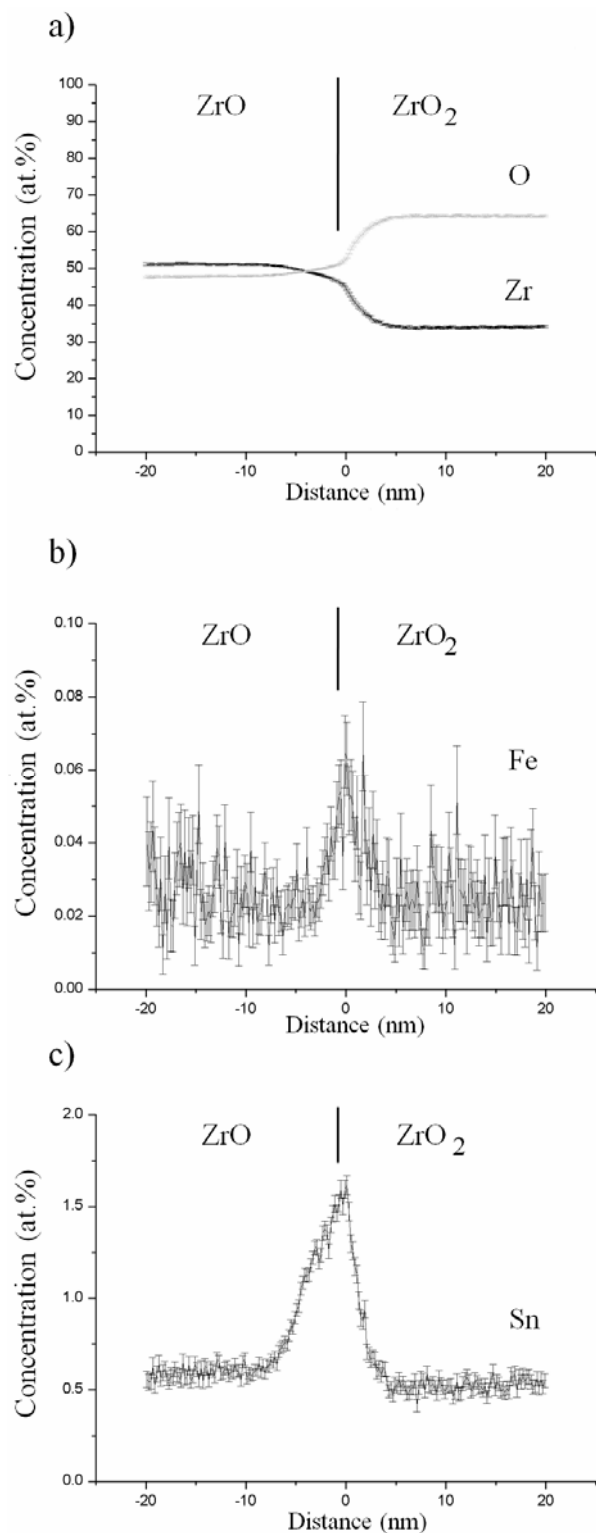


Figure 12: A 3DAP dataset in which a large area of ZrO-ZrO₂ interface was analyzed and averaged over the entire interface in the analysis volume using a proxigram, showing a) Zr and O, b) Fe, and c) Sn profiles.

This perhaps suggests that the columnar structure has a stronger intergranular cohesion, which has the effect of reducing crack propagation. Although it is difficult to be

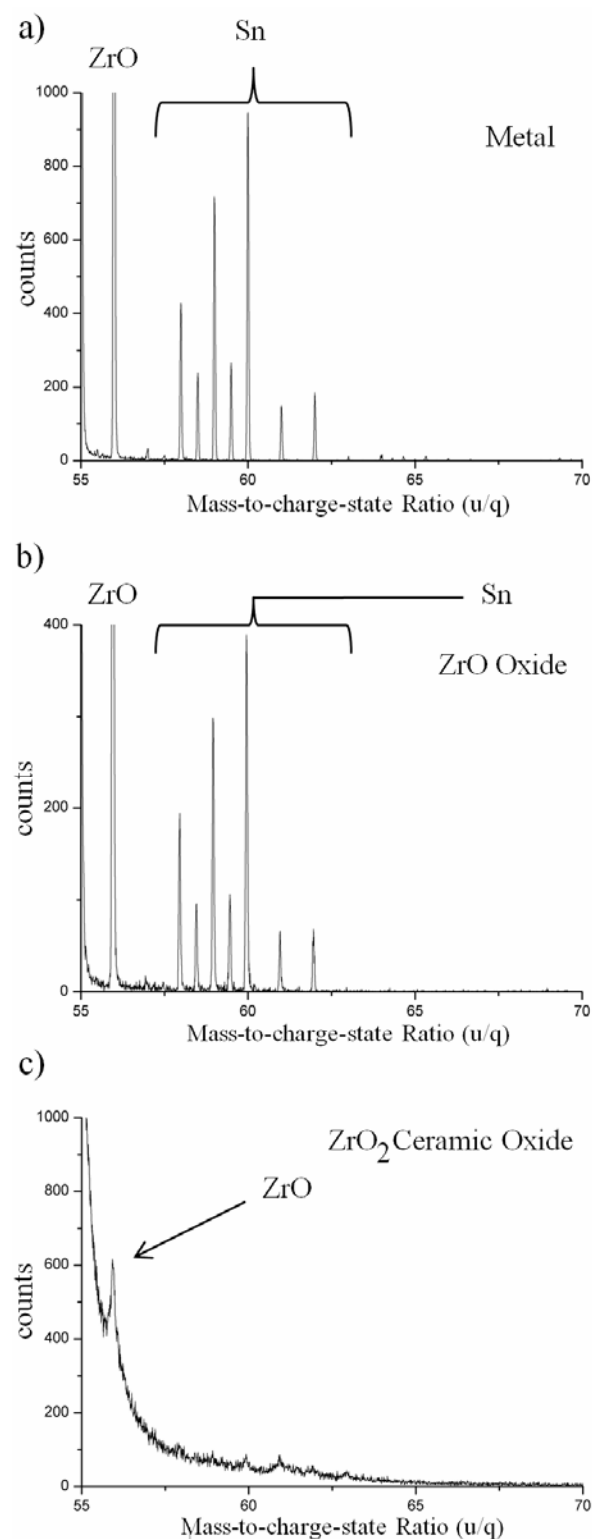


Figure 13: Mass-charge spectra of Sn²⁺ and the heaviest isotope of ZrO₂⁺ (at u/e= 56) in the; a) metallic, b) ZrO, and c) ZrO₂ regions. The poor thermal conductivity of the ZrO₂ region causes some ions to be delayed in their emission from the tip, producing tails on the spectra.

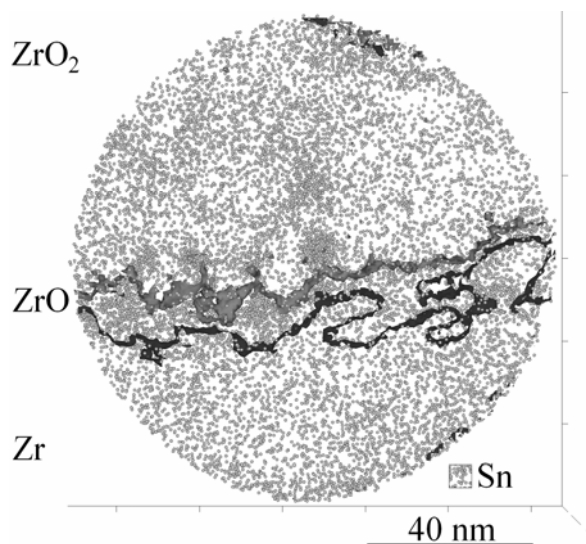


Figure 14: 3D atom map data showing the three-phase region at the interface. The intermediate ZrO layer is delineated between isosurfaces of constant concentration, marking the extremities of the metal and ceramic oxide regions. The tin atom map showing higher density in clusters at the interface. The apparent 'tin' concentrations in the ZrO₂ region are mainly noise, as seen in Figure 13c.

certain whether the pores and cracks seen in the TEM samples were already present in the bulk sample or formed during the TEM specimen preparation process, it should be noted that these cracks are systematically observed in similar locations while cross-sectioning the bulk sample in the FIB. In any case, the crack locations are likely to be places where high stresses were previously accumulated and later relaxed by the formation of cracks.

It has been reported that the first oxides formed on zirconium have a tetragonal or cubic metastable structure,⁴⁵ which is considered to be stabilized by high compressive stress⁴⁶ or small grain size⁴⁷ at the metal/oxide interface. Therefore, one of the possible stress accumulation/relaxation processes could be a phase transformation of initial tetragonal oxide stabilized at the metal/oxide interface to the monoclinic phase at the oxide some distance away the interface as the compressive stress decreases and the grain size increases. The shear deformation during this phase transformation could then lead to the formation of local porosity. Preferential growth of columnar monoclinic grains could be nucleated from the equiaxed grains at the interface that have preferred orientations with the underlying metal. The absence of further phase transformation and the higher intergranular cohesion between columnar grains could then reduce the porosity in the later middle and inner oxide. Such a process would explain the oxide and crack morphology that was observed using TEM.

IV. B. The metal/oxide interface

The existence of an intermediate layer between the zirconium matrix and stoichiometric ZrO₂ has been

previously observed by other workers^{19,21-24,48,49}, but with little agreement as to the composition of this layer. We believe that our results from z-contrast HAADF (Figure 9a), quantitative EELS and 3D atom probe analysis (Figure 9b and Figure) is the first convincing data on the stoichiometry of this layer. While previous EDX studies reported a smooth gradient of oxygen concentration across the metal/oxide interface,¹⁹ we find the oxygen level to be more or less constant (40-50 at. %) over a distance of about several tens of nanometers across the interface. Our confidence in this conclusion is enhanced by the fact that we obtain very similar quantitative compositional data from analysis techniques based on very different physical principles, and that the techniques we have used have intrinsically a high enough spatial resolution to detect composition variations on the nanometer scale. For the atom probe results there is excellent agreement with the known composition of the regions on either side of the intermediate phase. The oxygen content at the metal side of the metal/oxide interface is that expected in a saturated solid solution⁴⁰, and the ZrO₂ stoichiometry is accurately reproduced. This high solid solution oxygen content will have the effect of increasing the lattice parameter of the matrix and effectively forming a graded interface between the metal and sub-oxide. Oxygen also acts as a solid solution strengthener in zirconium and the additional oxygen in solution at the interface could thus enhance the ability of the metal substrate to resist stresses created by the formation of oxide. In the case of the TEM experiments, the measured oxygen concentration in the metal is higher than the known solid solution limit. We suggest that this could be a result of surface oxidation of the thin foils as it was found that the oxide content measured by EDX increased with the time between sample preparation and the TEM experiments.

The widths of the intermediate layer indicated by TEM imaging, EELS and atom probe experiments are in good agreement at 20-50 nm. We note, however, that our ability to explore a significant length of interface in each TEM sample reveals a significant variation in the thickness of this layer at different locations, and that, as shown in images like that in Figure 9, the suboxide has a complex 3D morphology.

Identification of the crystallography of the interfacial region has proved more difficult. Some of the interfacial grains were identified by micro-diffraction to be consistent with the crystal structure of monoclinic ZrO₂ or α -Zr, in agreement with results reported by Anada and Takeda⁴⁸ for pre-transition oxides of Zircaloy-4. Some other interfacial grains might be better identified to have a rhombohedral Zr₃O structure, as reported by Foord and Newcomb²¹ for pre-transition oxide grown on Zircaloy-4. The current study did not identify any grains with the ZrO cubic phase reported for the post-transition oxide of Zircaloy-2²³ or a ZrO amorphous layer a few nanometers thick containing unidentified crystallites.⁴⁹ What we can be confident of, however, is that there is no one dominant type of interfacial grain at the metal/oxide interface in our Zircaloy-4 samples, and that a good deal more analysis is required before we can with confidence describe the crystallography of these complex structures.

V. CONCLUSIONS

The preparation of TEM thin foils by focused ion beam milling has been shown to offer some important advantages for the study of oxides on zirconium alloys. Due to the large electron-transparent areas produced, the layered columnar/equiaxed oxide morphology was observed very clearly. Excellent homogeneity in sample thickness has been achieved, and this is essential for good EDX and EELS quantification. At the same time, the technique can also produce samples reliably with thicknesses down to 50 nm which is vital for EELS analysis and to improve the quality of electron diffraction patterns.

The 3D atom probe technique can provide detailed information pertaining to the nano-chemical distribution at localised regions of the interface, with around 100 nm field of view. We have developed a new technique for the reliable preparation of suitable samples for the analysis of metal/oxide interfaces that would have been regarded as impossible previously.

From the detailed observations conducted utilising this range of complimentary techniques, several characteristics of pre-transition Zircaloy-4 oxides have been observed.

The outer oxide contains a high concentration of equiaxed grains, typically 10-30 nm in diameter. The oxide developed later in the oxidation process consists of high aspect ratio, 200-400 nm long, columnar grains about 10-20 nm thick. Cracks and pores are much more common in the equiaxed outer oxide, and we suggest that cracks may form preferentially at grain boundaries of the equiaxed grains.

A very thin interface layer, a few tens of nanometers thick exists between the columnar ZrO_2 and the α -Zr substrate. Independent TEM and 3-D atom probe analysis demonstrate that this intermediate layer has an oxygen content close to ZrO , and that it is rather non-uniformly distributed along the metal/oxide interface. There are sharp chemical transitions at the boundaries of this region to both the ZrO_2 and metal regions. The oxygen content in the metal grains adjacent to the interface was found, as expected, to be close to that of saturated solid solution. No direct evidence from micro-diffraction was found for the presence of a cubic ZrO phase, neither was the layer found to be amorphous. Some of these interface grains could be matched with either $m\text{-ZrO}_2$ or $\alpha\text{-Zr}$ diffraction patterns, but a great deal more work needs to be carried out to properly understand the crystallography of this interface.

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