

Study of Oxidation Mechanisms of Zirconium Alloys by Electron Microscopy

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1 Introduction and literature review

1.1 Introduction

Zirconium and zirconium-based alloys were selected for use as nuclear fuel cladding and structural fuel assembly components in the nuclear reactors in the early 1950s [1, 2], especially in water-cooled reactors where the operation temperature range is $300 \pm 50^\circ\text{C}$ [3]. The main incentives come from the combination of low thermal neutron absorption cross-section, adequate corrosion resistance in high temperature water and reasonable mechanical properties in this material [2, 4].

The oxidation kinetics of zirconium and zirconium alloys is usually characterized by an initially decreased oxidation rate followed by a sharp increase in the oxidation rate after some time [5]. This change in kinetics is termed as “(kinetic) transition” or in many cases as “breakaway” [6-14]. After the transition the oxide changes to a friable grey one which tends to spall and finally leads to a rapid deterioration of the material [6].

Under conditions of high burnup and prolonged fuel campaigns, water corrosion and hydrogenation has become one of the main factors limiting the lifetime of zirconium alloys in the nuclear power reactor [15]. The improvement of corrosion behaviour of the zirconium alloys is obviously dependent on the extent of our understanding of the corrosion mechanisms, especially that of the breakaway process, which still remains incomplete and unclear in detail.

1.2 The current work

The current work described in this thesis is part of the EPSRC MUZIC project, which established the collaboration among several universities including Oxford, Manchester and the Open University to carry out a multidisciplinary study on the breakaway oxidation of zirconium alloys. The overall goal of the project is to further understand the mechanisms of

the oxidation and breakaway process, and a major strategy is to characterize the same corroded zirconium alloy cladding materials in many aspects by employing a variety of complementary analytical tools including advanced transmission electron microscopy (TEM), 3D atom probe, synchrotron X-ray diffraction, Raman spectroscopy, nano-indentation and in-situ electrochemical impedance spectroscopy etc.

This thesis describes the nano/micro-structural study and nano-analysis of the corroded zirconium alloys using up-to-date TEM and 3D focused ion beam (FIB) slicing and reconstruction techniques. The work mainly focused on the characterization of ZIRLO, which is a widely used commercial Zr-Nb-Sn-O-Fe alloy. Oxides grown on some other commercial Zr alloys and a test alloy (**See details in Section 4.1**) have been also included for comparison. In order to achieve reliable results, a great deal of work has been carried out first to optimize the experimental techniques and conditions. For example, a key issue for TEM characterization is the specimen quality. The most up-to-date sample preparation techniques using FIB have been employed in this work and the effect on the reliability of the resulting data studied. Other essential methodology development included quantitative electron energy loss spectroscopy (EELS) nano-analysis, electron diffraction data analysis and 3D FIB slicing data processing.

Following this introduction, a literature review on the oxidation of zirconium alloys and previous microstructural and microanalysis studies is given in the rest of this chapter. Chapter 2 describes working principles of FIB and the details of TEM sample preparation using FIB. Chapter 3 gives a description of the various TEM techniques used in this work and illustrates 3D microstructural characterization using FIB sequential sectioning and reconstruction. Information about the materials studied and the instruments used is summarized in Chapter 4. Chapter 5 describes the TEM investigations on oxide morphology, oxide phases and texture, crack and nano-scale porosity as well as some characterization of intermetallic precipitates (second phase particles) and hydrides. Chapter 6 focuses on the characterization of the

metal/oxide interface region, comprising a morphological study, EELS quantification of oxygen content and crystallographic identification. Chapter 7 is devoted to characterization using FIB sequential sectioning and reconstruction, where the 3D microstructure of the oxide, the cracks and the metal/oxide interface is studied in detail. Direct discussions relevant to the observations and results are incorporated in each results chapter, while a summary of main results and a more general interpretation of different aspects of my investigations focusing on the oxidation and breakaway mechanisms are given in Chapter 8. Some suggestions on future work can also be found in Chapter 8. It is frequently needed in this work to identify crystal structures of observed micro/nano-structures using electron diffraction and high resolution TEM (HRTEM). An error analysis on the measurement of lattice spacings using diffraction patterns and HRTEM images is given in Appendix A. Appendix B describes in detail the method and procedure for obtaining a reliable quantitative EELS characterization of oxygen content in the zirconium oxide samples.

1.3 Literature review

1.3.1 Zirconium and zirconium Alloys

The atomic number of zirconium is 40 and its atomic weight is 91.22. The absorption cross section for neutrons is the very low value of 0.18 barns [16], which is the most important advantage of Zr for its application as nuclear cladding materials. Pure zirconium has a hexagonal close-packed (HCP) crystal structure (α -phase) below 865°C. Above this transition temperature the body centered cubic (BCC) beta phase is stable. The melting temperature of zirconium is close to 1855°C.

In the 1960's, the Zircaloy series were introduced into commercial light water reactor cores [2, 3, 16]. Of these Zircaloy materials, Zircaloy-2 and Zircaloy-4 are still in use today. Another route of zirconium alloy development for fuel cladding used Zr-Nb alloys. The main

applications of Zr-Nb alloys are the Zr-1wt%Nb alloy in Russia and the Zr-2.5wt%Nb alloy in Canada. The ZIRLO alloy, Zr-1Nb-1Sn-0.1Fe, which was developed and selected as the advanced cladding material for Westinghouse fuel in the mid 1980s, has shown superior performance over Zircaloy-4 [1]. Other advanced alloys include low-Sn Zircaloy-4 variants, M5 [17], E635 [18] and HANA [19], but while their corrosion resistance may be improved, there are concerns about long term mechanical properties [5].

The nominal composition of typical zirconium alloys used as water reactor fuel assemblies and the reactor type in which they are used are summarized in **Table 1.1**.

Table 1.1 Nominal composition of typical zirconium alloys used as water reactor fuel assemblies [5, 15, 29]

<i>Alloys</i>	<i>Reactor Type</i>	<i>Nominal Composition (wt. %)</i>					
		<i>Sn</i>	<i>Fe</i>	<i>Cr</i>	<i>Ni</i>	<i>Nb</i>	<i>O</i>
Zircaloy-2	Boiling Water Reactor (BWR)	1.2-1.7	0.07-0.2	0.05 - 0.15	0.03 - 0.08	---	*
Zircaloy-4	Pressure Water Reactor (PWR)/ CANadian Deuterium Uranium (CANDU)	1.2-1.7	0.18-0.24	0.07 - 0.13	---	---	*
Zr-1% Nb (M5)	Pressure Water Reactor (PWR)	---	0.015 - 0.06	---	---	0.8-1.2	*
Zr-1% Nb (E110)	Russian design PWR (WWER) / Graphite-moderated Russian design BWR (RBMK)	---	0.006 - 0.001 2	---	---	0.95-1.05	≤0.1
Zr-2.5Nb	CANadian Deuterium Uranium (CANDU)	---	≤0.15	≤0.0 2	≤0.0 07	2.4-2.8	0.09-0.13
ZIRLO	Pressure Water Reactor (PWR)	0.9-1.2	0.1	---	---	0.9-1.13	0.09-0.15

* Oxygen content in all grades ranges from 1100 to 1400 ppm

1.3.2 Oxidation of zirconium and zirconium alloys

Pure ZrO₂ has a monoclinic crystal structure at room temperature and transitions to tetragonal and cubic at increasing temperatures. A temperature-pressure phase diagram of

ZrO₂ is given in **Figure 1.1a**. The schematic drawings of crystal structure which illustrated the atomic arrangement can be seen in **Figure 1.1b**.

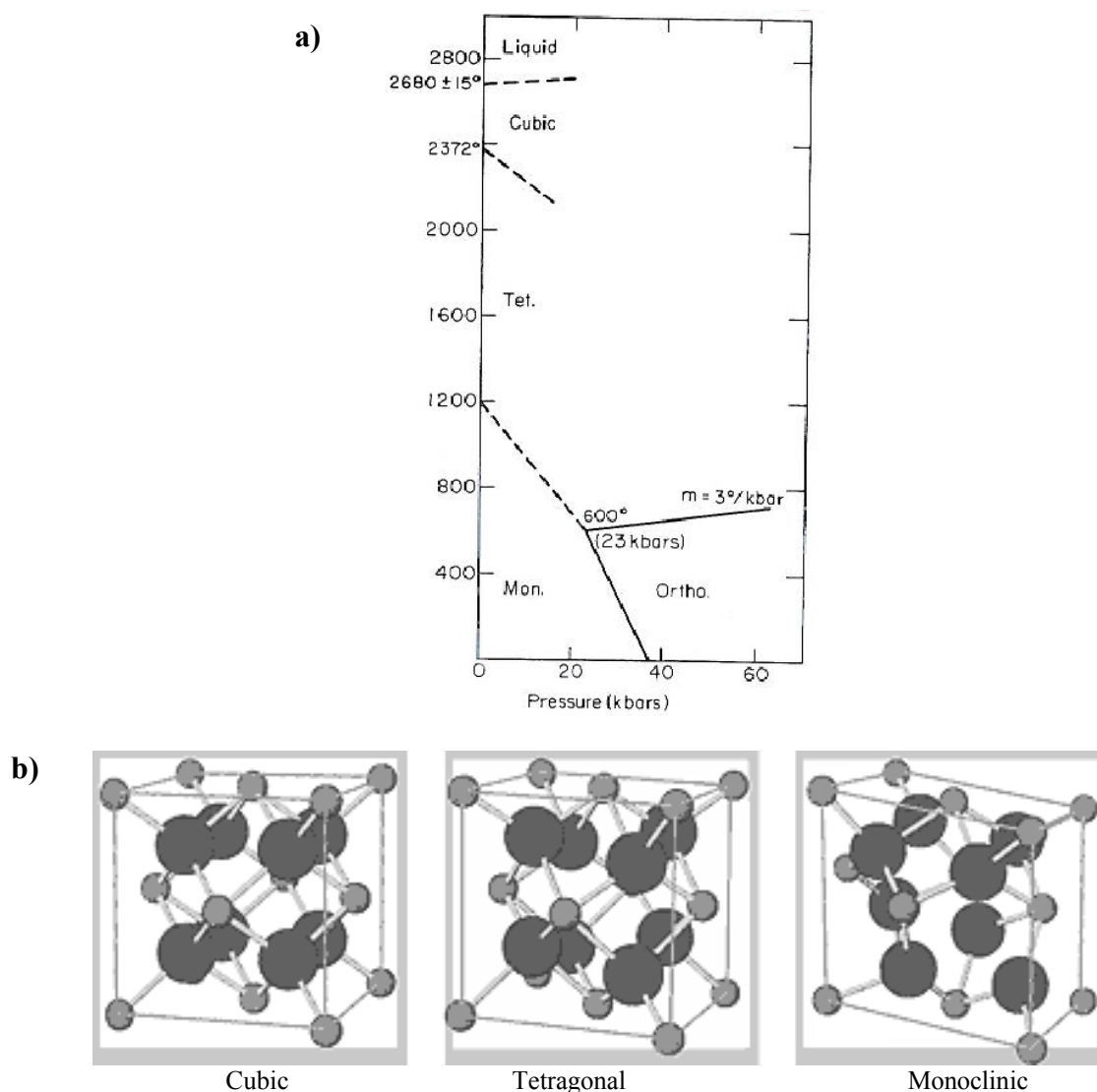


Figure 1.1 a) temperature-pressure phase diagram of ZrO₂ [20]. b) Schematic drawings of monoclinic, tetragonal and cubic crystal structure which illustrated the atomic arrangement [21]. Bigger and darker spheres = O atoms, and smaller and lighter ones = Zr atoms.

The growth of the oxide layer on zirconium has been shown to occur by diffusion of O²⁻ ions (via anion vacancies) through the oxide and formation of new oxide at the metal-oxide interface [16]. It is found that the diffusion of oxygen ions predominantly occurs at crystallite boundaries or at other easy paths in the oxide [22-24]. To achieve overall charge neutrality in the oxidation process, an electron current flows in the opposite direction to that of oxygen ion migration, i.e. from the interface to the oxide surface, and is proposed to occur via easy paths

associated with second phase particles in the oxide matrix [3, 25] or due to the semiconducting properties of the oxide [26]. However, the extent of coupling between the electronic and ionic fluxes remains unquantified. From the experiments that measure the potential drop across the oxide film during oxidation, it is concluded that in general electron transport is the rate-determining process, especially in early oxidation stages [2]. Beie et al [25] proposed that oxidation in the post-transition period was governed by oxygen anion diffusion in a “barrier layer” (with only small isolated pores) at the metal-oxide interface, and illustrated by a simple defect equilibrium argument that different rate-limiting mechanisms might exist at different locations in the oxide (**Figure 1.2**). Tupin et al. [27, 28] have carried out detailed studies to test the steady state and rate limiting step assumption in the pre- and post-transition stage for the steam oxidation of Zircaloy-4 and a ZrNbO alloy between 500 and 550 °C, and proposed different rate limiting steps for the two oxides. Their results are summarized in **Table 1.2**.

1.3.2.1 Oxidation kinetics

1.3.2.1.1 General aspects

The kinetics of high temperature oxidation are similar in shape for both zirconium and zirconium based alloys, and the similarity holds irrespective of the oxidising media for oxygen, air, water or steam [3, 16, 30]. The kinetics resolve into two distinct regimes, i.e. an initial period of slow corrosion rate and followed by corrosion at an accelerated rate. A general representation is shown in **Figure 1.3** [5]. The point at which the kinetics change from the first mode to the second has been variously termed the “breakaway”, “transition time”, or “breakdown” [2, 5-14]. Differences in alloying elements and oxidising media were shown to be the major influence on changes in the time for this transition to occur and/or the oxidation rate. For example, the tin content is believed to cause the early transition observed in the

oxidation kinetics of Zircalloys [31]; the time to transition for high-purity zirconium is much longer in oxygen than in air [32]; higher oxygen or water pressures result in a transition at thicker oxide thickness [27, 32], and oxidation of alloys with 1 wt% Nb at 400-500°C showed lower pre-transition oxidation rates in air than in steam [33].

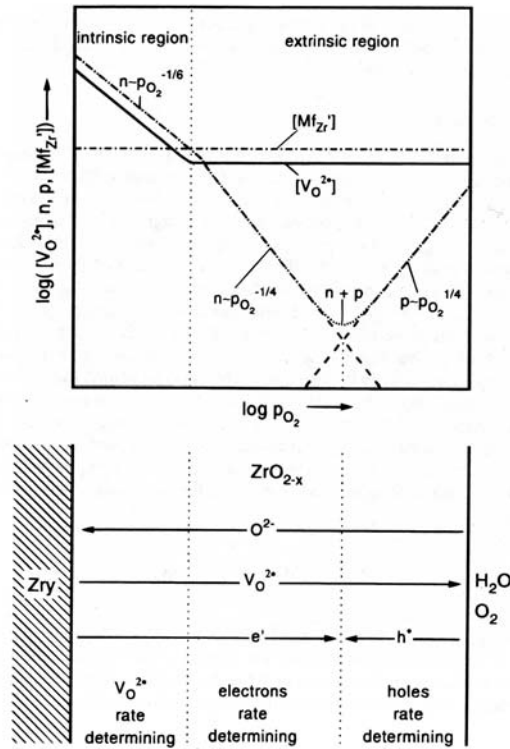


Figure 1.2 Concentration of charge carriers in ZrO_{2-x} as a function of oxygen partial pressure (top), and corresponding transport barrier layer on Zircaloy (bottom) [25].

1) Pre-transition Region

Before transition, the kinetics may be described by the empirical equation

$$\Delta m = kt^n \quad \text{Equation 1.1}$$

where Δm is the weight gain, t is the time and k and n are constants for a given temperature.

The rate constant k is related to the activation energy for the rate-controlling process in the pre-transition region and can be derived from the temperature dependence of oxidation rate.

Table 1.2 Test of steady state and rate limiting step assumption in the pre- and post-transition stages for water vapor oxidation of Zircaloy-4 and a ZrNbO alloy [27, 28].

	Zircaloy-4		ZrNbO	
Oxidation stage	Pre-transition	Post-transition	Pre-transition	Post-transition
Steady state assumption	Valid	Probably	Valid	Not determined
Rate limiting step assumption	Valid	Not valid	Valid	Valid
Proposed rate limiting step	Diffusion of oxygen	N.A	Diffusion of absorbed OH groups	An interface step different from that in pre-transition stage, or diffusion through a layer with constant thickness

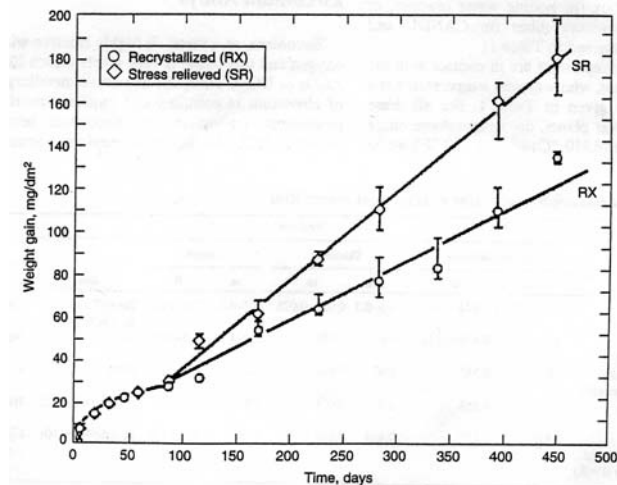


Figure 1.3 A general representation of oxidation kinetics of zirconium and its alloys [5].

It has been shown by various investigators that n can be either fitted with $1/2$ or $1/3$ in the pre-transition period. Furthermore, Dawson et al. [32] reported that the pre-transition stage of the oxidation of Zircaloy-2 in oxygen and water vapour could be divided into three periods with 2 extra “transitions”: firstly parabolic kinetics changed to a second parabolic rate with a different rate constant at a weight gain $\sim 1 \text{ mg/dm}^2$, then cubic kinetics followed at a weight gain $\sim 10 \text{ mg/dm}^2$ before the kinetics finally transitioned to linear at $\sim 30 \text{ mg/dm}^2$. It is currently believed that although the pre-transition oxide is regarded as a diffusion barrier, high

temperature oxidation of zirconium deviates from ideal lattice diffusion controlled parabolic behaviour [2, 34].

The cubic growth rate has been related to reduced oxygen diffusion during the oxide growth, by formation of randomly distributed cracks localized at or near oxide/metal interface [32, 35], or the reduction in the crystalline boundary area due to the evolution of the oxide grain shape and the growth of the grain size [2, 36]. An attempt has been made by Yoo et al [37] to give a quantitative description and prediction for the parabolic to cubic transition by taking into account the stress gradient in addition to the oxygen concentration gradient as diffusional driving forces.

2) Post-transition region

The post-transition stage is characterized by an accelerated oxidation rate. For zirconium alloys, the transition generally starts when the oxide thickens to about 2 μm [2]. While a near linear rate is often assumed in the post-transition region, a similar equation to that for pre-transition region can be used to model the kinetics [5]:

$$\varepsilon = \varepsilon_0 \cdot t \cdot \exp(-\Delta H / RT)$$

where ε is the oxide thickness, ε_0 is an experimental kinetic constant and ΔH the activation enthalpy. Typical values of these parameters are: $\varepsilon_0 = 0.5$ to 2×10^8 $\mu\text{m}/\text{day}$ and $\Delta H = 110$ to 120 kJ/Mol , which are similar to those for the diffusion of oxygen in zirconia [5]. By modelling the experimental corrosion data, Maroto et al. [38] also showed that the linear post-transition kinetics can be fitted with the kinetics of the diffusion of oxygen vacancies through a dense “barrier layer” with constant thickness.

1.3.2.1.2 Corrosion of zirconium alloys in high temperature water and steam

Most studies on corrosion of zirconium alloys have been focused on conditions of high temperature water and steam, since zirconium alloys are mainly used in LWRs. Typical reactor environments in which zirconium alloys are used are shown in **Table 1.3**.

Table 1.3 Typical temperatures and pressures in reactor environments [5]

Reactor Type	Coolant Temperature °C	Coolant Pressure MPa
Pressurised Water Reactor (PWR)	290-335	15.5
Boiling Water Reactor (BWR)	275-285	7
CANadian Deuterium Uranium (CANDU)	265-310 (Heavy water)	10
Russian design PWR (WWER)	290-320	15.7
Graphite-moderated Russian design BWR (RBMK)	270-284	6.7

Uniform corrosion, which refers to the formation of a uniform oxide, is observed in the PWR, while nodular corrosion, which takes the form of locally thicker patches grown on the uniform oxide, is usually observed in BWRs and also occasionally in PWRs if the oxygen content in the primary coolant is high [39]. Nevertheless, only uniform corrosion will be focused on in this thesis.

1) Characteristics of Zircaloy Corrosion

A black coherent oxide film is formed following an initial appearance of interference colors in the pre-transition period. After transition, a gray or white oxide replaces the black oxide. Transition can start at single points before spreading over the whole surface (**Figure 1.4**).

The exponent n in **Equation 1.1** was reported to lie in the range 0.25-0.6 for the corrosion of Zircalloys in high temperature water or steam [3]. Many studies have reported that a cubic law is more likely at lower temperatures, while a parabolic law is clearer at higher temperatures. The temperature that separates the two behaviours appears to be in the range of 900-1000°C [40-42]. This trend has been related to the monoclinic to tetragonal oxide phase transformation at about 1000 °C, which changes the oxygen diffusivity in the ZrO_2 lattice [42].

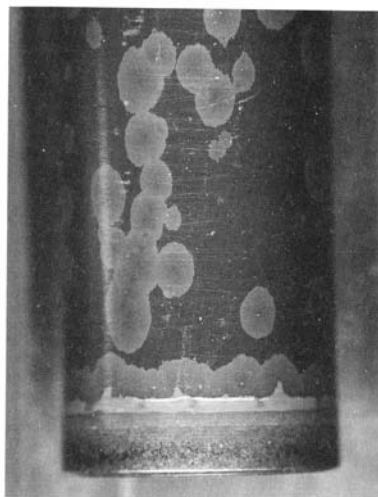


Figure 1.4 Appearance of corroded Zircaloy tube exposed to high-pressure water containing 70 ppm LiOH at 350 for 140 days [25].

At least two different modes of development of transition have been observed in the oxidation of Zircalloys, according to the summary given by Cox [2]. The first mode is found in aqueous solutions at 300-360°C, with a sharp increase in oxidation rate and a successive cycle of apparently pre-transition corrosion periods, such as first observed in the corrosion of Zircaloy-2 in 360°C water by Griggs et al. [43] and other studies [38, 44, 45]. An example is given in **Figure 1.5**. The rate constant for each cycle could be fitted with one value. The cyclic growth will eventually be replaced by a linear rate. This was suggested to be a result of different oxidation rates at different locations [38]. Maroto et al. [38] found that the rate constant of the post transition linear growth (starting from an oxide thickness of 6.4 μm) for Zircaloy corrosion in steam at 435°C was the same as that of the pre-transition cycle until the oxidation rate increased at higher weight gains of 280 mg/dm² (corresponding to a thickness of about 18.7 μm). A similar second increase in the linear rate in the post-transition regime was also reported by Hillner et al. [46] in the prolonged high temperature water (316-360 °C) oxidation of Zircaloy-2 and Zircaloy-4 (**Figure 1.6**). It was found that the post-transition rate increased from a lower linear rate to a higher one at ~30 μm and this was termed by the author as “a second transition” and “stage 2 kinetics”.

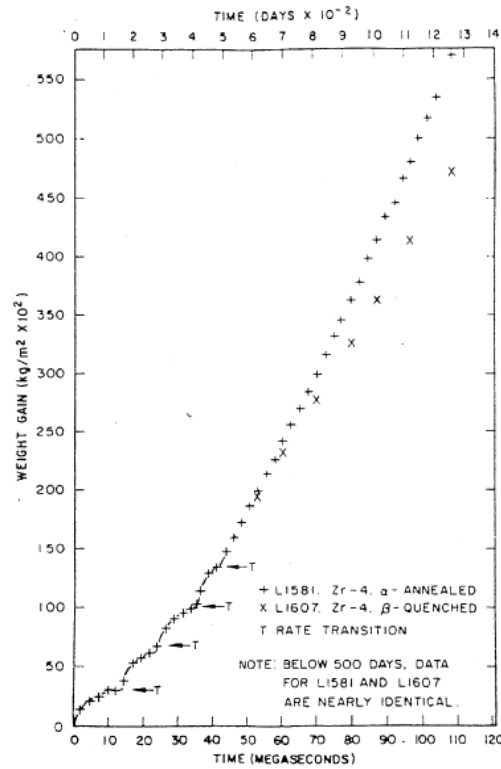


Figure 1.5 Cyclic nature of post-transition corrosion of Zircaloy-4 in 633 K water [2].

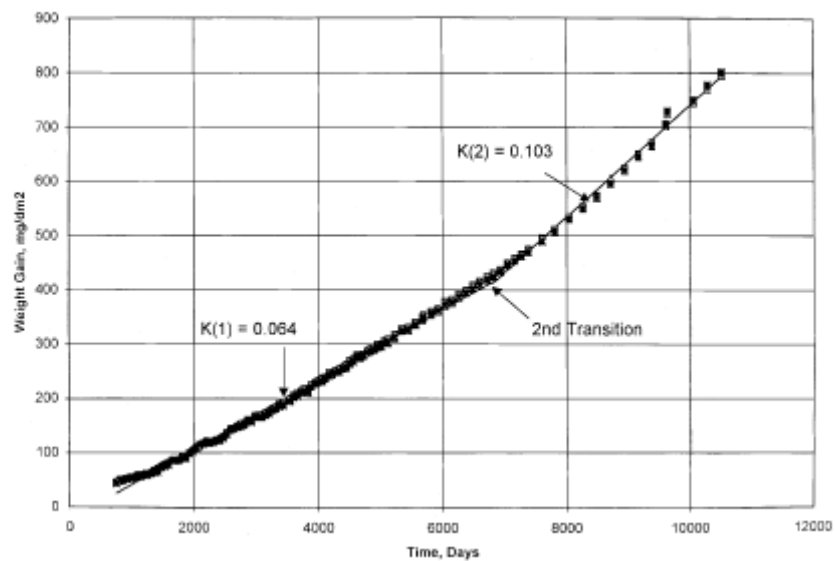


Figure 1.6 Weight gain as a function of exposure time for a Zircaloy-2 oxidized in water at 316°C [46].

At higher temperatures in oxygen or low-pressure steam, a more gradual change from pre-transition kinetics to an accelerated linear corrosion process is observed. In this case, the transition can take place over the whole pre-transition period, and the post-transition rate actually often shows a slowly increasing rate instead of being precisely linear. It was argued

that the apparently linear rate at high temperature still has cyclic nature and might be merely a representation of a condition where the transition process occurs on a small scale across the surface and the weight gain averages out as a result of different stages of oxidation over larger areas of the specimen [3, 47]. **Figure 1.7** shows a representation of this hypothesis.

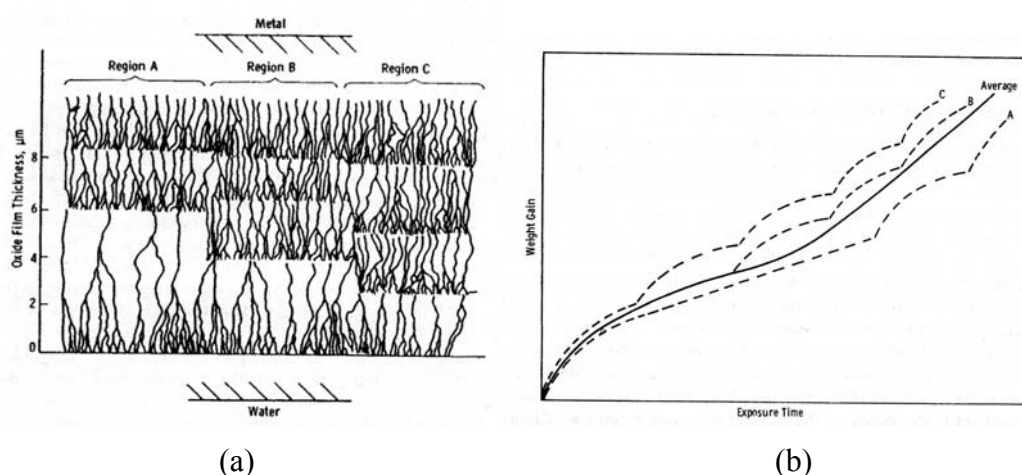


Figure 1.7 Relation between the structure of the oxide film and multiple rate transitions in the corrosion kinetics of Zr alloys. (a) schematic of the grain structure through the thickness of an oxide layer. (b) schematic of the local corrosion kinetics for the three regions shown in (a) and the macroscopically observed linear post-transition corrosion rate [47].

2) Characteristics of niobium containing Zr-alloy corrosion

Many studies [1, 19, 38, 48-57] have reported that Zr-Nb based alloys with suitable heat treatment can show a major improvement in corrosion rate over Zircaloy-4. **Figure 1.8** shows a comparison of the post-transition rates of Zr-1Nb, Zr-2.5Nb, ZIRLO and Zircaloy-4 in autoclave corrosion tests at various temperatures (589-727 K).

Kim [57] reported the oxidation behaviours for Zircaloy-4 and ZIRLO in the temperature range 700–1200 °C in steam. The results showed the oxidation resistance of ZIRLO below 1200 °C was superior to that of Zircaloy-4. In long term autoclave water and steam corrosion tests, ZIRLO has been shown not to exhibit a second breakaway (transition) in contrast to Zircaloy-4 [1]. The oxidation rate of ZIRLO was better than Zircaloy-4 in 633K water but worse in 672K and 700K steam prior to the onset of accelerated corrosion in Zircaloy-4.

Lin et al. [56] showed that oxidation was faster for a Zr-2.5Nb alloy than for Zircaloy-4 when oxidized in an autoclave at 623K with lithiated heavy water. Maroto et al [38] also reported that in the temperature range 265-435°C, the water autoclave corrosion of Zr-2.5Nb had a higher corrosion rate than Zircaloy-4 and did not show the cyclic behaviour seen in Zircaloy-4. The higher corrosion rate and absence of cyclic corrosion were attributed to faster oxidation of β -Zr present in the Zr-2.5Nb alloy.

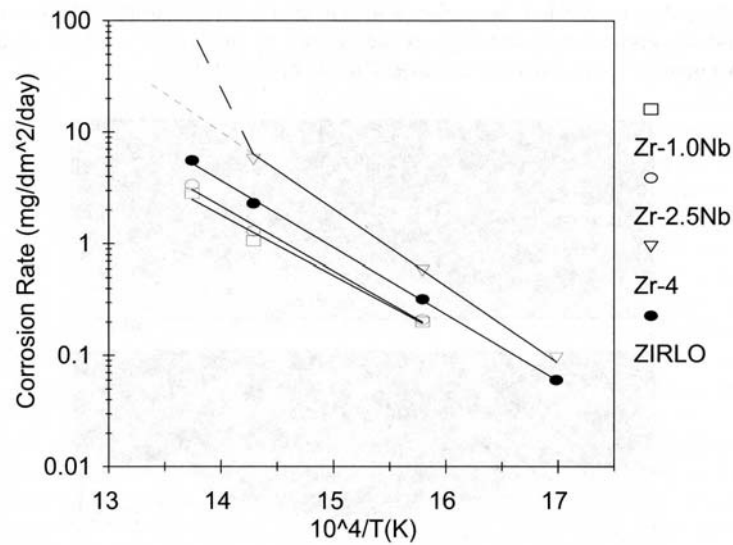
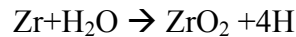


Figure 1.8 Comparison of the post-transition rate of Zr-1Nb, Zr-2.5Nb, ZIRLO and Zircaloy-4 in autoclave corrosion test at various temperatures [1].

1.3.2.2 Hydrogen absorption

The oxidation of zirconium in high-temperature water follows the reaction:



Part of the released atomic hydrogen dissolves into zirconium metal to form a solid solution at high temperatures and will precipitate as zirconium hydride at lower temperatures. Usually δ -hydride ($\text{ZrH}_{1.66}$) or γ -hydride (ZrH) is reported in the α -Zr matrix. The equilibrium δ -hydride has a greater tendency to form with increasing hydrogen content in the metal and/or decreasing cooling rate [58, 59]. Northwood and Lim [59] found that at slower cooling rates

and higher H contents radial (i.e., through-wall) hydrides tended to form in the Zr-2.5Nb tube, which could lead to through-wall cracks.

The hydrides are brittle at low temperatures, which could result in a reduced ductility of the alloy. Garde et al. [60] found that the local hydride precipitate volume fraction was a better parameter than the average hydrogen concentration level to evaluate the effects of hydride on ductility, and that there was a critical volume fraction of local hydride precipitates below which the ductility of Zircaloy-4 could be maintained above a certain minimum value. It was reported that the extent of embrittlement depended not only on the volume fraction of hydride present, but also on its morphology and in particular the orientation of hydrides with respect to the applied stress [59, 61, 62].

Charquet et al. [63] reported the hydrogen absorption kinetics of Zircaloy-4 in 400 and 500°C steam. They found that the hydriding rate increased but the absorption ratio with respect to oxygen weight gain decreased with increasing corrosion rate, and related this observation to an assumption that the diffusion of hydrogen is slower than oxygen diffusion in a barrier oxide layer. The final heat treatment, the cumulative annealing parameter, the tin content and the Fe/Cr ratio were found to have little additional intrinsic effect on hydrogen pick up.

Warr et al. [64] found that the thin oxide formed in steam at 400°C on Zr-2.5Nb acted as an excellent hydrogen permeation barrier, with a much lower diffusion coefficient of hydrogen than the bulk alloy. Enhanced transportation of hydrogen up to the metal-oxide interface was related to the presence of a network of interconnected pores extending to the interface [64, 65].

Krishna et al. [66] observed predominantly grain boundary hydrides in Zircaloy-2 subjected to hydride formation through gaseous hydrogen charging. They found that low CSL (coincident site lattice) boundaries were generally resistant to hydride formation and elastically harder grains also arrested the formation of hydrides.

The effects of hydrogen absorption on corrosion rate have been investigated by many workers. Kim et al. [67] found that the hydrides locally precipitated on the Zircaloy-4 cladding outer surface initiated in-reactor corrosion rate enhancement depending on the extent of the hydrides. Blat and Noel [68] reported that hydrogen precharging of a Zircaloy-4 above the solubility limit induced an increase in corrosion rate in steam at 400°C, especially for high cathodic potential hydrogen charging.

Oskarsson et al. [69] studied the pre-transition behaviour of pre-hydrided Zircaloy-2 and found that the oxidation of massive surface hydrides resembled the oxidation of zirconium metal. They then concluded that the accelerated oxidation of zirconium alloys cannot be due to an increased oxidation rate of the hydride itself compared to the metal, but a combined effect of, for example, interfacial roughness and hydride precipitation. Garde [70] indicated that the corrosion rate acceleration observed for Zircaloy-4 in autoclaves at long times was associated with the onset of hydride precipitation and subsequent hydride fracture at the metal-oxide interface. However, SEM morphological observations of hydrides by Blat and Noel [68] did not support this mechanical degradation mechanism.

Lelievre et al. [71] suggested from neutron diffraction analysis that the precipitation of hydride and transfer of hydrogen from intermetallic precipitates to Zircaloy matrix grains could activate the transformation of tetragonal to monoclinic zirconia, which would lead to formation of strained zones, voids or fractures allowing more effective oxygen diffusion and higher corrosion rates. In turn, Takeda et al [72] reported that oxides on zirconium alloys containing more tetragonal ZrO_2 showed lower hydrogen pickup, and suggested that SPPs affects hydrogen absorption indirectly by modifying solute concentrations in the matrix.

Bossis et al. [17] reported that hydrogen pick-up in an advanced Nb-containing alloy M5 was lower than that in Zircaloy-4, and the difference increased with burn-up. It was noted that

the difference could be explained by the different localizations of the reduction reaction of protons in M5 and Zircaloy.

1.3.2.3 Impact of alloying elements

During the development of zirconium alloys for nuclear reactor applications, numerous studies have been done on the effects of alloying additions on the oxidation behaviour [1, 3, 5, 16].

1. Tin

Sn is added to zirconium to improve its corrosion resistance by counteracting the negative effects of nitrogen impurity in the metal and also improving the yield stress and creep resistance. However, it is found to cause an early transition and an increased post-transition rate for uniform corrosion in oxygen. In high temperature water (400°C and above), the behaviour of Zircaloy-2 is found to be worse than that of alloys containing less tin. Long-term uniform corrosion tests in 360°C water and 400°C steam for Zircaloy-2 and -4 based alloys showed that tin significantly increased the post-transition corrosion rate [45].

Garde et al. found that the in-PWR corrosion resistance of Zircaloy-4 improved when the Sn content was reduced to the lower limit of the ASTM range [73]. Etoh et al. [74] found that decreasing the content of tin showed improved corrosion resistance both in BWR and in autoclaves. It was found that the negative effect of tin was more pronounced in high burn-up in-reactor corrosion [17].

A negligible effect of decreased Sn content was reported on the high-temperature steam oxidation kinetics for Zircaloy-4 cladding [42]. Garzarolli et al. [75] found in out-of-reactor tests that Sn shows a beneficial effect at the lower temperature (<300°C) but is detrimental at higher temperatures.

Electrochemical impedance measurements suggested a decrease in the ionic and electronic resistance of the dense oxide layer with increasing tin contents [76], which could enhance the oxidation rate, but the mechanism of this effect is not clear. The stable oxidation state was calculated to be Sn^{4+} and so can not to directly affect the semiconducting properties of ZrO_2 as an extrinsic dopant [77]. It was speculated that Sn may stabilize other aliovalent alloying elements in the oxide lattice [26].

Harada et al. [45] considered that tin might stabilize monoclinic zirconium oxide, but Barberis [36] and Beie et al. [25] suggested that tin stabilizes the tetragonal phase.

2. Iron, chromium and nickel

The role of the transition alloying elements Fe, Cr and Ni in affecting the corrosion resistance is not resolved. It was thought that the addition of Fe, Cr, and Ni improved the plasticity of the oxide and thereby allowing the protective oxide to attain greater thickness before breakdown [78]. Other models proposed that the addition of Fe, Cr and Ni (as well as other alloying elements that have normal oxidation states other than IV) increases the conductivity of the oxide [26] or enhances defect (such as anion vacancy) populations and migration [77].

Small amounts of Fe, Cr, and Ni, of the order of 0.05-0.2%, are generally correlated to good behaviour [8, 19]. The increase of the total content of Fe and Cr from 0.3% in Zircaloy-4 to 0.7% was found to improve the mechanical properties without affecting the corrosion resistance [79], but the increase of the total content of Fe, Cr and Ni in Zircaloy-2 from 0.34% to 0.4% decreased the corrosion resistance at 450° in air [80].

Control of the uniform corrosion resistance has been reported by adjusting the Fe/Cr ratio of the matrix for Zircaloy-4 [76, 81] and for a niobium-containing alloy [79], and the Fe/Ni ratio of the matrix for Zircaloy-2 [72, 76]. It was found that the hydrogen uptake decreased with

increasing iron additions [82] or Fe/Cr ratio [72], and a decrease in Ni addition to Zircaloy-2 [72, 83].

A supersaturation of these solute elements in the matrix was found in earlier work to be detrimental to uniform corrosion [84-88]. One recent observation reported the opposite effect, where a much higher contents of Fe and Cr than their maximal solubility in the α -Zr matrix led to superior uniform corrosion resistance of Zircaloy-4 [89].

3. Niobium

Niobium has higher solubility in α -Zr matrix than Fe, Cr, and Ni, which was thought to be a reason for the superior corrosion resistance of Zr-Sn-Nb alloys (e.g. ZIRLO and M8) over Zircalloys in lithiated water [89].

The effective valence of Nb ions in the Zr sub-lattice of the oxide has been estimated by X-ray adsorption near edge spectroscopy (XANES) to be between 2 and 4, which means that Nb can be considered either as a hypovalent or isovalent defect [90].

Low-niobium alloys have improved strength compared with Zircalloys, and the corrosion resistance was found to be optimum at about 2-2.5% Nb addition for the oxidation of Zr-Nb binary alloys in steam [3].

1.3.2.4 Impact of second phase particles

The alloying elements used for nuclear applications such as O, Cr, Fe, Ni, Nb and Sn have extensive solubility in β -zirconium. In the α phase, oxygen, tin and niobium have very limited solubility. The transition metals (iron, chromium and nickel) are almost insoluble in the equilibrium α phase and form intermetallic precipitates (SPPs).

In the PWR or static water autoclave, the uniform oxide growth rate was shown to be increased by keeping the precipitate size small [75, 80, 88, 91-93]. Thus, large precipitates (larger than 150 nm) are required for good resistance to uniform corrosion for pressurized

water conditions [5]. A contrary observation in a simulated BWR condition was given by Bojinov et al. [94], where a better corrosion resistance was achieved in Zircaloy-2 with the highest number of small SPPs. The oxide studied in their work should be in the pre-transition region (oxide thickness $\sim 0.3 \mu\text{m}$), which might explain this discrepancy.

For the Zr-Nb-based alloys, the effect of the SPP size distribution on uniform corrosion was shown to be opposite to that of Zircaloy-4, i.e. a uniform distribution of fine SPPs (with needle-like morphology [1]) is beneficial to optimum corrosion performance [1, 48, 55, 79, 95, 96]. A necessary condition was reported to be the complete precipitation of β -Nb content above the solubility level from the matrix [1]. This was found to result in a reduction of both electronic and ionic conductance of the oxide [97]. Several studies have shown that the highest weight gain was related with the lowest SPP volume fraction, being more obvious in steam corrosion than in air [98, 99].

Intermetallic precipitates are believed to act as cathodic sites because they are more noble than the surrounding Zr; as a result SPPs form galvanic couples with the Zr matrix. By considering this electrochemical concept, together with mechanical factors and passivity of the reaction surface, Weidinger et al. [100] developed a model capable of explaining the correlation between corrosion resistance and SPPs for Zircalloys.

The hydrogen uptake behaviour is also dependent on intermetallic precipitates. Bossis et al. [101] using SIMS found that the preferential paths for hydrogen penetration were in or close to nonoxidized precipitates. Coarse precipitates compared to fine precipitates [102], or $\text{Zr}(\text{Fe},\text{Cr})_2$ compared to $\text{Zr}_2(\text{Fe},\text{Ni})$ [82] were both found to give a larger amount of hydrogen uptake. These results have been explained by precipitates in the oxide film acting as the window for hydrogen absorption, with larger intermetallic precipitates or $\text{Zr}(\text{Fe},\text{Cr})_2$ retaining their unoxidized stage for longer.

1.3.2.5 Impact of heat treatment

The effect of heat treatment, especially the β -solution treatment and the intermediate and final annealing, is mainly on the microstructure, such as the size and distribution of second phase particles, and on the solute concentration in the zirconium alloy matrix.

β -solution treatment is a three step process: first of all an α to β phase transformation through furnace heating, secondly a homogenisation period in the β phase field for dissolving the second phase precipitates and finally a β to α phase transformation by cooling (β quenching) the specimen in water or gas [103].

Massih et al. [103] reported that a lower β -quenching rate leads to a superior uniform corrosion rate due to the formation of larger and a lower number density of SPPs. The opposite was reported by Yao et al. [89]. It was noted the fast β -quenching treatment significantly slowed down the development of pores to cracks in oxide films and reduces the uneven growth tendency of the oxide, leading to a reduced corrosion rate. Since these studies didn't give values of the rate of β -quenching that were employed, it is not known if they are consistent with the results reported by Charquet [81] who found an optimum range of quenching rates from the β -phase of about 10-100 °C/s for maximum uniform corrosion resistance. It was noted that when cooling rates were too low, extensive precipitate-free regions were obtained, while excessively rapid quenching led to martensitic structures, both of which were detrimental to uniform corrosion resistance. Massih et al. [103] introduced a parameter that is the mean lamella thickness formed upon β -quenching, and showed that the effective quenching rate can be correlated to it. Regarding nodular corrosion, fast β -quenching is usually beneficial [75, 104, 105].

Increase of annealing time after β -quenching below a critical temperature [106] leads to a decrease in solute contents in the matrix and an increase in SPP size (**Figure 1.9**).

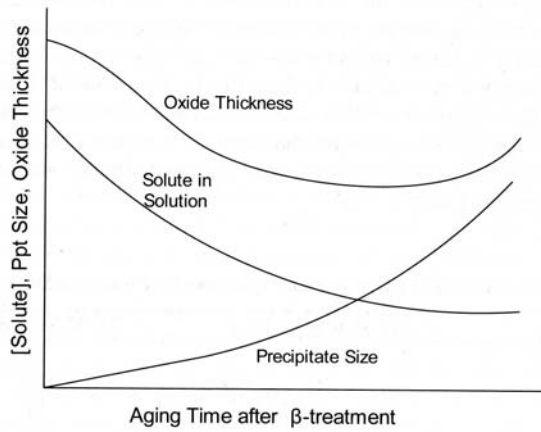


Figure 1.9 A schematic of the effects of annealing on the microstructure and corrosion resistance [1].

An increase in the final anneal temperature has been found to result in a decrease in the creep strain, due to the effects of recovery and recrystallization, which can be used to compensate for the loss of creep resistance due to Sn reduction [1].

To effectively correlate the integrated effects of all the heat treatments after beta-quenching with the precipitate size and distribution in the alloy and the corrosion performance of Zircaloy, a cumulative annealing parameter approach has been developed by Garzarolli et al. [107]. The general expression for the cumulative annealing parameter (CAP) A is:

$$A = \sum A_i = \sum (t_i \exp(-Q / RT_i))$$

where t_i is the time and T_i the temperatures of each heat treatment following the β -quenching, Q is the activation energy, and R is the gas constant. A Q/R value of 40000 has been widely used.

Typical values of the A parameter are in the range of $1-5 \times 10^{-17}$ h for PWR and $0.1-1 \times 10^{-18}$ h for BWRs, corresponding to, respectively, precipitate diameters of 200-500 nm and 50-80 nm [5, 105]. The volume fraction of SPPs was found to increase very rapidly when $A > 10^{-19}$ h and saturated at $A \sim 10^{-17}$ h [108].

Generally, the uniform corrosion resistance of Zircaloys increases with an increasing A parameter [72, 109]. On the other hand, prediction using definite A values appears not to be

possible [87]. Contrasting observations for uniform oxidation (increasing corrosion resistance with a decreasing A) [72] or poor correlations between the A parameter and corrosion behaviour were also found [72, 110].

For zirconium-niobium alloys, heat treatment is optimized when the formation of β -Zr precipitates is avoided and an equilibrium microstructure (precipitation of β -Nb from the matrix) is obtained [5, 53, 111, 112]. The presence of β -Zr is undesirable as it was found that small cracks were induced at the metal-oxide interface between the large β -Zr regions and the oxidized α -Zr matrix during oxidation [112]. Therefore, tempering at temperatures lower than the monotectoid transformation at 888K is required [96, 111, 113-117]. Kim et al. reported for Zr-1.1Nb-0.05Cu corroded in 673K steam that the corrosion behaviour was affected more by the intermediate annealing as well as the final annealing temperature than by the intermediate cold reduction schedule [96]. An increase in the intermediate anneal temperature was found to increase the creep resistance for ZIRLO, probably due to the formation of SPP clusters which can be more effective in impeding dislocation movement [1].

1.3.3 Microstructural characterization and microanalysis

To understand these corrosion mechanisms, microstructural and microanalysis studies on zirconium alloys and their oxides have been intensively carried out.

1.3.3.1 Oxide morphology

1.3.3.1.1 Pre-transition

General observations [19, 25, 69, 80, 89, 118-123] are that the pre-transition film is compact with some micro-cracks or pores but no large cracks; the grains are mainly columnar monoclinic (but may be intermixed with equiaxed grains) with a good intergranular cohesion. Foord and Newcomb [121] suggested from electron diffraction that although the size of

columnar grains appear to be 5-30 nm in width and 200-400 nm in length, in fact one can identify very wide twinned columnar grains that are decorated by finely spaced twin boundaries (**Figure 1.10**).

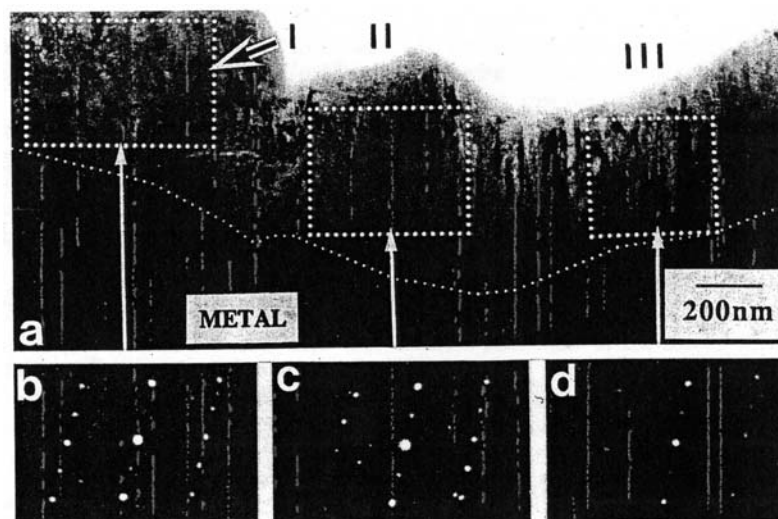


Figure 1.10 Bright field micrograph from a large area of the oxide scale grown on Zircaloy-4 in air at 773K (a), which is clearly one grain of oxide as indicated by the diffraction patterns from areas I, II and III shown in b, c and d respectively.

The transformation from columnar grains to equiaxed grains at the outer part of the oxide was reported. [25, 89, 124, 125]. Bossis et al. [101] showed from SIMS and EIS experiments that there was a porous outer layer of about 0.5-0.6 μm in the pre-transition thin oxide ($\sim 1 \mu\text{m}$) and that the porosity in the inner layer was not connected to the outer surface. Discontinuous arrays of 1-2 nm pores aligned along the columnar monoclinic grain boundaries ~ 600 nm away from the metal-oxide interface have been reported by Kubo and Uno for a $\sim 1.3 \mu\text{m}$ Zircaloy-2 oxide grown in 400 $^{\circ}\text{C}$ steam [86]. The diameter of grain boundary pores was found to be slightly larger than that of pores within the oxide grains [86]. Large cavities or cracks were also found in some cases [25], but they were considered likely to be produced during the sample preparation process.

Oskarsson et al. [124] found that the pre-transition oxides on five different Zircaloy alloys consisted of mainly columnar grains in autoclave tests at 360 $^{\circ}\text{C}$ (higher weight gain), but a

mixture of columnar and equiaxed grains at 288°C (lower weight gain). The columnar grains formed at 360°C were found to be 3-4 times long as those at 288 °C.

A morphology composed of mainly equiaxed oxide grains in the pre-transition period was reported by some workers [23, 69, 89, 126]. Hsieh et al. [126] reported that the initial columnar grains formed until the oxide thickness was about 2.5 µm and the largest ones formed at the time of minimum corrosion rate before transition. Equiaxed grains were found to be present in the oxide on more corrosion-resistant alloys in some studies [89], but the opposite in other work [23]. No correlation between the morphology and corrosion resistance has been reported in some other studies [69]. Therefore, no clear conclusion can be drawn from these studies on the link between the presence of equiaxed grains and the corrosion resistance.

1.3.3.1.2 Post-transition

1) Multilayer structure

The fact that post-transition oxide is characterized by an inner dense layer and an outer part with more cracks and pores has been widely observed by SEM, TEM, and was consistently indicated by EIS [25, 38, 50, 76, 80, 127-131]. Electrochemical impedance measurements sometimes indicated a three-layer model, with a compact inner-most layer, a micro-pores middle layer and a porous outermost layer [132]. Ishii and Sykes [80, 133] observed a thin plate structure of twins perpendicular to the interface with lateral cracks at the middle section of the oxide layer on Zircaloy-2 oxidized in 450° air.

A bigger thickness of the dense inner layer has been correlated to a better corrosion resistance [38, 120, 134]. From electrochemical impedance measurements, Maroto et al. [38] found that the thickness of the inner dense layer at first increased with oxidation time, decreased at the transition, then remained constant in the linear growth post-transition period.

It was noted that the thickness of the dense layer can vary between different measurement techniques. Bossis et al. [101] reported a similar decrease of inner layer thickness at transition, but an increase in thickness and decrease in protective power of the layer after transition, associated with the formation of cracks very close to the metal-oxide interface.

For thick oxides, a periodic layer structure (**Figure 1.11**) suggesting periodicity in the oxide growth has been observed by optical microscopy [19, 38, 43, 51, 135], SEM [136] and indicated by micro X-ray diffraction [135, 137] and electrochemical impedance measurements [76]. It was found the periodicity increased with decreasing oxide thickness or corrosion rate [19, 51, 137], and lack of periodicity in oxide growth was correlated with accelerated corrosion rates in Zircaloy-4 and Zr-2.5Nb in lithiated water [135] or with lower corrosion resistance of a low tin Zircaloy-4 compared to M5 [17, 135]. The observation in SEM and TEM of cracks parallel to oxide surface distributed in the oxide with a similar periodicity to that mentioned above, and a layered columnar-equiaxed-columnar structure in the oxide appears to be related to the periodicity in the oxide growth [17, 19, 101, 138, 139]. These periodicities have been related to the multiple transitions observed in the oxidation kinetics [19, 43, 138].

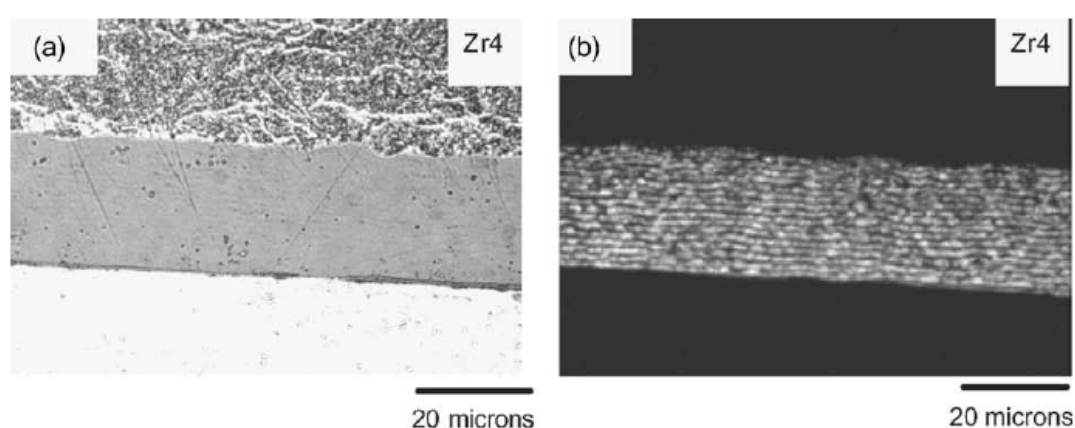


Figure 1.11 Optical micrographs, in a) reflected and b) transmitted light for oxides formed in 360 °C water for 784 days on Zircaloy-4, showing the periodic growth of the oxide [137].

2) Pores and cracks

Besides common lateral cracks parallel to the oxide surface, radial cracks have also been observed that start from the oxide surface and go through the middle part of the oxide [32, 133] sometimes as far as the interface [134, 140]. It was considered that lateral cracks could prevent the oxidation reactions if they are closed, while vertical cracks promote oxidation [141, 142]. Cox and Donner [139] reported that large areas of thick post-transition oxide films did not show lateral cracks when the oxide was sealed in epoxy and then fractured. Based on this observation, they suggested that the uncracked form is the normal state of such an oxide. Abolhassani [143] reported that in an in-situ ESEM experiment no cracks were found at the surface of the oxide formed on Zircaloy-4 in water vapour at 700°C for 65 min, but cracks were observed in the same sample by ex-situ TEM. Therefore, the cracks observed in the oxide are likely to be artefacts of some sample preparation methods. Nevertheless, their locations are still thought to identify weak locations in the oxide film and reflect the stressed nature of the oxide [25, 89, 119, 122, 138].

There was evidence that the inner layer could contain porosity [25, 127-129, 132, 144]. It was found that the porosity slightly increased in the post-transition oxide compared to the pre-transition oxide [132]. The pores or small cracks measured by porosimetry [144] were in the range of 1-1.5 nm. Beie et al [25] showed on Zircaloy-4 tested at 420°C that the small pores formed on grain boundaries near the metal-oxide interface were closed and had no connection with the oxide interface. However, Cox and Yamaguchi [127] have studied replicas of the metal-oxide interface of a thick oxide on Zircaloy-4 after chemical removal of the metal and fractured cross-sections of the oxide, and show images suggestive of interconnected porosity with high density. But the apparent size of these features were often 80-100 nm in width, compared to the nano-size pore reported by other studies. Ramasubramanian et.al. [145] have also inferred from SIMS depth profiles that show the incorporation and exchange of stable

isotopes of H, Li, and B into the oxide that microporosity must be present right down to the metal-oxide interface for Zircaloy-2 oxidized in 400°C steam.

Ploc [146] has divided the types of pores they observed in oxide on Zr-2.5Nb alloy into 3 main types – flake, ribbon and stress cracks. The flake porosity is seen predominantly at grain boundaries in the oxide, often at the top of columnar grains, while the ribbon pores are interconnected over 100s of nm and can run towards the metal-oxide interface. The flake-like pores at the top of the oxide columns were also observed in a Zr-2.5Nb oxidized in 400 °C steam for 24 hours [64].

The appearance of micropores and cracks has been related to the accelerated corrosion behaviour at transition [3, 38, 101, 127]. Garzarolli et al. [119] concluded from impedance measurements that at transition the pore size in the dense inner layer was extremely small. Correlation between higher corrosion rate and higher amount of cracks and pores in the oxide has been reported [25, 89, 119, 123], except that no correlation between large surface cracks and post transition corrosion kinetics were found [127]. For example, Warr et al. [64] reported that for pure zirconium oxidized in 400 °C steam for 24 with high hydrogen absorption, a network of interconnected pores extending to the metal-oxide interface was present. Ploc and Newcomb [147] have reported that for the oxides grown on Zr-2.5Nb with different level of carbon and other impurities, the amount and extent of coarse pores was higher in the oxide grown on the alloy containing more impurity and showing higher deuterium absorption. Also, the porosity increased with increasing exposure time.

3) Grain morphology

The oxide usually consists of both columnar and equiaxed grains. Columnar grains are often more dominant in the inner part and equiaxed grains are more seen at mid-thickness and at the oxide surface [19, 25, 138]. The columnar structure was found to extend up to the interface in some cases or be replaced by higher fraction of equiaxed grains in some other cases.

The columnar grains are usually highly textured, growing perpendicular to the interface. An orientation of 45° growth of the columnar grains to the interface was reported in the oxide of a Zr-0.5Sn-0.53Nb alloy which had a better corrosion resistance compared to standard Zircaloy-4 [123]. Either $[001]_m$ or $[100]_m$ crystallographic axes have been usually found to align along the growth direction of the oxide [125, 135, 148, 149]. The orientation of $[-111]_m$, $[111]_m$ and $[020]_m$ axes were also studied by X-ray diffraction or TEM [125, 138, 150]. $[-111]_m$ and $[111]_m$ were found to lie about $30-50^\circ$ and $50-70^\circ$ away from the growth direction, respectively. An orientation of 70° away from the oxide growth direction was reported for the $(020)_m$ axes [125]. A detailed HREM investigation [148] has shown that special grain boundaries (low-angle and twin), which would be expected to have little free volume, mainly exist in the orientated columnar growth texture, as opposed to the case in random oriented structure. It was indicated that when the degree of grain-to-grain misorientation increases, the corrosion resistance decreases [138].

Park et al. [7] investigated by HREM the grain microstructure in the oxide grown on Zircaloy-4 in 1000°C steam. In this particular simulated loss of coolant accident (LOCA) oxidation condition, the breakaway transition was found to occur at $\sim 700\text{ mg/dm}^2$ weight gain (oxide thickness of $\sim 40\text{ }\mu\text{m}$). The authors found that pre-transition oxide grains were smaller with unclear and uneven grain boundaries while in the oxide grown during the transition to breakaway the grains were larger with flat and clear grain boundaries and nano-pores at grain triple points, which was considered to favour oxygen diffusion and crack formation and propagation.

Anada et al. [93, 120] and Wadman et al. [151] found that the columnar grains transformed to fine equiaxed grains near lateral cracks and incorporated intermetallic precipitates. Generally, a decrease in the fraction of equiaxed grains (or the extent of undisturbed growth of columnar grains) corresponds to lower weight gain and corrosion rate [17, 23, 118, 121,

152], and the transformation from columnar grains to equiaxed grains at some point in the oxide is suggested to be associated with the corrosion transition [93, 119, 120, 123]. One contrary observation was reported by Yao et al. [89], where columnar grains were almost not evident in the oxide layer on a beta quenched Zircaloy-4 specimen that showed superior corrosion resistance.

The positive effect of columnar grain structure could be a result of the reduced grain boundary diffusion of oxygen ions due to smaller grain boundary volume between columnar grains [93, 148], or fewer associated pores or cracks [19, 23, 123, 138] due to stronger intergranular cohesion between columnar grains [25, 118].

4) Grain sizes

The size of columnar grains reported by TEM studies ranges from 5 to 90 nm in width and 100 to 500 nm in length [17, 25, 118, 121, 126, 138, 152]. The aspect ratio appears to remain constant (~ five) [138]. The size of equiaxed grains are reported by TEM to be in the range of 15-50 nm [25, 118, 126, 138]. Very fine grains (around 10nm) were found at some preferential locations such as the metal-oxide interface [119, 152]. The grain sizes deduced from the broadness of peaks in XRD analysis are usually much smaller [36, 119, 138], probably because the broadness of peaks is increased by other factors like inhomogeneities of crystal size and local stress.

It appears that larger grain size (especially that of columnar grains) is correlated to better corrosion resistance [17, 19, 25, 93, 119, 123, 126, 138, 153]. It was suggested that the oxide grain size increased with decreasing solute concentration in the matrix due to less segregation of solute elements to the oxide grain boundaries during oxidation [138].

5) Oxide phase

The tetragonal phase has been reported to be found mainly at the oxide/metal interface by many workers using X-ray diffraction analysis [153-156], Raman spectroscopy [24, 157, 158]

and TEM [119, 120, 123, 125]. Godlewski et al. [24] noted that the tetragonal phase was observed throughout the oxide thickness before transition and that the phase transformation began at the outer oxide surface at transition point. Employing synchrotron X-ray diffraction, Yilmazbayhan and Motta [137] have found a periodic intensity variation of the tetragonal phase at different depth in the oxide layer, with the same period of oxide layer thickness such as in **Figure 1.11**. Some work showed the tetragonal phase was also present several μm from the interface in thick oxides on Zircaloy-2 [132], or only at the outer part of the oxide instead of near the interface in a low-tin Zircaloy-2 [45].

Yilmazbayhan et al. [138] indicated that the tetragonal oxide was normally associated with small (equiaxed) grains for the three oxides they investigated (Zircaloy-4, ZIRLO and Zr-2.5Nb). Wadman et al. [123] observed a few columnar tetragonal grains and equiaxed monoclinic grains in the outer part of the oxide layer in a standard Zircaloy-4. A twinned grain structure with pores at the column ends was associated with the tetragonal to monoclinic phase transformation [123, 159, 160]. Wadman et al. [123] found that this structure was not in the majority throughout the oxide and also existed in pre-transition oxides.

A monotonic decrease in the fraction of tetragonal oxide with oxidation time was usually found [24, 36, 71, 119, 156, 161-163]. Some of these studies indicated a more abrupt decrease of the tetragonal fraction at transition [24, 119], while some others found smooth decrease at the kinetic transition, indicating no sudden evolution associated with the transition [36, 71, 156, 163]. Furthermore, some studies [56, 158] found that the tetragonal fraction followed the multiple transitions in the oxidation kinetics, i.e. decreased at the first transition and then increased again up to a new kinetic transition. A presence of a maximum in this fraction at the kinetic transition were also reported [38].

Many works showed that higher fraction of tetragonal phase was correlated to lower corrosion resistance [25, 36, 119, 121, 124, 137, 153], while some others showed the opposite

[56, 113, 132]. The disagreement between reported results might result from two factors: first, a texture correction was not used in the calculation method for the tetragonal phase fraction in most cases (except in [137]); secondly, the resolution of different techniques (bulk X-ray diffraction $\sim 2 \mu\text{m}$, micro-beam synchrotron radiation diffraction $0.2 \times 0.3 \mu\text{m}$) could result in different sensitivity to the actual tetragonal phase gradient through the oxide.

By analyzing electron diffraction patterns, Beie et al. [25] reported that the monoclinic and tetragonal phases in the surface part of a pre-transition Zircaloy oxide had an orientation relationship of $\{-111\}$ and $\{111\}$ m-ZrO₂ parallel to $\{111\}$ t-ZrO₂, which would be expected if t-ZrO₂ transforms to m-ZrO₂ via a diffusionless process. However Kim et al. [125] using high voltage electron microscopy (HVEM) reported that no definite crystal orientation relationship was found between the tetragonal phase and the connected monoclinic phase in the outer part of a Zr-0.4Nb oxide (thickness $\sim 2.2 \mu\text{m}$).

1.3.3.2 Oxide-metal Interface

1.3.3.2.1 Interface morphology

The growth of oxide grains at the interface has been shown to be strongly dependent on the orientation of underlying metal grains, especially in the early stage of oxidation [23, 38, 56, 121, 122, 143, 164]. This could lead to observations such as the development of structural heterogeneities at the very early stage of oxidation of pure zirconium [22]. When the oxide thickens, information about the grain orientation with respect to the matrix is usually lost and a common observation is that protrusion zones form. Foord and Newcomb [121, 122] found that the columnar grains were more laterally developed and textured in the lower part of the oxide near the interface than in the outer part of the oxide, and indicated that a loss of information on the texture of base metal was correlated to a sharp increase in the rate of

oxidation. Bossis et al. [101] showed that the cracks close to the interface were preferentially formed over delayed portions of the oxidation front, i.e. over the convex part of the interface.

A typical ‘cauliflower-like’ morphology of the interface for post-transition oxide has been often observed by SEM [23, 89, 132], see **Figure 1.12**. It is reported [132, 165] that this morphology develops at later oxidation stages from a structure observed at an early stage of oxidation via a needle structure. Higher corrosion resistance appears to be correlated with either more slowly developing cauliflower structure [132, 165] or no such kind of development [23], but the formation of this structure was not found to be directly correlate to the kinetic transition [132].

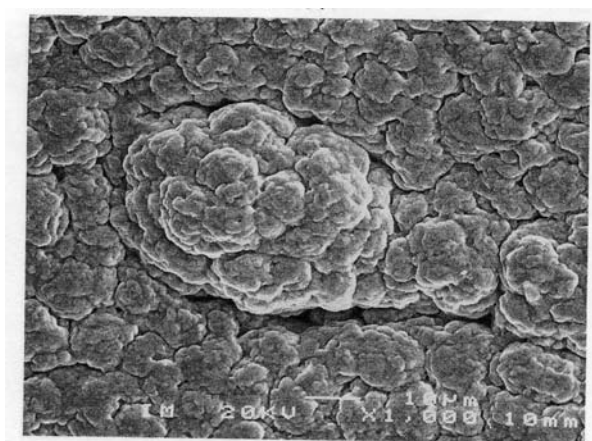


Figure 1.12 The cauliflower structure of the metal-oxide interface oxide of a Zirconium alloy [132].

Gebhardt et al. [134] reported that the interface showed spherical crystal agglomerates for fast-corroding standard Zircaloy-4 in a PWR, but crystal platelets for slowly grown oxides.

The roughness of the interface has been found to have several levels at the same time, especially for thick oxides and fast-corroding oxides [23, 134, 136]. At the first level, the interface exhibits steep hills and ridges. At higher magnifications, it can be observed that the surface of the deep hills is actually covered by mini-hills (or flat cusps) with smaller diameter. The mini-hills can also be resolved into finer details, which correspond to the roughness of the surface of columnar grains. A schematic representation of this kind of morphology is shown

in **Figure 1.13**. Some correlation between the dimensions of these structures and the oxidation behaviour has been indicated [134].

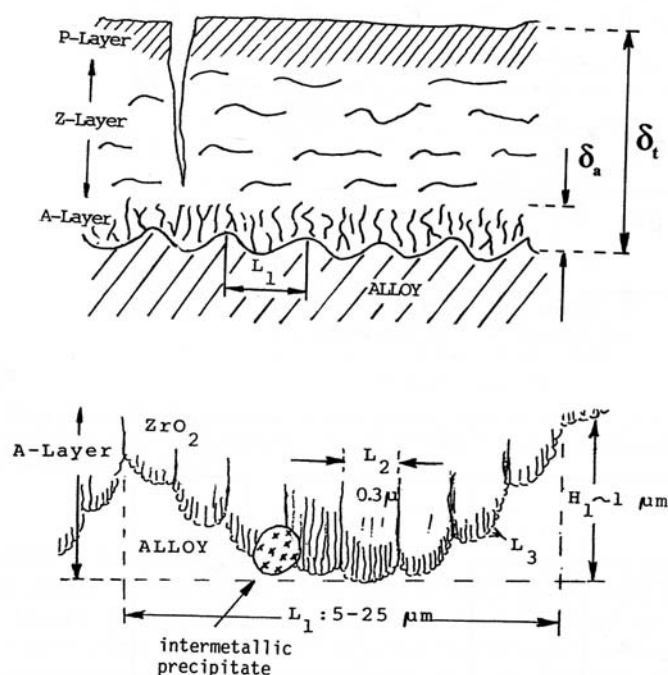


Figure 1.13 Semi-schematic representation of the oxide morphology on zirconium-based alloys after uniform corrosion, showing roughness at different scale levels [134].

A high extent of roughness of the interface has been related to the higher growth rate of the oxide [19, 23, 89, 101, 123, 127, 134, 152, 166]. Yilmazbayhan et al. [138] found that the metal-oxide boundary was more well-defined for slower corroded Zr-2.5Nb and ZIRLO than for faster corroded Zircaloy-4.

In Zr-Nb based alloys that contains a metastable Nb-rich, bcc β -Zr phase, it has been found that the oxidation of the β -Zr phase is faster than that of the α -Zr phase [167], leading to the formation of oxide ridges that penetrate into the underlying metal substrate at the β -Zr regions (a 'jigsaw' interface) [38, 50, 152, 168, 169]. It was noted that the ridges eventually reached some limiting depth of penetration due to the decomposition of the β -Zr to ω -phase at a later oxidation stage. When the oxide grows, these ridges eventually coalesce resulting in an array of coarse ridges and holes over the whole interface [38, 168]. This microstructure was also considered to result in a better stress distribution along the interface, which would lead to

a lower crack density close to the interface and to slower oxygen diffusion, and thereby a slower corrosion rate [152]. However, Bohmert et al. [50] argued from the thermodynamic point of view that such an irregular interface provides a path for faster oxygen diffusion.

1.3.3.2.2 *Intermediate layer at interface*

An intermediate layer has been reported by TEM at the interface with a complex structure or/and stoichiometry different to that of bulk oxide and bulk metal [25, 50, 64, 72, 80, 120, 121, 123, 125, 134, 138, 170]. Angle-resolved XPS measurements [171, 172] show similar results, although epitaxial growth of m-ZrO₂ on the zirconium grains was found in some other studies [25, 126, 133].

1) Composition of the intermediate layer

The presence of an oxygen-rich region at the metal-oxide interface has often been reported and described by some authors as a suboxide phase [101, 120, 123, 138, 173].

Yilmazbayhan et al. [138] reported from EDX measurements that the oxygen content at the metal-oxide interface decreases gradually from approximately the stoichiometric ZrO₂ level (~67 at. %) in the bulk oxide to the level of oxygen solid solution in Zr (29 at. %) over a significant distance, which varies from ~160nm to ~560 nm in oxides grown on Zircaloy-4, ZIRLO and Zr-2.5Nb. It was not clearly stated in their study whether the examined oxides were pre- or post-transition oxides. They speculated that this might be evidence for the presence of a Zr₃O phase. Rather than a gradual decrease in oxygen content over the interface region, Bossis et al. [101] reported a plateau in composition at ~ 40 at. % O for a pre-transition oxide on the Zircaloy-4 alloy widely used for cladding the nuclear fuel in light water reactors, and identified it to have the crystal structure of the ω-Zr phase. Wadman et al. [123] showed microstructure/diffraction evidence for the presence of a crystalline sub-oxide layer in the oxide grown on a Zr-0.23Fe0.2V alloy (although there was no information about

the oxidation stage of this oxide), which they suggested could create a barrier for hydrogen migration. The oxygen content of this layer was measured by EDX to be around 40-50 at. % but consisted of analyzing only two data points. Abolhassani et al. [152] measured EDX line profiles of oxygen concentration across the metal-oxide interface in three post-transition oxides grown on different Zr alloys. This data showed an oxygen deficient zone in the oxide near the interface and also the indication of oxygen contents higher than the solid solution limit in the metal near the interface. From these observations, they concluded that a combination of thermodynamic and kinetic processes was rate controlling in the corrosion mechanism, but there was a large amount of scatter in the compositional data in the sub-oxide region. Beie et al [25] reported using EDX microanalysis that the oxygen concentration decreased continuously over a distance of 1 μm from the bulk oxide level to a constant non-zero value in the metal (due to the surface oxidation of TEM samples) for a post-transition Zircaloy-4 uniform oxide. My own interpretation of their data suggests that over ~ 100 nm we move from the stoichiometric ZrO_2 level in the bulk oxide to the level of oxygen solid solution in Zr. They also showed a sudden decrease of the oxygen content within the metal directly beyond the interface for a nodular Zircaloy-4 oxide.

2) Crystallography of the intermediate layer

Different structures of the intermediate layer have been observed and some correlations with different oxidation type or stage have been suggested. Beie et al [25] showed an epitaxial growth of m- ZrO_2 on the zirconium grain for a post-transition oxide formed Zircaloy-4 in steam at 420°C. Wadman et al [123] reported tetragonal ZrO_2 at the metal-oxide interface for pre-transition Zircaloy-4 oxide formed in an autoclave at 400 °C and not for a post-transition oxide.

Warr et al. [64] reported a discontinuous layer of amorphous material (~ 10 nm thick) at the metal-oxide interface in the Zr-2.5Nb oxide grown in steam at 400°C for 24 h (should be pre-

transition oxide), and argued that it reduced the rate of hydrogen permeation via grain boundaries and the rate of hydrogen transfer from the oxide into the bulk alloy. Ploc [174] suggested the possible presence of highly defected or nearly amorphous oxide growing on the metal for thin oxide (<200 nm) formed in dry oxygen at 300 °C. Garzarolli et al. [119] reported the observation of tetragonal oxide recrystallized from an amorphous inner layer for a Zircaloy-4 oxide formed in oxygen at 400 °C (should be post-transition oxide) and monoclinic oxide recrystallized from possibly an amorphous layer for a nodular Zircaloy-4 oxide formed in steam at 500 °C.

Iltis and Michel [170] reported electron diffraction data for a ~5 µm Zircaloy-4 oxide formed in oxygen at 873 K that demonstrates the existence of an ordered phase which the author proposed to be an oxygen solid solution in ω-Zr with a composition of Zr₃O. Yilmazbayhan et al. [138] have attributed a combination of Zr₃O and tetragonal oxide precipitates to the suboxide they observed in oxides grown on Zircaloy-4, ZIRLO and Zr-2.5Nb based on parallel micro-beam synchrotron radiation diffraction data [135]. Foord and Newcomb [122] have observed a saw-tooth structure for a pre-transition oxide grown on Zircaloy-4 in pure oxygen at 500 and identified the structure to be rhombohedral Zr₃O (a = 0.563 nm and c = 1.559 nm), which varied depending on the oxygen content. It was also found that this structure was absent after transition.

By contrast, the saw-tooth structure observed at the metal-oxide interface in both pre- and post-transition Zircaloy-2 oxides formed in air at 450 °C by Ishii and Sykes [80] has been identified to be ω-Zr. Bossis et al. [101] also reported ω-Zr with a banded structure at the interface for a post-transition Zircaloy-4 oxide formed in a water autoclave at 415 °C. Foord and Newcomb [121] reported an oxygen rich ω-Zr with a lath-like morphology at the interface and noted that this phase was only found in the oxide formed on the alloy with a higher corrosion resistance.

Using X-ray diffraction, Furuta and Motohashi [175] reported a ZrO cubic phase ($a = 0.462$ nm) for a Zircaloy oxidized in steam at 1273 K. A similar phase with $a = 0.44$ - 0.46 nm was also reported at the metal-oxide interface in the post-transition oxide of Zircaloy-2 formed in water at 350 °C [176].

Anada and Takeda [120] reported from HRTEM observations at Zircaloy-4 metal-oxide interfaces a quasi-equiaxed tetragonal ZrO₂ layer and below a substoichiometric layer (of small monoclinic ZrO₂ grains and unidentified grains similar to α -Zr). They also stated that this two layer structure was present in a pre-transition oxide of Zircaloy-4 formed in an autoclave but disappeared after transition, while the layers remained stabilized in the oxide of more corrosion-resistant alloys such as Zircaloy-2 and 1Nb-Zircaloy-4. Similar observations using HRTEM of an unidentified structure at the metal-oxide interface was also reported by Kim et al. for a pre-transition Zr-0.4Nb oxide formed at 360°C in water [125].

1.3.3.3 Second phase particles

1.3.3.3.1 Second phase particles in the metal matrix

The main second phase particles present in Zircaloy-4 have been reported to be Zr(Fe,Cr)₂ Laves phase having either C14 (hcp MgZn₂ type) or C15 (fcc MgCu₂ type) structure, and stacking faults are often observed in both phases [177-179]. Some work reported the presence of ZrFe₂ type precipitates in Zircaloy-4 [180].

For Zircaloy-2, Zr(Fe,Cr)₂ precipitates were reported in most cases, with the hexagonal C14 structure [181, 182], and occasionally with the cubic structure [183].

The hexagonal C14 phase particles were shown to be dominant at grain boundaries and to have a round shape while the cubic phase ones were mainly found to be within the grains and have irregular shapes [183]. According to Pearson [184], the FCC structure is the high-temperature modification of the Zr(Fe,Cr)₂ phase while the hexagonal structure is the low-

temperature form. Thus it was indicated that hexagonal Zr(Fe,Cr)_2 forms at later stage of processing by grain boundary diffusion leading to its preferential growth along grain boundaries [183].

Shaltiel et al. indicated that the crystal structure of $\text{Zr(Fe}_x\text{Cr}_{1-x})_2$ is hexagonal if $x < 0.8$ and fcc if $x > 0.9$ [185]. Versaci and Ipohorski [136] found the presence of a polytype structure within the Zr(Fe,Cr)_2 precipitates, consisting of alternate packing of hexagonal and fcc layers, and attribute this to possible fluctuations of Cr and Fe concentrations.

$\text{Zr}_2(\text{Ni,Fe})$ is another major type of precipitate reported for Zircaloy-2. The structure is usually based on the body-centred tetragonal (BCT) Zr_2Ni Zintl phase [181, 182, 186, 187].

The Fe/Cr ratio in Zr(Fe,Cr)_2 in the Zircaloy-4 metal matrix is reported to be approximately 2 [109, 136]. Vander Sander and Bement [179] showed α annealed (at 800°C) Zircaloy-4 contained Zr(Fe,Cr)_2 precipitates with the Fe/Cr ratio being 2.5. Arias et al [188] showed that depending on the different heat treatments applied to the samples in their experiments, the Cr/Fe ratio of Zr(Fe,Cr)_2 second phase particles varied from 0.1 to 1.7 in Zircaloy-4 and from 0.8 to 1.7 in Zircaloy-2, and the Ni/Fe ratio of $\text{Zr}_2(\text{Ni, Fe})$ varied from 0.5 to 0.9.

For niobium containing alloys, hexagonal Zr(Nb,Fe)_2 , and cubic $(\text{Zr,Nb})_4\text{Fe}_2$ have been reported as the main types of intermetallic precipitates [15, 51, 99, 189]. $\beta\text{-Nb}$ precipitates are often present in commercial Zr-Nb based alloys [51]. Northwood et al. [59] found that the formation of Zr_2Fe precipitates was favoured by higher Fe content and larger $\alpha\text{-Zr}$ grains in a standard Zr-2.5Nb pressure tube. Work on SPPs in niobium-containing alloys has been focused on the development of phase diagram of binary and ternary niobium containing Zr alloys [98, 99, 189-192]. From these studies, various precipitates have been reported.

The typical precipitates observed in Zircaloy-2, Zircaloy-4 and ZIRLO and their crystal structure information is shown in **Table 1.4**.

Table 1.4 Typical precipitates observed in Zircaloy-2 and Zircaloy-4 and their crystal information.

Alloy	Precipitate	Crystal Structure	Lattice Parameter (Å)		
			a	b	c
Zircaloy-2	Zr(Fe,Cr) ₂	HCP [181-183]	5.079		8.22
	Zr(Fe,Cr) ₂	FCC [183]	0.7212		
	Zr ₂ (Ni, Fe)	BCT [181, 182, 186]	6.499		5.270
Zircaloy-4	Zr(Fe,Cr) ₂	HCP (C14)[177]	5.034-5.075		8.209-8.275
		FCC (C15) [177]	7.015-7.084		
	Zr ₂ (Fe,Cr)	HCP [179]	5.079		8.279
ZIRLO	β-Nb	BCC [51]	3.322		
	Zr(Nb,Fe) ₂	Hexagonal [99]	5.366		8.792
	(Zr,Nb) ₄ Fe ₂	Cubic [99]	12.15		

1.3.3.3.2 Second phase particles in the oxide

A large amount of TEM work has shown that the intermetallic precipitates are incorporated into the oxide and oxidize gradually as the oxide thickens [19, 80, 86, 109, 119, 133, 193-196]. During oxidation of Zr(Fe,Cr)₂, iron in the precipitates becomes oxidized first and diffuses faster than chromium out into the oxide, resulting in a decreasing Fe/Cr ratio in the precipitate with oxidation time [109, 119, 193, 195].

The oxidized precipitates were found to be composed of mainly nanocrystallites (a few nanometers in size) at the beginning of the oxidation, and be nanocrystalline and amorphous at later stage [193, 194]. The crystallites were also found to possess strong textures [197]. The size of the oxide crystallites was found to increase with oxidation temperature [196].

At an early stage of the oxidation of the precipitates, metallic bcc iron can segregate at the precipitate/matrix interface as precipitates while most of the chromium remains homogeneously distributed within precipitates [86, 119, 193, 195, 196]. The heterogeneous distribution of iron was also observed using EELS [119]. Precipitation of metallic chromium at the precipitate/matrix interface was also sometimes reported [193]. After long oxidation times (for precipitates at the outer porous part of the oxide), the metallic iron-rich bcc phase is

absent and a depleted zone of Fe near the oxidized precipitate could be found, indicating iron dissolution into the matrix. Fe_2O_3 (and probably Cr_2O_3) could be formed near the periphery of the precipitate [86, 196]. Cox and Sheikh [196] found that at higher temperatures (500°C) the diffusion of iron was enhanced so that it diffused further into the matrix and formed a high-Fe solid solution in cubic ZrO_2 at some distance from the oxidised intermetallic precipitate. They also found associated silicon segregation at the boundaries of the agglomerates of iron oxide at the higher temperature and suggested that Si might enhance the diffusion of Fe^{3+} in ZrO_2 . A schematic representation of this evolution is shown in **Figure 1.14**.

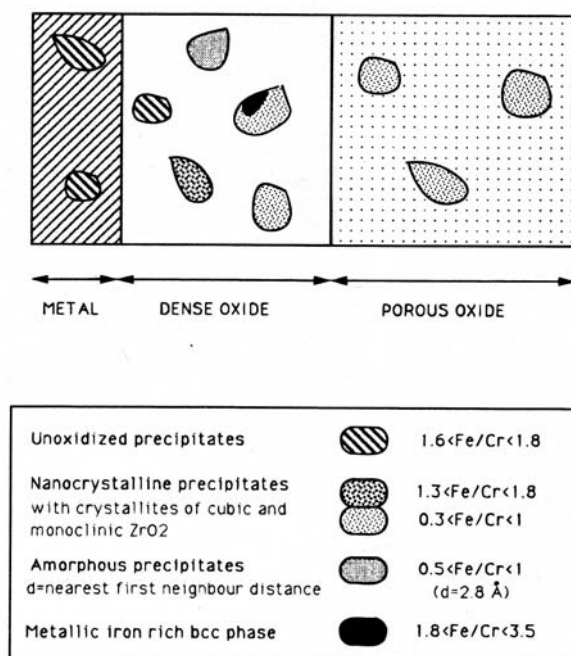


Figure 1.14 Schematic view of the structural and chemical composition evolutions experienced by the $\text{Zr}(\text{Fe,Cr})_2$ precipitates during their incorporation in the Zircaloy-4 oxide layer formed in-autoclave [193].

Similar observations were also obtained using SIMS [101, 119], AES [198, 199] or by studying the oxidation behaviour of isolated intermetallic particles using X-ray diffraction and Mössbauer spectroscopy [200].

For $\text{Zr}_2(\text{Fe,Ni})$ precipitates, a similar process of oxidation has been observed [86, 196-199]. Iron was again found to diffuse faster than nickel. However, it segregates near the periphery of the oxidized precipitate and forms an oxide layer, while Ni is depleted near the surface of the precipitate and oxidized via dissolution in the matrix zirconia. With increasing oxidation

time, both iron and nickel could be oxidized inside the precipitate. Cox and Sheikh [196] found that the behaviour of nickel in $Zr_2(Fe,Ni)$ precipitates in Zircaloy-2 during oxidation strongly depended on the precipitate size. For small particles, migration out of the particle occurred and agglomerates of mixed Fe/Ni oxide were formed, while for large ($\geq 1 \mu m$) particles these agglomerates remained inside the original particle boundary. Li et al. [197] found that $Zr_2(Fe,Ni)$ precipitates oxidized faster than $Zr(Fe,Cr)_2$ precipitates during the oxidation of a zirconium alloy in an autoclave at 360°C.

A general model for the oxidation behaviour of both $Zr(Fe,Cr)_2$ and $Zr_2(Fe,Ni)$ type precipitates has been given by Hatano et al. [198, 199]. The main considerations were different chemical affinity of the alloying elements to oxygen and different diffusivities of the elements in zirconia.

Cubic (or tetragonal) ZrO_2 with small amounts of monoclinic ZrO_2 has been reported to be the structure of the oxidized precipitates [138, 193, 197, 200, 201]. Garzarolli [119] reported the cubic phase in the core of the precipitate and monoclinic phase in the peripheral zones and matrix surrounding the precipitate. Possible stabilization factors were thought to be dissolved Fe in the ZrO_2 [201] and size effects [193]. An orthorhombic structure was found for a Fe-Cr-rich precipitate oxide in Zircaloy-2 [45]. Garzarolli [119] found that the precipitates at the metal-oxide interface in a Zircaloy oxide were either amorphous or poorly crystallized cubic ZrO_2 . Amorphous ZrO_2 was also reported by Li et al. to be present in the $Zr_2(Fe,Ni)$ precipitate oxide [197].

In similar behaviour to precipitates in Zircaloys, the β -Nb precipitates incorporated in the oxide remain metallic near the metal-oxide interface, and are oxidized gradually with time [17, 112, 195, 202]. Detailed HREM investigation revealed that β -Nb in a Zr-1.5Nb alloy changed to a mixed structure in both amorphous and β - NbO_2 phase at the initial oxidation stage (corroded in 360°C water autoclave), then to the amorphous structure at the middle stage and

finally to fully oxidized crystalline oxide [112]. Yilmazbayhan [138] found that the β -Nb precipitates in ZIRLO and Zr-2.5Nb become amorphous within the oxide layer and eventually dissolve during oxidation. Similar amorphization was observed for the oxidation of Zr-1%Nb [195] and Zr-2.5Nb and Zr-20Nb [202]. Park et al. [19, 51] reported from TEM work that the β -Nb in a Zr-1.1wt%Nb-0.05 wt%Cu alloy was oxidized more slowly than the Zr(Fe,Cr)_2 in Zircaloy-4, and related this observation to the lower oxidation rate of the Zr-1.1wt%Nb-0.05 wt%Cu alloy.

Cracks were often reported to be associated with the second phase particles [51, 93, 120, 122, 123, 151]. It was suggested that the cracks could be caused by the additional stress build-up due to the oxidation of SPPs [133].

1.3.4 Breakaway mechanism

It has become clear with accumulating experimental results that the breakdown transition is related to a degradation of an oxide, which is dense in the initial oxidation stage (at least near the metal-oxide). For the kinetic transition to happen, defects, either pores or microcracks or both, must develop to decrease the thickness of the dense part of the oxide. Cox [2] reviews the experimental data the oxidation of Zr alloys in steam showing changing the pressure of the oxidising environment only controls the rate of oxidation in the post-transition stage, and comments that “Such a change is possible only if some of the cracks or pores in the oxide propagated right up to the oxide/metal interface”. Several possible mechanisms that have appeared in the literature are discussed below.

1.3.4.1 Mechanical breakdown of the oxide

The most straightforward mechanism is simply the mechanical breakdown of the oxide as a result of a built-up stress with increasing oxide thickness [16, 43, 203]. For the oxide film

grown on the zirconium alloy substrate, the presence of a large compressive stress at the metal-oxide interface is expected due to the large Pilling-Bedworth ratio (~ 1.56) for formation of the oxide on the metal. The stress continually experienced by the oxide finally induces microcracks when it exceeds the critical stress level which the oxide can mechanically sustain. Cracks that run parallel to the metal-oxide interface may be initiated by decohesion of a weak metal-oxide interface and buckling of the oxide [204]. An undulated metal-oxide interface may locally introduce cracks parallel to the metal-oxide interface as a result of normal tensile stress concentrated on the top of a convex part of the interface [205]. It should be noted that cracking along the compressive stress axis in a confined heterogeneous brittle solid loaded under uniaxial compression may also be a possible mechanism [206].

However, the horizontal crack layer must be connected to the surface by a network of transverse cracks to render the bulk of the oxide not protective. One of the possible mechanisms has been reviewed by Cox [2]. In this hypothesis, a balancing increment of tensile stress is created in the pre-existing oxide layer as each new oxide layer forms at the metal-oxide interface, so the compressive stress decreases towards the oxide outer surface. Finally a tensile stress will be present in the surface layer of the oxide that will initiate cracking from the surface. However, Cox commented that “this cracking should only propagate to the neutral stress axis in the oxide leaving a thick uncracked inner barrier layer”. Other mechanisms that can cause surface crack initiation and propagation might also be present, such as reactions of the oxide surface with OH^- group, as illustrated in **Figure 1.15** [207].

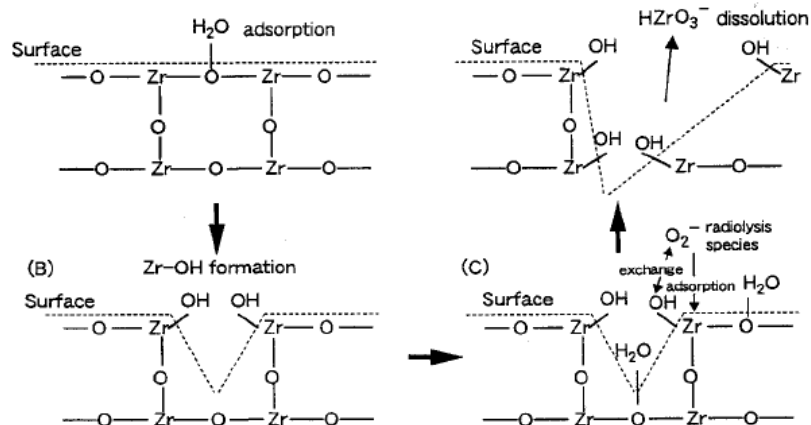


Figure 1.15 Model of dissolution process of zirconium oxide film into water [207].

1.3.4.2 Tetragonal to monoclinic oxide phase transformation

An alternative mechanism thought to be responsible for the breakaway transition is related to phase transformation of the oxide. This hypothesis, which was proposed at the very beginning of work in this area [16] and has been the main concern since then, assumed that at transition an initially stabilized tetragonal zirconia transformed to monoclinic zirconia which induces porosity because of the stresses and 3-5 % volume expansion accompanying with transformation [208]. Specifically, the pores are formed by a shear resulting from the twinning required by the transformation. The relevant evidence is the finding of the sudden decrease in the tetragonal volume fraction in the oxide upon transition [24, 119], and the observation of the disappearance of a tetragonal oxide interface layer after transition for some less corrosion-resistant alloys [120, 122]. Modelling work based on this transformation mechanism [209] also seems to give a reasonably good prediction of the weight gain at transition for the oxidation of Zircaloy-4 in air between 600-1000°C.

However, there are still many aspects that remain unresolved. Firstly, rather than phase transformation causing pores and cracks, Hutchinson and Lehtinen [141] proposed that the transformation should stop the propagation of a crack. What they observed was that a thick oxide formed on Zircaloy has a microstructure composed of primary and secondary crack-free

veins that appear lighter in SEM images, as schematically shown in **Figure 1.16**, and that all cracks were found to be arrested on reaching a vein. Similar observations have also been reported later by Bossis et al. [17]. These veins were considered to consist initially of tetragonal zirconia in a monoclinic oxide matrix and thus be the locations where the phase transformation had happened. The primary veins were argued to be caused by the inhomogeneous stress distribution due to the scalloped shape of the metal-oxide interface, and the secondary veins were thought to nucleate at suitably-sized second-phase particles. According to this mechanism, the breakaway of the oxide film, depending on the evolution of the cracks, will be determined by the pattern of the veins so that the role of precipitates could be explained. In this sense, the tetragonal to monoclinic transformation would be beneficial since it stops the crack propagation and increases the oxide toughness. This would be similar to the mechanism suggested by Harada et al. [45], who also believed in a positive role of the phase transformation, based on the accompanying stress relief effect. However, Hutchinson and Lehtinen didn't specify in this mechanism how the cracks would be initiated.

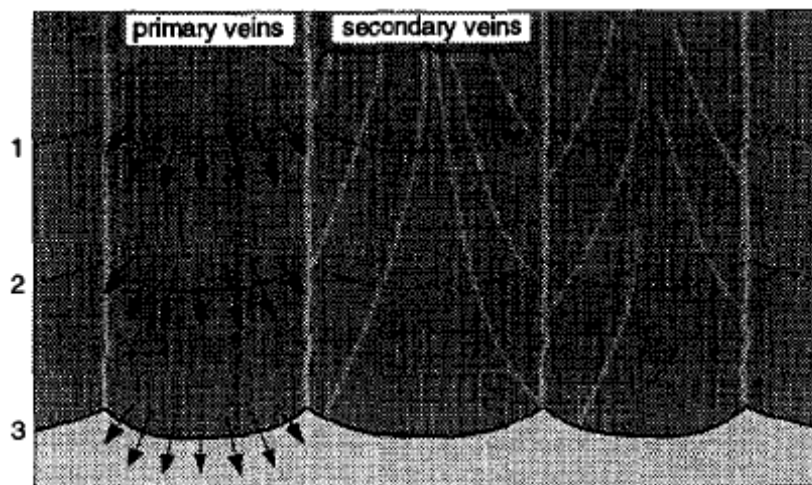


Figure 1.16 A schematic of primary veins and secondary veins observed in the thick oxide of Zircalloys [141].

Secondly, related to the first point, it is not known how exactly the phase transformation influences the corrosion resistance. For example, contradictory results have been reported regarding the correlation between the amount of tetragonal phase and the corrosion resistance

(see point 5 in **section 1.3.3.1.2**). Very recently, Qin et al. [210] have proposed a model based on the thermodynamics of the transformation, trying to formulate a correlation between different factors including grain size, stress and microstructure. The model is satisfactory to explain some experimental results but not others.

Finally, it is not yet clear what mechanism is stabilizing the high temperature stable tetragonal zirconia polymorph at room temperatures. It has been known in general that the tetragonal phase can be stabilized by high stress [211], or small grain size (smaller than 25-30 nm) [36, 212-214], or defects (induced by dopants) [215-218].

Godlewski [158] and Zhang et al. [156] found that the stress in a uniform oxide gradually increases before the transition, but drops sharply after the transition. Certainly this observation can be correlated to mechanical cracking of the oxide layer as a result of stresses generated during oxidation, but it also led to the thought that the main factor for the stabilization of tetragonal zirconia was the large compressive stress [24, 25, 71, 119, 156, 157, 219]. When the oxide thickens, it is suggested that the compressive stress decreases towards the oxide surface and becomes insufficient to stabilize the metastable tetragonal zirconia, inducing the phase transformation to monoclinic zirconia. On the other hand, it has been shown that for t-ZrO₂ powder that a macroscopic compression can in fact induce microscale shear stresses and maybe tensile stresses in the individual grains (**Figure 1.17**), and generate the tetragonal to monoclinic transformation [208]. Similar effects may be present for an oxide film grown on the Zr substrate, where there is a bi-axial compressive stress along the plane parallel to the metal-oxide interface while the oxide growth direction is expected to be nearly stresses free. Therefore, the effect of compressive stress in the oxide for stabilizing tetragonal oxide could be 2-fold, which may be related to the fact that some studies [69, 124, 132, 140, 163] found that tetragonal phase was stabilized in the absence of high compressive stress.

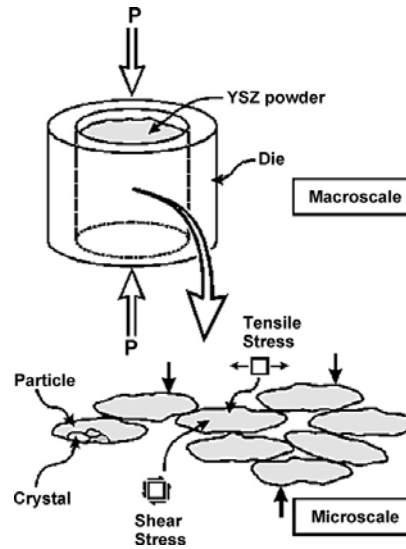


Figure 1.17 A schematic illustration showing how particle-to-particle contact can generate microscale shear stresses and tensile stresses although the macroscopic applied stress in compression [208].

Regarding the size effect, Barberis [36] has proposed a model to evaluate the evolution of the oxide phase and the grain size during autoclave corrosion assuming two competing phenomena; the creation of a constant fraction of tetragonal phase at the metal-oxide interface as a result of the oxidation process, and the disappearance of the tetragonal phase in the oxide layer due to autoclave annealing. The model agrees with some experimental results, such as the steep monotonous gradient of the fraction of tetragonal phase from the oxide/metal interface to the outer surface in corrosion films and the increase of the proportion of tetragonal phase with tin content at a given oxidation time. It also predicts that the higher the corrosion resistance, the lower will be the content of tetragonal phase for a given oxide thickness. The author concluded that the major controlling factor on tetragonal phase stabilization was the oxide grain size. In fact the crystal size would be expected to influence the pressure-temperature phase diagram of zirconia, as discussed by Bounier et al. [220]. However, the size effect would fail to explain some other observations, such as presence of small monoclinic grains.

Furthermore, it is found that chemically stabilized (usually by Y or Ca) t-ZrO₂ ceramics transform to m-ZrO₂ when exposed to moisture due to leaching of the stabilizing element,

which results in a degradation of the ceramics [215]. In oxides grown on zirconium alloys, the defects induced by dopants like Fe^{3+} and Nb^{5+} have been associated with tetragonal stabilization in the vicinity of the precipitates [193, 221]. However, it was also suggested that the concentration of dopant in the oxide was too low to stabilize the tetragonal phase but sufficient to affect the destabilization process [222]. Therefore, the exact role of these alloying solutes in phase transformation-induced breakaway needs to be clarified.

1.3.4.3 Dissolution of alloying elements in the oxide

Cox [2] has suggested another possible mechanism which considers the dissolution of alloying elements present in the zirconium oxide. SnO_2 is found concentrated in the oxide crystallite boundaries and Fe_2O_3 and Cr_2O_3 are formed by the oxidation of intermetallic precipitates, and they are thought to be much more soluble in high temperature water than ZrO_2 , possibly resulting in the formation of pores and cracks by selective dissolution. However, this hypothesis again lacks clear experimental evidence.

In conclusion, none of proposed breakaway mechanisms are supported by enough evidence. Without further critical experiments it is unlikely that more mechanistic understanding of corrosion of zirconium alloys will be achieved.

2 TEM Sample preparation

In this chapter TEM sample preparation using focused ion beam (FIB) milling will be described.

2.1 *Focused ion beam (FIB)*

Systems for ion beam milling utilizing FIB have been commercially available for more than ten years and are mostly applied in semiconductor research. The fundamental working principle of FIB is very similar to the scanning electron microscope (SEM), except that instead of an electron beam a finely focused beam of ions is applied [223]. A schematic setup of a FIB is shown in **Figure 2.1**. Currently the most widespread ion sources are liquid metal, especially gallium ion sources [224]. The ion beam is emitted from the source and focused onto the sample surface by a set of electrostatic lenses. The beam can have very high current density (tens of nanoamperes in a modern FIB) with a very small energy spread, and a spot size of the order of a few nanometers can be achieved, allowing very high precision milling.

When the gallium (Ga^+) primary ion beam hits the sample surface, it sputters the sample material as either secondary ions or neutral atoms. Secondary electrons are also produced at the same time. The physical sputtering process dominating at high ion beam currents enables the removal of material during FIB milling. If the finely focused ion beam is raster scanned over a substrate at low current, the generated secondary ions or electrons can be utilized for imaging. Localized deposition of both metal and insulator materials can also be carried out using FIB by chemical vapour deposition (**Figure 2.2**) [225]. A precursor gas is sprayed by a gas injector to be adsorbed on the surface, which is then decomposed by the primary ion beam and leaves the desired reaction product on the surface as a thin film.

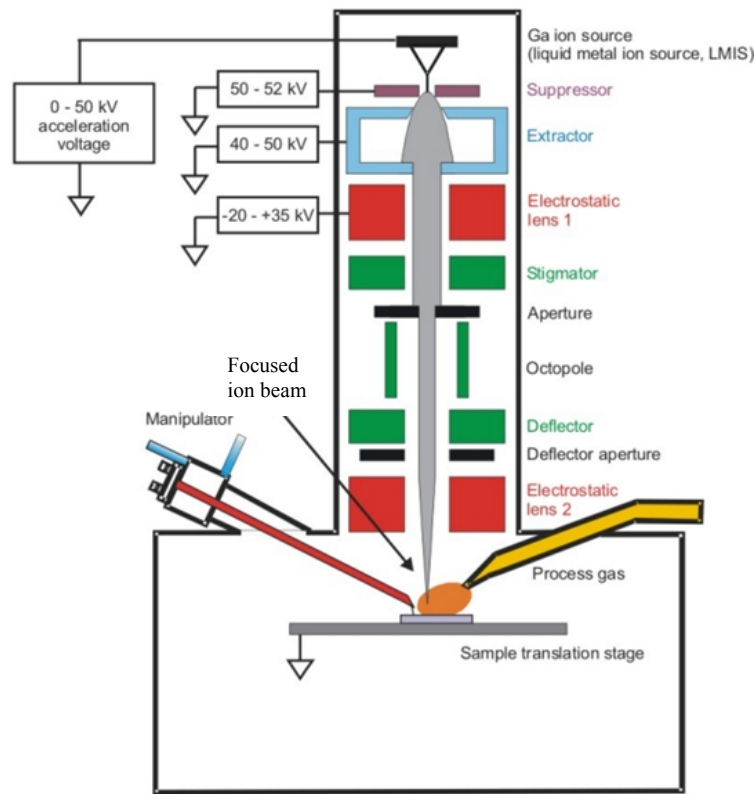


Figure 2.1 A schematic setup of a FIB instrument [223]

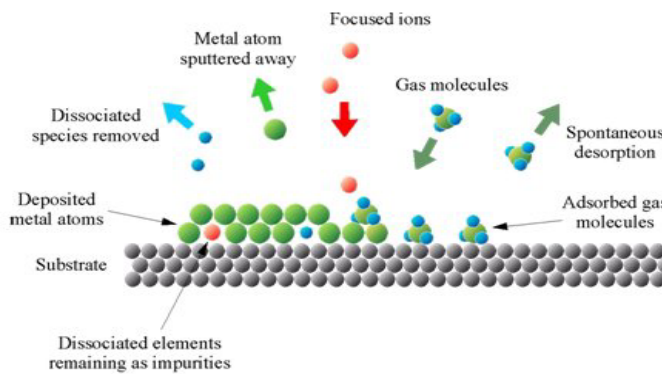


Figure 2.2 Gas assisted deposition [225].

More recently, ‘Dual beam’ FIB instruments (**Figure 2.3**), which consist of both a FIB column and an SEM column, have offered the ability to monitor ion milling processes in real time by imaging with an electron beam. This not only allows a higher image resolution with the finer electron beam but also prevents the surface damage that would be produced when imaging with an ion beam. This is particularly important for TEM sample preparation where surface features are often the area of interest. In addition to the secondary electron detectors, it

is also possible to include other detectors to collect various signals such as X-rays, back scattered electrons etc.

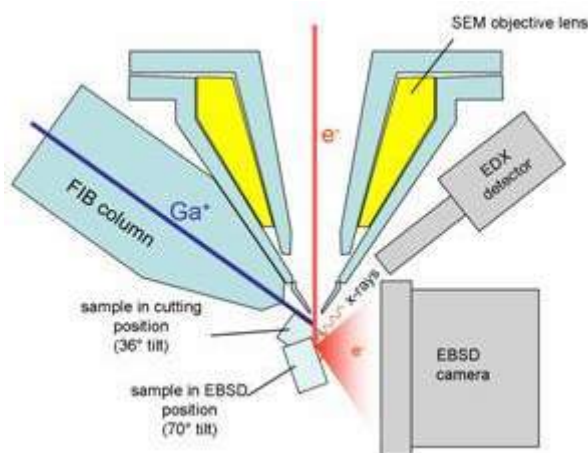


Figure 2.3 Schematic image of a dual beam FIB-SEM system with an EDX detector and an EBSD camera [226].

2.2 Sample preparation using FIB

Sample preparation methods for TEM have a large influence on microstructural investigation, for example the presence of cracks [139], details at metal/interface [227] and the analysis of second phase particles [122, 179, 189]. In general metallurgical studies, FIB is now a very common technique for TEM specimen preparation due to a number of big advantages over more conventional methods [228], including the precise selection of the target area, the possibility of making large electron-transparent areas with nearly parallel sides and high throughput and reliability. This technique, however, has not yet seen wide use in the study of zirconium oxidation. Little TEM work has employed this technique for preparing thin foils [19, 152].

In this work, the in-situ lift-out (INLO) FIB method [228, 229] was employed for the preparation of TEM foils. First a Pt or C layer was deposited over the target area to protect the top surface of the resulting specimen. After that three trenches were milled at the selected site to create a lamella typically about 15-20 μm in length and 7-8 μm in depth. For thin oxides (a few μm), the sample is orientated such that the oxidized surface is perpendicular to the FIB

ion beam. For samples that have a thicker oxide layer, the bulk sample is cross-sectioned and subsequently polished to mirror finish, and the cross-sectioned surface is orientated perpendicular to the ion beam. Therefore, in both cases the lamellae produced between the trenches can contain the oxide/metal interface, as shown in **Figure 2.4a**. The membrane is then milled from both sides to about 1-2 micrometers in thickness. At this stage, an in-situ micro-manipulator is employed to transfer the piece of specimen to a TEM half-grid inside the FIB chamber (**Figure 2.4b**). This is achieved by depositing a Pt layer to first weld the manipulator probe to the lamella, and then to weld the lamella to the grid. Final FIB thinning of the foil to electron transparency is performed at progressively lower ion beam currents when the sample is on the grid (**Figure 2.4c**). Thicker regions are left on purpose at the side and the bottom of the specimen to prevent bending caused by the release of the high stresses stored in the oxide.

In **Figure 2.4c**, some curtaining effect can be seen in the bottom of the sample. This type of artefact can be a result of change in sputtering rate across the sample surface due to differences in materials, specimen topography or crystal orientation [230, 231]. In this study, the observed curtaining effect usually starts from $\sim 5\text{ }\mu\text{m}$ below the sample surface, and is mainly caused by the insufficient milling dose from beam tails or presence of cracks or other topographic features in the region above [231]. Due to the protection of the deposited Pt or C layer, the curtaining induced by the cracks present in the oxide can be minimized.

A main advantage of the FIB technique in general is the ability to produce TEM specimens with a large electron transparent area with an almost uniform thickness. For example, a TEM thin foil with an electron transparent area about $11\text{ }\mu\text{m}$ by $6.5\text{ }\mu\text{m}$ was finally obtained from the lamella shown in **Figure 2.4c**. The INLO method allows further thinning of the specimen if it is found to be necessary after initial examination in the TEM. This is done by tilting the specimen ± 10 degrees and milling the whole specimen area from both sides under a 5 kV Ga beam.

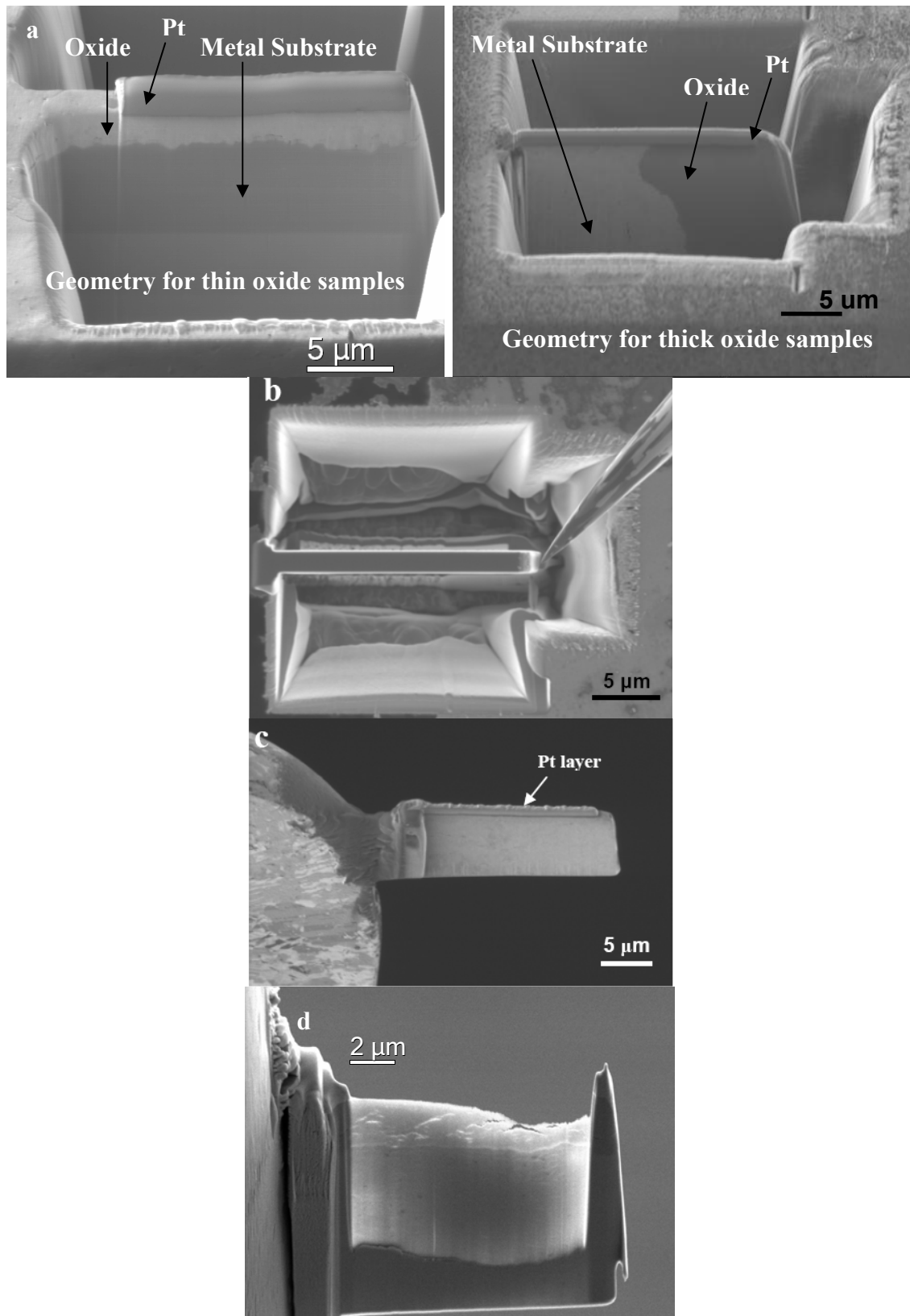


Figure 2.4 Procedure of the in-situ lift-out method for preparing TEM thin foils. a) Tilted images show geometry of trench, sample orientation and the slices in the trench. b) The lamella is thinned to about $2\ \mu\text{m}$. The internal micromanipulator is welded to the thin foil for transferring the specimen to a TEM grid. c) The lamella is welded to the TEM half-grid and thinned to be electron transparent (d).

With care, the foil can be thinned to a thickness of 100 nm or less, which is not only required for EELS and HRTEM but also very important to avoid the complex images that result when the specimens are thicker than the characteristic scale of the microstructure – in this case the very fine grain size in the oxide scale, 10-50 nm.

The most common artefacts that happen to the FIB prepared samples are Ga ion implantation, carbon contamination, and sample damage such as the formation of an amorphous layer that may extend several tens of nanometers into the material [228, 232]. Low-energy Ga polishing and plasma cleaning have been found to be effective in reducing the damage layer and the contamination [228, 233, 234] and it is possible to produce specimens with large electron transparent regions that reveal sub-angstrom information without carbon contamination [235, 236]. In this work the TEM specimens were always cleaned using a 5 kV or 2kV ion beam at $\pm 10^\circ$ to remove the beam damage. After the cleaning, no obvious Ga implantation can be detected in the TEM samples, as shown in the energy dispersive X-ray (EDX) spectrum obtained from the oxide of a typical thin foil (**Figure 2.5a**). The amorphous layer at the edge of the sample is ~ 3 nm thick, as shown in a typical high resolution transmission electron microscopy (HRTEM) image (**Figure 2.5b**). From this measurement, the amorphous layer on top of each side of my samples can be estimated to be about ~ 3 nm, although this may be an underestimation for the centre part of the specimen as the ~ 3 nm layer was measured from the sample edge. A similar width of the amorphous layer (~ 2 nm) was reported for Si specimen polished with FIB at 5 keV [237]. And a summary of the thickness of the damage layers for Si in different milling conditions is shown in **Table 2.1** [238].

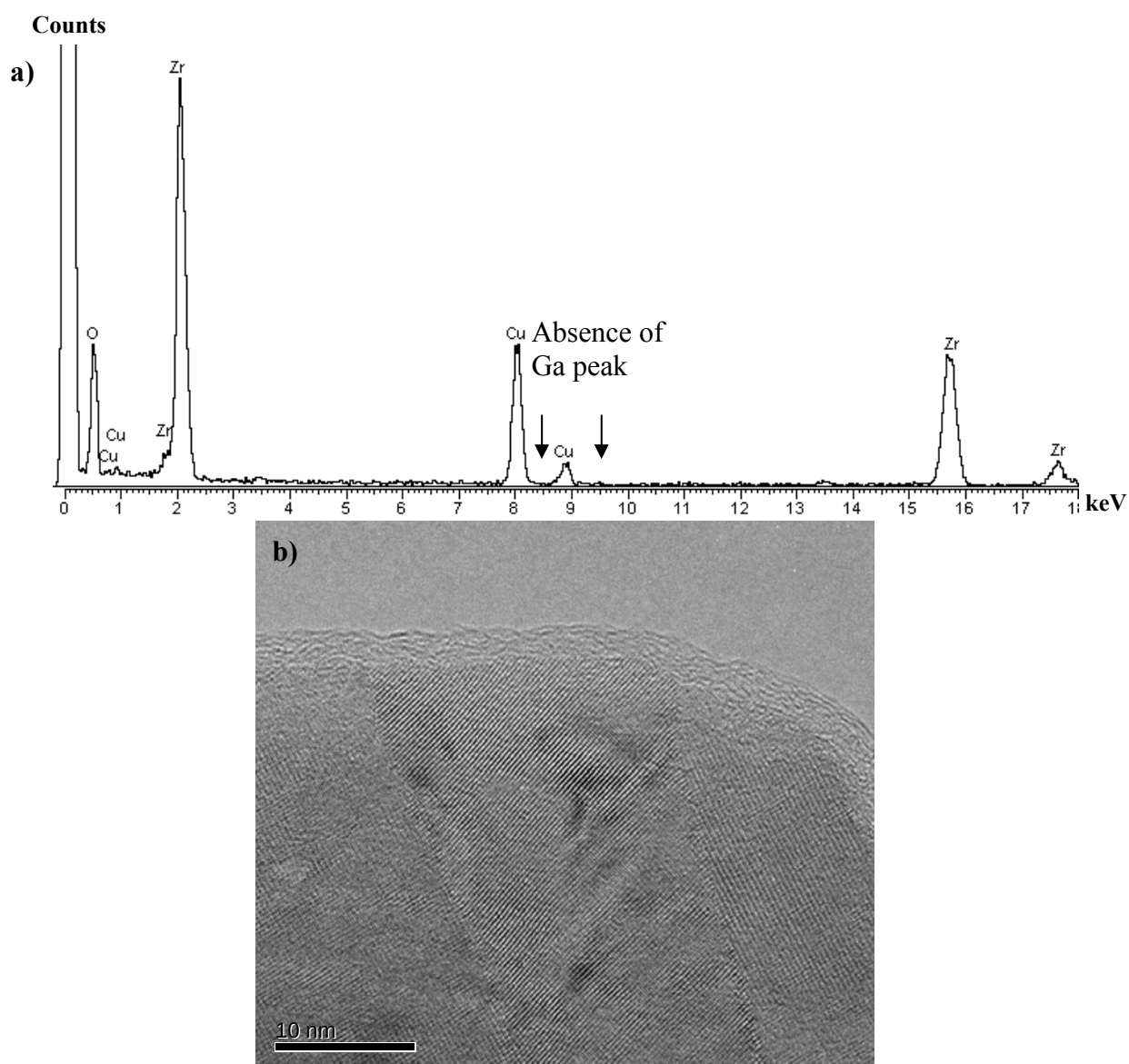


Figure 2.5a) EDX spectra obtained from the oxide and the metal of one thin foil showing no obvious Ga implantation. b) HRTEM image at the edge of a sample, revealing a ~3 nm thick amorphous layer.

Table 2.1 Experimental and calculated data for damage depths of silicon etched using 10–50 keV gallium ion beams, where (Cal) indicates calculated data and (Exp) indicates experimental results [238].

Reference	10 keV	30 keV	50 keV
Boxleitiner (Cal)	9 nm	19 nm	31 nm
Boxleitiner (Exp)	8 nm	17 nm	25 nm
Ishitani (10) (Cal)		10 nm	
Kato (7) (Exp)	10 nm	21 nm	
Langford (14) (Exp)		20 nm	
Mardinly (Cal)		30 nm	
Mardinly (Exp)		28 nm	
McCaffrey (Exp)			22 nm
Rubanov (Exp)		30 nm	
Walker (Exp)	6 nm	28 nm	

3 Techniques and methodology

The experimental techniques and data analysis methods involved in this work are described in this chapter. After an introduction on the interaction between electrons and materials, the basic principles and main techniques of transmission electron microscopy (TEM) will be given. Finally 3D microstructural characterization using FIB sequential sectioning and imaging is described.

3.1 *Interaction of electrons with matter*

In TEM high-energy electrons are used to irradiate a specimen about 100 nm thick or less. The incident electrons can interact with the specimen in many different ways and generate a wide range of secondary radiations and particles from the specimen, as illustrated in **Figure 3.1**. Most incident electrons pass directly through the specimen remaining in the direction parallel to that of the incident beam to form the non-deflected direct beam. Many others will be scattered elastically or inelastically by the electrons or the nuclei of the atoms in the specimen. Both the direct beam and the scattered electrons, and most of the other generated secondary signals, can be detected in different types of electron microscope, providing structural and chemical information on the material. Details of some of the aspects relevant to this work will be described in the following sections.

3.2 *TEM instrumentation*

After the electrons pass through the specimen they form an image which is magnified by several subsequent electron-optical lenses. This image can be observed directly on a fluorescent screen or on a CCD camera. A schematic of a TEM instrument, showing the location of a thin sample, the principal lenses within a TEM column, and the ray path for

bright-field imaging is illustrated in **Figure 3.2**. The most important functional units of a TEM are:

1. Illumination system composed of electron source and condenser lenses;
2. Specimen stage for shift, tilting and rotation;
3. Image formation system that consists of objective lens and aperture, intermediate and projective lenses, and
4. Image recording system formed by the screen and photo recorder (camera or video).

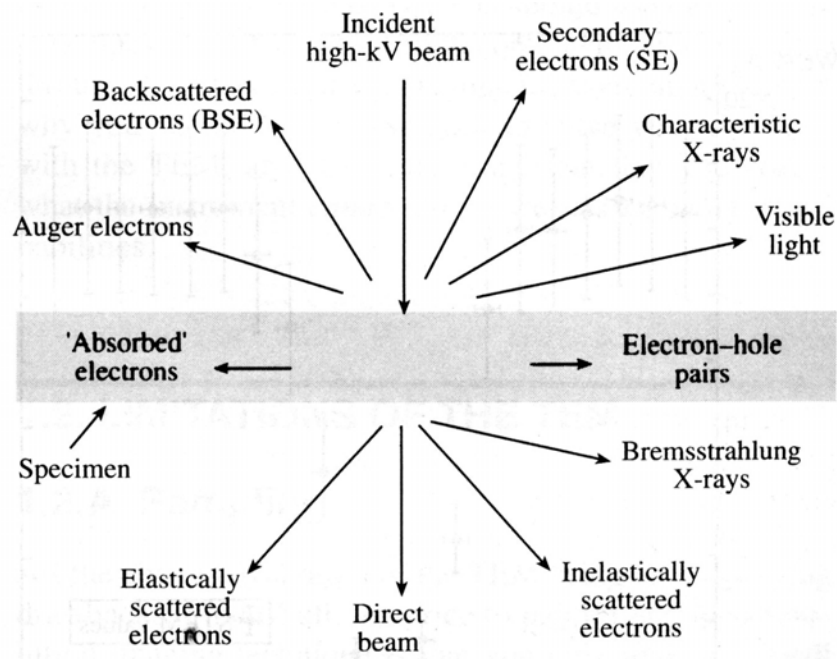


Figure 3.1 Possible signals generated from a primary electron interacting with a thin specimen [239].

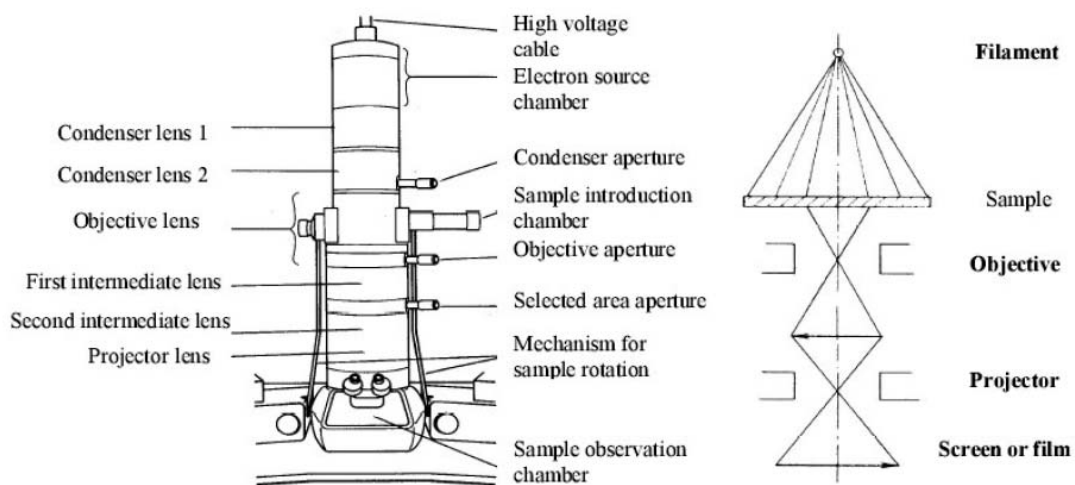


Figure 3.2 Schematic diagram of TEM and its optics [239]

The adjustment of condenser lenses can produce either a parallel illumination or a focused convergent beam on the specimen. The objective lens then takes the electrons passing through the specimen, focuses the electrons which have the same direction to create a diffraction pattern (DP) in the back focal plane and recombines them to form an image of the specimen in the image plane where all electrons emerging from the same point in the specimen converge to a same point (**Figure 3.3**). Finally the intermediate lens can be adjusted to either project the diffraction pattern or the image onto the screen through the projector lens, enabling the microscope to be operated in either diffraction mode or imaging mode.

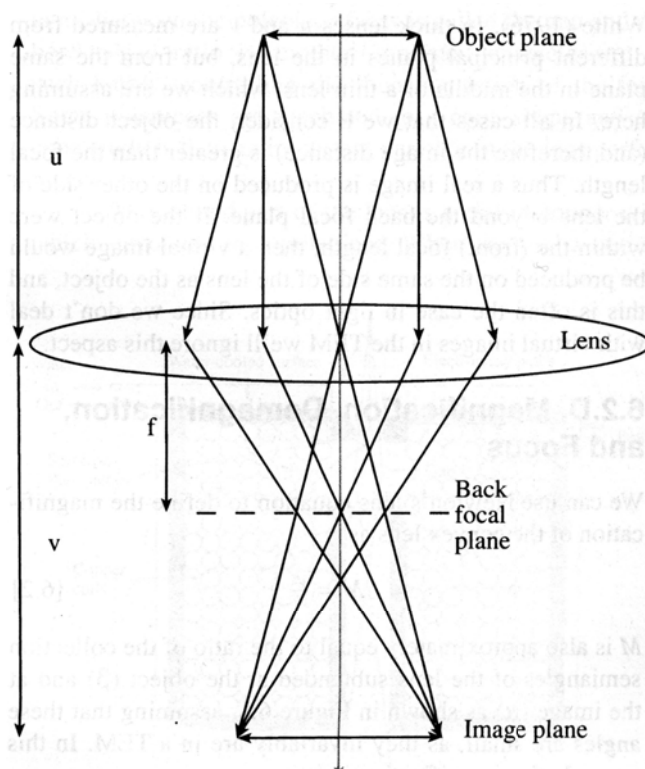


Figure 3.3 Ray diagram showing the function of the objective lens [239].

3.3 Micro/Nano structure imaging

3.3.1 Diffraction contrast in bright-field/dark-field images

The elastic scattering at low scattering angles is primarily from interaction of the primary electrons with the electron clouds of sample atoms, and has strong dependence on the

scattering angle. For crystalline materials, the intensity of the scattered beam is a maximum at specific angles where the crystal planes are orientated such that the Bragg-diffraction condition of the electron wave by the crystal planes is satisfied. This is the mechanism responsible for (Bragg-) diffraction contrast, which depends on the crystal structure and sample orientation.

By selecting either the direct beam or some of the diffracted beams for forming the image, we can produce either bright-field (BF) or dark-field (DF) images (**Figure 3.4**) [239]. The selection of diffracted beams can be done either by physically moving the objective aperture or by tilting the incident beam so that the diffracted beam travels down the optic axis. The latter is sometimes specified as centered dark-field (CDF) imaging and is the usual way to do DF image in the TEM. This mode can avoid the aberration and astigmatism suffered by the off-axis electrons in the displaced-aperture DF mode.

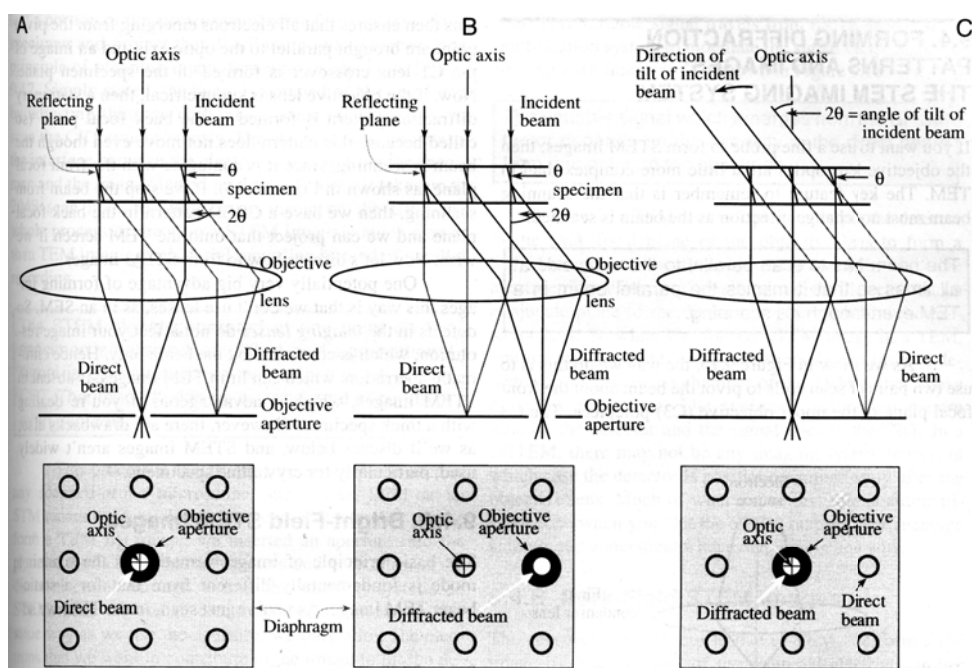


Figure 3.4 Ray diagram showing (A) a BF image formed from the direct beam, (B) a displaced-aperture DF image formed with a specific off-axis scattered beam, and (C) a CDF image where the incident beam is tilted so that the scattered beam remains on axis. [239]

In BF and DF images of a crystalline material, both Bragg-diffraction contrast and mass-thickness contrast are present, and compete with each other. The mass-thickness contrast

arises from incoherent (Rutherford) elastic scattering of electrons, and depends on the atomic number Z and the sample thickness. Therefore, an area that is thinner, and/or has lower Z and/or is not in Bragg-diffraction orientation, appears brighter in the BF image and darker in the DF imager. Within a single phase, if the variation of thickness is small diffraction contrast dominates. The best diffraction contrast can be achieved if two-beam conditions are set up where only one specific diffracted beam is strongly excited.

3.3.2 Fresnel contrast

Fresnel contrast in the defocused condition has been used in this work in order to study nano-porosity in the oxide. Pores less than 10 nm in diameter can be best imaged using Fresnel contrast [240], and this method is regarded as the only way to image voids smaller than 1/20 of the foil thickness when there is no associated strain field [241].

The contrast originates from the difference in the inner potential of the matrix and the cavity and depends on the thickness variations in the direction of the incident electron beam. When the image is over-focused, black fringes appear around the periphery of a cavity and the cavity is white; when the image is under-focus, white fringes appear around the cavity and the cavity is black (**Figure 3.5**). Specimen surface craters can produce similar phase contrast [241], but this is minimized in the FIB-prepared TEM samples where an almost homogeneous thickness with very little surface roughness can be achieved.

3.4 Identification of crystal structures

3.4.1 Electron diffraction techniques

The electron diffraction pattern can be obtained in several ways. The most usual one is to form a selected area diffraction pattern (SADP), which contains electrons diffracted from a selected area confined by the selected area diffraction aperture. The pattern exhibits sharp

spots as it is obtained with a parallel beam. The size of the area from which the electrons are diffracted depends on the size of the selected area aperture, which in many cases is not small enough to study only an area we are interested in. The smallest size of the selected area aperture is ~800 nm for the microscope most used in this work. One way to overcome this limitation is to use micro-diffraction where a convergent beam is used to limit the region of the specimen from which diffraction information is obtained. This mode gives rise to a diffraction pattern in the form of disks instead of sharp spots. When adjusting the convergence angle 2α by changing the size of the condenser aperture (C2 aperture), the diffraction pattern can change from one in which all disks overlap to one in which individual disk are resolved (Figure 3.6).

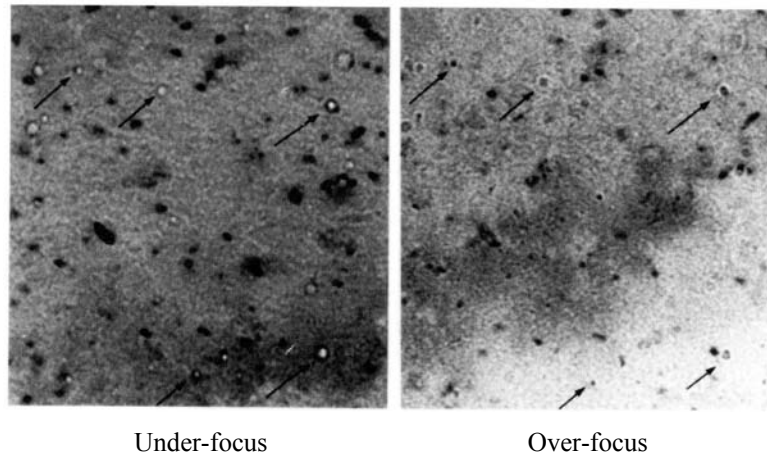


Figure 3.5 Surface craters in molybdenum, produced by irradiation with Sb_3^+ ions. The same area is shown, imaged in bright-field conditions in both underfocus and overfocus conditions. Some craters are arrowed. They show Fresnel phase contrast behaviour typical of cavities.[241]

At the Bragg-diffraction condition, we have

$$\frac{2\sin\theta_B}{\lambda} = \frac{1}{d_{hkl}} = |\underline{g}_{hkl}| \quad \text{Equation 3.1}$$

where θ_B is the Bragg angle, λ is the wavelength of the incident electron beam, d_{hkl} is the distance between a set of parallel (hkl) atomic planes where the Bragg-diffraction occurs, and $\underline{g}_{hkl}$ is the diffraction vector from the central spot O to the first diffraction spot G associated

with the specific (hkl) planes in the diffraction pattern (**Figure 3.7**). The vector $\underline{g}_{hkl}$ is generally defined as a vector in reciprocal space which has a length equal to $1/d_{hkl}$ and an orientation normal to the (hkl) planes, but will only produce corresponding diffraction spots G when the (hkl) planes are orientated at the Bragg-diffraction condition. Therefore by careful analysis of diffraction patterns we can determine the spacing of crystal planes for crystalline materials that are characteristic of the crystal structure, and angles between diffraction vectors which also carry structural information.

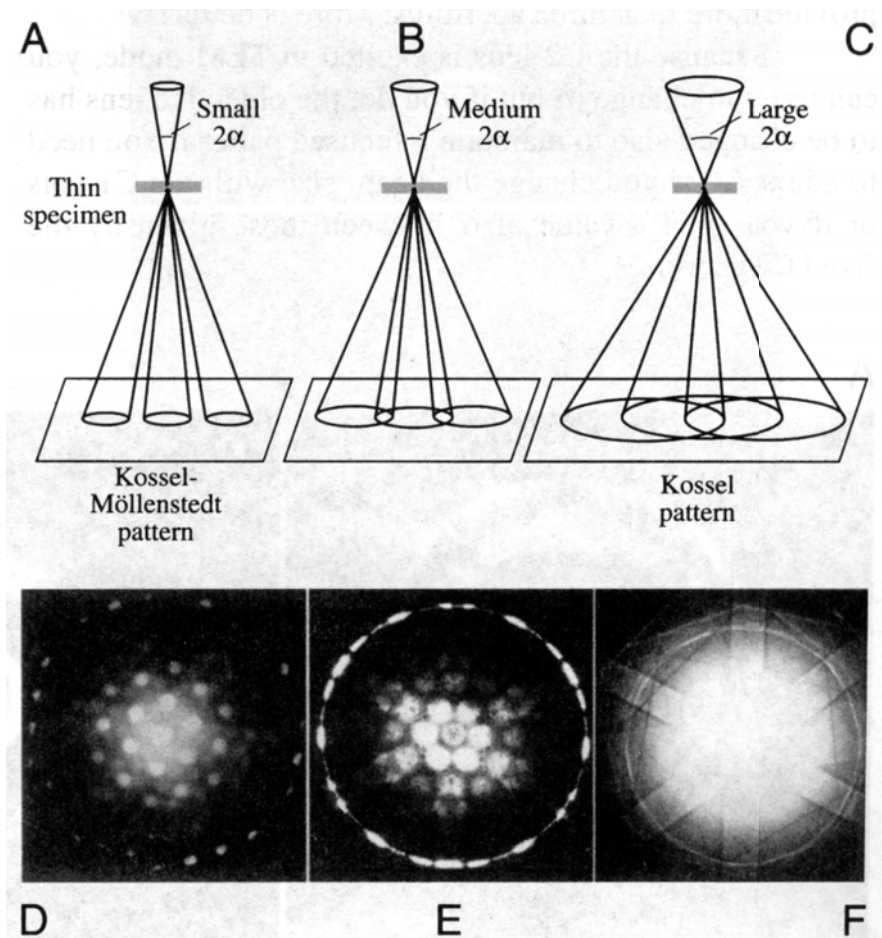


Figure 3.6 9 (A)-(C) Ray diagram showing how increasing the C2 aperture size causes the CBED pattern to change from one in which individual disks are resolved to one in which all the disks overlap. (D)-(F) show what happens to experimental patterns as larger C2 is selected. [239]

In practice, one measures the lengths D of diffraction vectors $\underline{g}$ as well as the angles γ between the vectors from a recorded diffraction pattern. One example of an experimental

micro-diffraction pattern is shown in **Figure 3.8**. The crystal spacing (d) giving rise a particular g vector is related to D via the following equation:

$$D \cdot d = \lambda \cdot L \quad \text{Equation 3.2}$$

where λ is the wavelength of the incident electron beam and L is the camera length between the specimen and the image recording device (eg. film or CCD camera). In order to achieve accurate measurement of the lattice spacing, the camera length used in this work has been carefully calibrated using a Si sample for which the crystal structure and plane spacings are known. Phase identification can then be carried out by comparing the experimental values with reference data available for phases with known crystal structures.

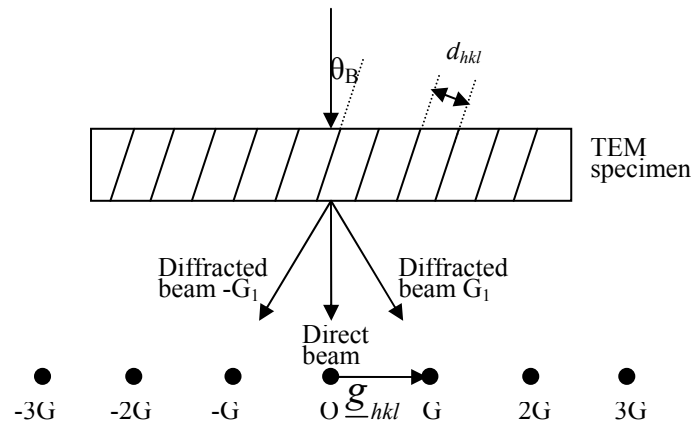


Figure 3.7 Notations for Equation 3.1

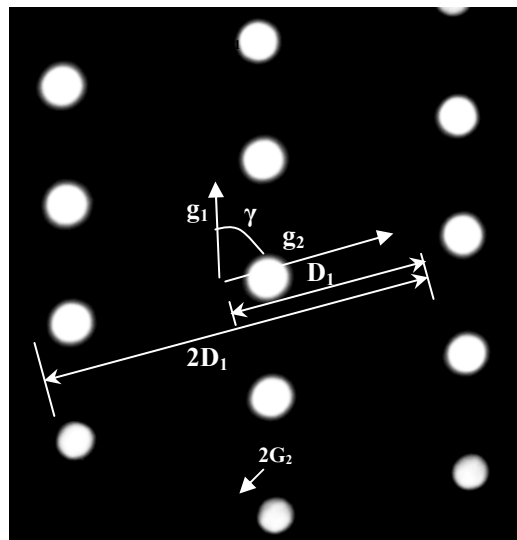


Figure 3.8 One example of an experimental micro-diffraction pattern.

3.4.2 High resolution TEM (HRTEM)

In high resolution TEM, phase contrast, which arises from the difference in the phase of the electron waves, is utilized to image thin specimens at atomic resolution. Instead of just using a single beam for imaging as for BF/DF mode, a number of beams are selected. The phase contrast along one direction x for a very thin specimen can be described by the following equation considering the interference of two beams, the central (000) beam and one diffracted beam g [239]:

$$I = A^2 + B^2 + 2AB \sin(2\pi \underline{g}' x - \pi s t) \quad \text{Equation 3.3}$$

where I is the intensity, A is the amplitude of the direct beam, B is a parameter related to the amplitude of the diffracted beam, and depends on s and the extinction distance for the diffraction vector $\underline{g}$; s is the excitation error which describes the deviation from exact Bragg diffraction, t is the specimen thickness and $\underline{g}' = \underline{g} + s$ along the x direction. As a result of this equation, the contrast comes from the sinusoidal oscillation in intensity along x (i.e. normal to $\underline{g}'$) with a periodicity of $1/\underline{g}'$. When s is set to be zero, the periodicity is equal to $1/\underline{g}$ or d . In this way the HRTEM images carry lattice spacing information about the specimen. The change of periodicity caused by a non-zero s is usually not noticeable if, as in most experimental conditions, s is much smaller than $\underline{g}$. It is also clear from the equation that non-zero s and thickness (t) variations will cause a shift of the lattice fringes along the x direction, for example in the case of bending of the specimen.

In this work HRTEM has been used to identify the lattice spacings in nano-scale grains where the resolution of the micro-diffraction technique is not sufficient. In addition, HRTEM is also useful to study the crystal orientations at the nanometer scale.

3.4.3 Error estimation on analyzing diffraction patterns and HRTEM images

It is important to estimate the errors when electron diffraction patterns or HRTEM images are used to identify crystal structures, because the possible candidate structures can be similar, for example the monoclinic and tetragonal oxide seen later in **Figures 5.10-5.12**, and the identification of the suboxide phase at the metal-oxide interface as will be shown in **section 6.3**. The details of the error analysis are described in Appendix A. It is found that in general the error ranges from $\sim \pm 0.0005$ nm to $\sim \pm 0.02$ nm, which depends on several factors including the pixel size of the analyzed digital images, the lattice spacings to be measured, the uncertainty in measuring positions of diffraction spots, and deviations from a perfect diffraction pattern due to instrument instability or other experimental and sample issues such as small thickness variation, local lattice strains etc. In most cases, the error on lattice spacing measurement is smaller using micro-diffraction patterns than from the analysis of HRTEM images. In HRTEM, the optimum magnification was found to be $\times 400\,000$ - $500\,000$.

3.5 STEM

In scanning TEM (STEM) mode, a fine probe is formed and scanned over the specimen. The formation of a very fine probe is realized by introducing a condenser-objective lens (C3), as shown in **Figure 3.9**. The convergence semi-angle α and the collection semi-angle β are important parameters related to quantitative STEM work. The scanning of the beam is enabled by two pairs of scan coils which pivot the beam about the front focal plane of C3 pole piece and thereby ensure the beam is always parallel to the optic axis during scanning. The STEM signal is generated point-by-point from the specimen, recorded by the detectors and finally displayed after proportional amplification at equivalent points at the CCD camera or CRT to form a complete image of the scanned area.

Different type of images can be obtained using different detectors. A BF image forms when a BF detector is inserted where only the direct beam in the diffraction pattern is used. When an annular detector, which has a hole in the middle and surrounds the BF detector, is used, all the scattered electrons will be detected, forming the annular dark-field (ADF) image. If an annular detector is configured to only detect electrons which have been scattered through large angles ($>5^\circ$), then a so-called high-angle annular dark field (HAADF) image is formed. In the last mode, the image contrast depends mostly on atomic number (Z) and is often called Z contrast because in this case coherent scattering is negligible [239]. Therefore, a Z-contrast image can provide elemental information to help identify different phases.

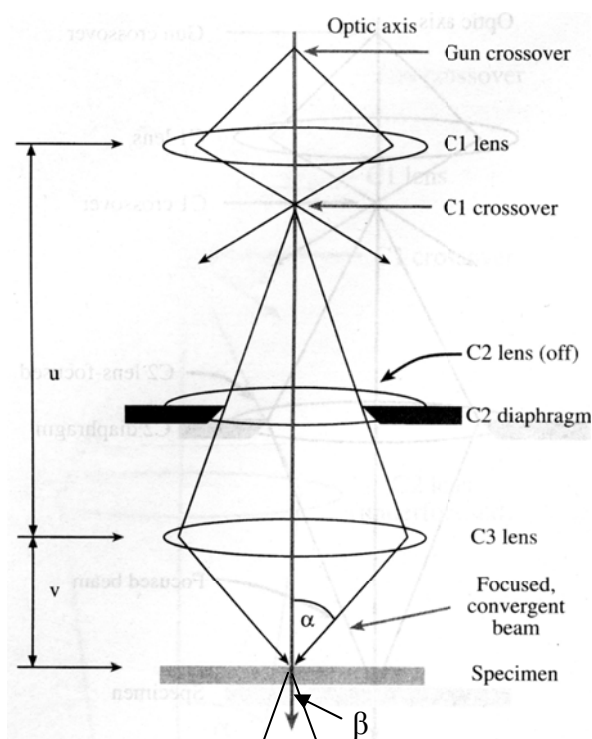


Figure 3.9 Use of the objective pole piece as a third condenser lens (condenser-objective lens C3) gives the smallest possible probe and large convergence angles. The large u/v ratios gives the maximum demagnification of the image of the gun crossover.[239]

3.6 Analytical (S)TEM

As we have mentioned in **section 3.1**, inelastic scattering of the incident electrons can happen when they interact with the specimen. During this process, the electron loses some

energy and the lost energy can be transferred to the specimen exciting secondary signals such as X-rays, secondary electrons etc. The two important analytical (S)TEM techniques, energy-dispersive X-ray spectroscopy (EDX) and electron energy loss spectroscopy (EELS), are related to the analysis of characteristic X-rays and the energy lost by electrons in the undiffracted beam respectively. Both techniques can be used in TEM or STEM mode. The latter mode offers better spatial resolution and the capability of elemental mapping (electron spectroscopic imaging (ESI)).

3.6.1 EDX

When an atom in the specimen is ionized by an incident electron, an electron in an inner shell may be ejected and create an electron hole, leaving the atom in an energetically excited state. In order to lose its excess energy, an electron from an outer, higher-energy shell then fills the hole, resulting in the emission of an X-ray photon characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, which allows the elemental composition of the specimen to be measured. At the same time, the incident electrons can also produce a continuum of bremsstrahlung X-rays if they are slowed by interaction with the nucleus. The incoming X-rays generate electron-hole pairs in a detector which comprises an intrinsic semiconductor (in most cases Si) proportional to the energy of the X-rays and produce charge pulses when separated by an applied bias. These pulses can then be processed so that EDX spectra are recorded in the form of X-ray counts versus X-ray energy, such as shown in **Figure 2.5a**. The characteristic X-rays appear as Gaussian peaks superimposed on a background of bremsstrahlung X-rays.

In general EDX is simple to use and a qualitative interpretation of the data is straightforward. Because a single spectrum can cover a wide range of energy, EDX is good for a quick overview of the elements present in the specimen. Because the intensities of EDX peaks depend on the properties of the TEM/EDX system, accurate quantification will need the use of

a standard with known composition to obtain a sensitivity factor [239] for specific X-ray peaks of an element, applicable for the same X-ray peak obtained with the same EDX detector and the microscope operating at the same accelerating voltage. For light elements that have low-energy X-rays, the sensitivity factor is highly dependent on absorption of X-rays in the detector and within the specimen itself. This absorption effect is difficult to correct quantitatively with high accuracy [242]. In addition the X-ray fluorescence yield, which measures the probability of X-rays competing with Auger emission, is much lower for light elements and so limits the detection sensitivity [243]. As a result, the quantification of light-element EDX analysis is not as good as for heavier elements.

3.6.2 EELS

Because the electrons lose energy by different mechanisms during the inelastic scattering process, a lot of information about the specimen can be obtained by analyzing the electrons that have lost energy. The energy loss (ΔE) can be measured by a spectrometer as schematically shown in **Figure 3.10** which separates the electrons according to their kinetic energy and produces EELS spectra in the form of the scattered intensity as a function of energy losses. **Figure 3.11** shows a schematic of EELS spectrum, which can be divided into three parts: the zero-loss peak at $\Delta E=0$ contains electrons that retain the original beam energy; the low-loss region in the spectrum usually refers to the energy-loss up to about 50eV, and the high-loss region of the spectrum above about 50eV reflects inelastic interaction where the incident electrons ionize the inner or core shell electrons. Different characteristic features are present in these different parts due to different mechanisms and can be utilized to give analytical and structural information of materials [239, 242].

For qualitative analysis, one just compares the experimental spectra with reference spectra by looking at the family of edges belonging to the particular elements. Quantitative EELS

analysis can be carried out based on the following equations assuming a single ionization event of the k shell electron [242]:

$$N = \frac{I_k}{\sigma_k I_T} \quad \text{Equation 3.4}$$

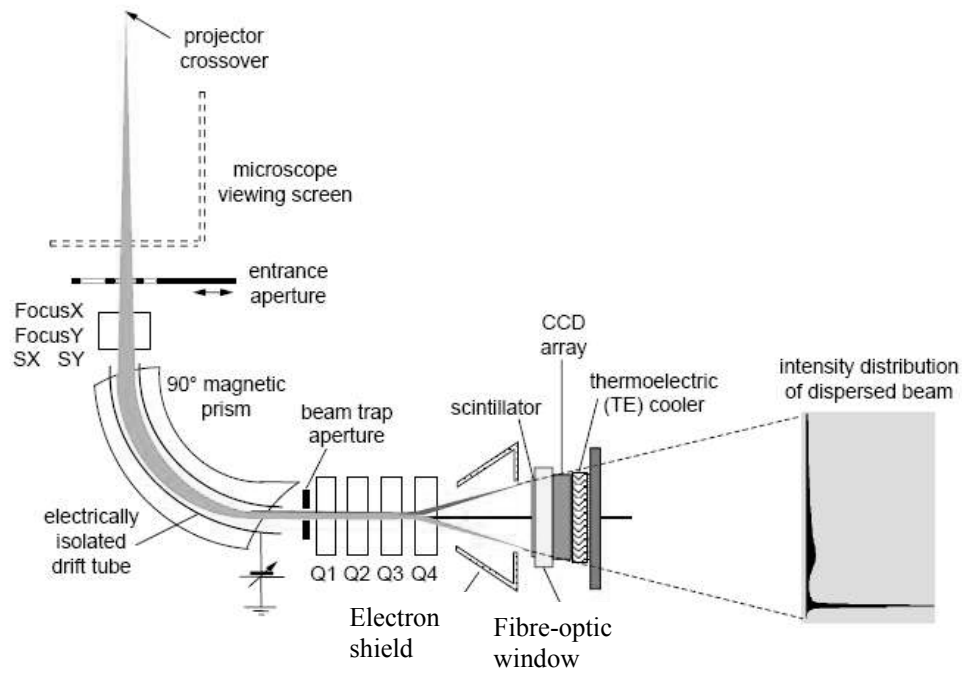


Figure 3.10 Schematic of an EELS spectrometer [244]

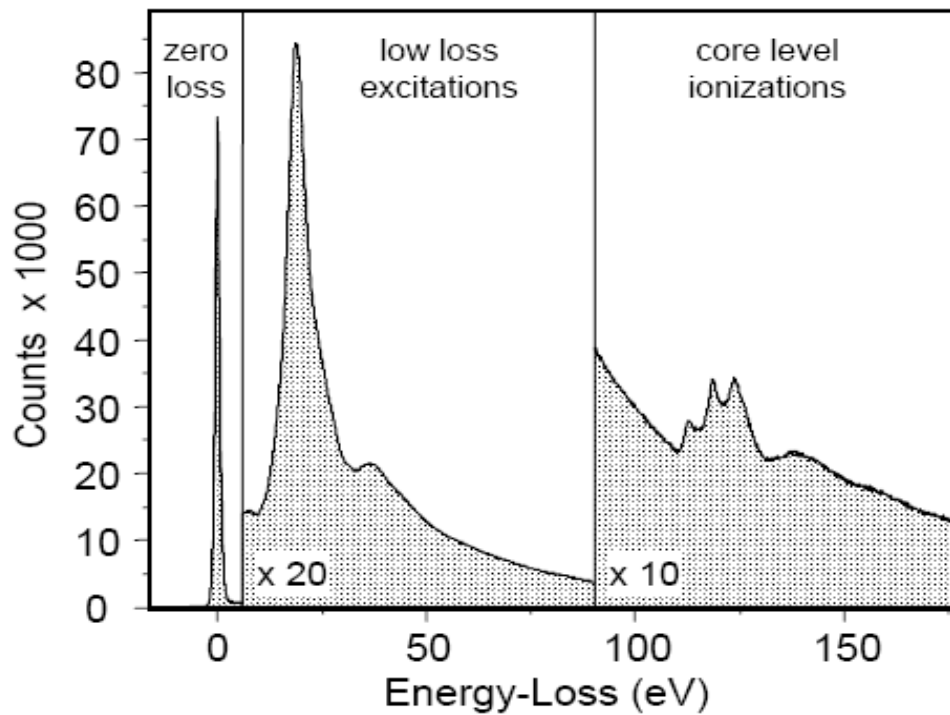


Figure 3.11 Schematic of an EELS spectrum

where N is the number of atoms per unit area of the specimen (thickness t) that contribute to the K edge in the spectrum, σ_k is the ionization cross-section of the K shell and I_k and I_T are the k-shell intensity above background and the total transmitted intensity respectively. For a binary system, the relative composition can be calculated by the following expression without knowing I_T :

$$\frac{N_A}{N_B} = \frac{I_k^A \sigma_k^B}{I_k^B \sigma_k^A} \quad \text{Equation 3.5}$$

In reality, we only collect electrons entering a limited solid angle β . During the analysis, the background is not precisely known and the intensity is usually integrated over a certain range of energies. Therefore, quantification depends on the choice of β and the way the background subtraction and intensity integration is carried out.

Compared to EDX, EELS is not as easy to use and only a certain range of energy region can be measured at one time. Interpretation of data also often requires more careful data processing. Another challenge is that the specimen thickness suitable for EELS is typically much smaller than for EDX due to the bigger background intensity in EELS and the problem of multiple scattering in thick specimen which prevents quantitative analysis. However, EELS measurement can offer better energy resolution of below 1eV. The spatial resolution is also better in EELS due to much less severe beam broadening. The entrance aperture of the spectrometer in EELS can limit the volume of the specimen from which the electron are scattered and detected, while in EDX no such limiting aperture exists and electrons scattered through large angles also generate X-rays which contribute to the signal. The important aspect of EELS for this work is its better capability of quantifying light elements because the limitations with EDX mentioned in **Section 3.6.1** are not issues for EELS. It will be shown in **section 6.2** how accurate quantification of oxygen content in my samples using EELS was achieved.

3.6.3 EFTEM

In energy-filtered TEM (EFTEM), an energy range is selected and a TEM image is recorded with electrons only of this energy by using an energy filter [245]. This procedure can be repeated at a number of energy loss settings and leads to a 3D data cube (Figure 3.12), where the first two axes correspond to the x - y position on the specimen plane, and the third axis is the energy-loss. Every pixel on the TEM image contains an EELS spectrum over an energy range. In this way, qualitative and quantitative elemental mapping can be obtained through the use of element-specific ionization edges.

If only the zero-loss beam is used, all inelastically scattered electrons will be filtered, which can help to increase contrast and resolution in TEM images and electron diffraction patterns. If an unfiltered image is divided by a zero-loss image, a relative thickness map in units of electron mean free path λ (t/λ map) can be obtained, which is useful for checking thickness changes in the specimen.

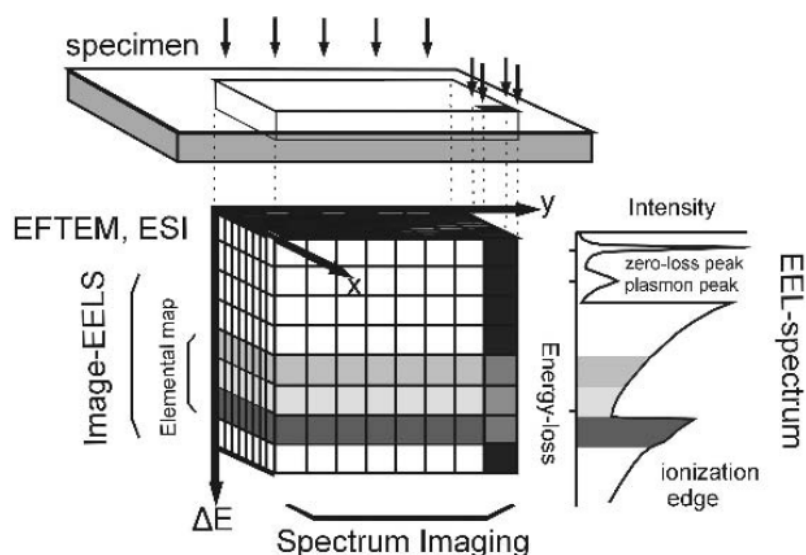


Figure 3.12 Schematic of the three dimensional (3D) data space that is obtained from the EFTEM [246].

3.7 3-D characterization using FIB sequential sectioning

By performing serial sectioning and imaging, modern dual-beam FIB instruments can produce two-dimensional image datasets suitable for the reconstruction of microstructures in three dimensions [247]. The analyzed 3D volume can be $\gg 1000 \mu\text{m}^3$ while nanometer image resolution can be routinely achieved at the same time. There have been an increasing number of applications of this method in studying different kinds of material microstructures, [248-251]. In this work, characterization of cracks in oxidized zirconium samples and the morphology of metal-oxide interface was carried out using this method. This provided a quantitative description of the oxide microstructure including crack density, crack distribution and interface roughness.

During the FIB sectioning, samples were orientated such that the focused Ga ion beam was at normal incidence (defined as the x direction) to the metal-oxide interface, and SEM secondary electron (SE) images were taken of each sequential x–y 2D slice at a tilt angle of 54° (**Figure 3.13a**).

Before sectioning, a protective coating of carbon was deposited on the area of interest, and then three staircase trenches were made in front of and at the sides of the volume of interest (**Figure 3.13b**). The front trench was made to reveal the cross-section of the oxide for subsequent imaging, and the two side ones to provide space to accommodate re-deposited materials during the sectioning process. To achieve a balance between an adequate image quality and a reasonable data acquisition time, a beam current of 700 pA was used to carry out the sectioning.

When the sectioning depth along the y dimension is greater than the oxide thickness, the SEM images are complete cross-sections containing the whole oxide from the outer surface into the metal substrate below the metal-oxide interface. An example of a typical 2D SEM image from an oxide grown on ZIRLO SR tube is shown in **Figure 3.13c**.

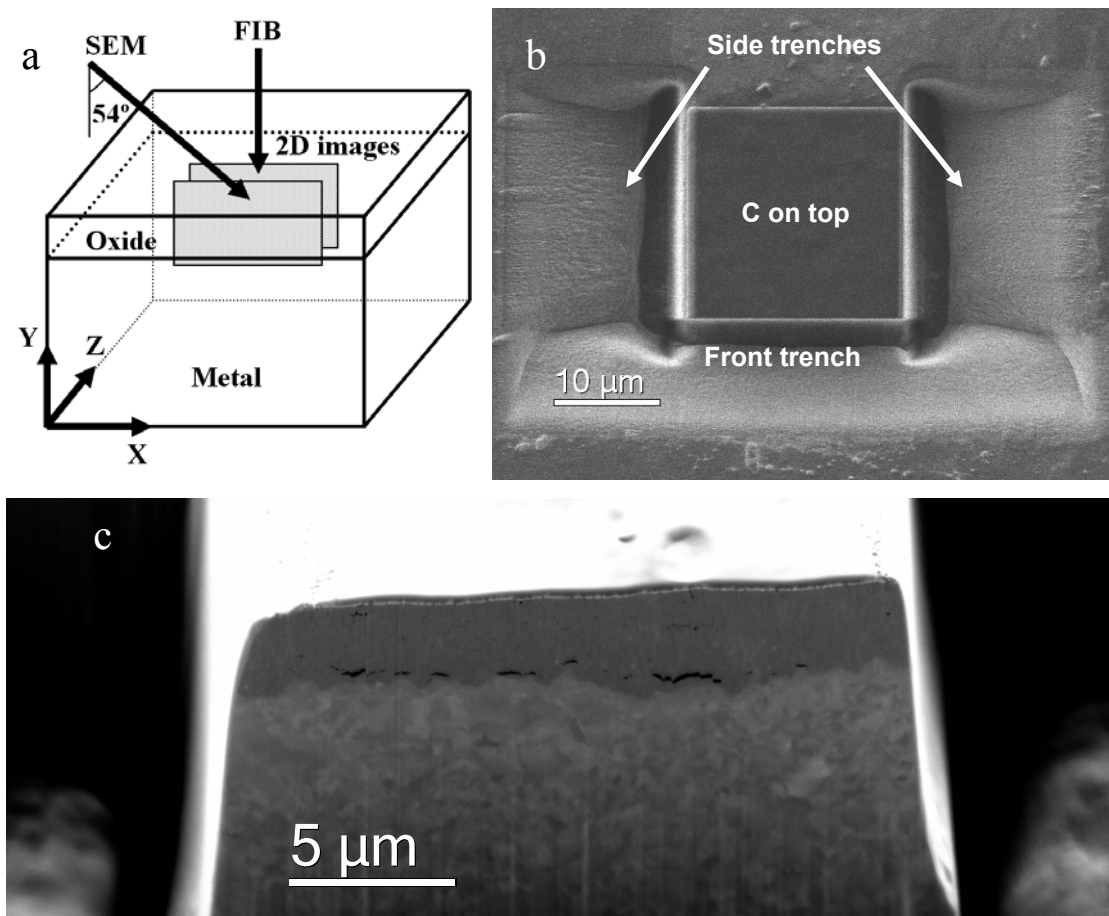


Figure 3.13 (a) Schematic of FIB serial sectioning and SEM imaging geometry. (b) Preparation for sectioning. A protective coating of carbon is deposited on the area of interest, and three staircase trenches are made in front of and at the sides of the volume of interest. The front trench is to reveal the cross-section of the oxide for subsequent imaging, and the two side ones to provide space to accommodate re-deposited materials during the sectioning process. (c) A typical 2D cross-sectional SEM image.

2D SE images obtained by FIB sequential sectioning were aligned and corrected for drift following a method previously described [252]. Then an area containing the region of interest with its top edge coinciding with the sample surface is extracted from each image and arranged into a 3D dataset. The 3-D reconstruction was carried out using the Mercury Software Avizo 6.1 program. The different regions of interest appearing in the 2-D images including the boundaries of each crack and the metal-oxide interface were defined manually as no automated segmentation method I tried could allow reliably for the significant channelling contrast in the SE images.

4 Materials and instruments

4.1 Materials

Autoclave corroded oxide samples of different kind of zirconium alloys were provided by the partners in the MUZIC project. **Table 4.1** lists the details of all the samples involved in this work, including the composition of the metals, oxidation conditions etc.

Table 4.1 List of materials investigated in this work. Bulk compositional data courtesy of Goodfellow Cambridge Ltd, EDF Energy, Westinghouse Electric Company Ltd. and Jianfei Wei, University of Manchester.

Alloys	Composition (weight percent)	Oxidation condition	Oxidation time
ZIRLO recrystallized (RXA) sheet	Zr-0.66 Sn-0.09Fe-0.92Nb- 0.01Cr	autoclave at 360 °C	Up to 180 days
ZIRLO stress-relieved (SR) tube	Zr-(0.89-0.92)Sn-0.09Fe-(0.87-0.91)Nb- 0.01Cr	autoclave at 360 °C	Up to 180 days
Zr-4 recrystallized (RXA) sheet	Zr-1.28Sn-0.22Fe-0.11Cr	autoclave at 360 °C	Up to 220 days
Zr-4 recrystallized (RXA) tube	Zr-1.28Sn-0.22Fe-0.11Cr	autoclave at 360 °C	90 days
Sheet Zr-Ti-Nb model alloy	Zr-0.98Nb-0.05Fe-0.21Ti	autoclave at 360 °C	1 day
Zircaloy-2 sheet	Zr-(1.2-1.7)Fe-(0.05-0.15)Cr-(0.03-0.08)Ni*	autoclave at 415 °C	660 day

** Specific composition data not provided for these samples, published data for commercial Zircaloy-2 used*

4.1.1 Oxides grown on ZIRLO

Standard ZIRLO sheet and tube were supplied by the Westinghouse Electric Company. The sheet material had undergone a final heat-treatment in the recrystallized (RXA) condition and

the tube materials in the stress-relieved (SR) condition. Details of the fabrication process can be found in [253-255]. The final anneal created a fine, equiaxed microstructure. An optical micrograph of the electrochemically etched RXA ZIRLO sheet material is shown in **Figure 4.1**.

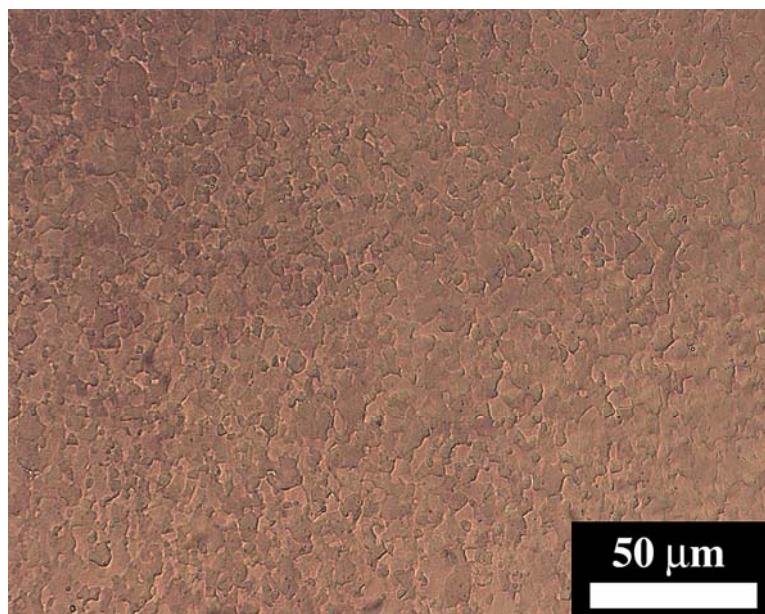


Figure 4.1 Electrochemically etched ZIRLO RXA sheet material. Courtesy of Jianfei Wei, University of Manchester

A large number of identical specimens of the alloys were subjected to aqueous corrosion in a static autoclave and subsequently removed after incremental periods of time up to 180 days. The corrosion testing was conducted by Jianfei Wei of Manchester University at the EDF research facility at Les Renardières near Paris. The static autoclave was operated at 360 °C and 18 MPa using the primary water chemistry for a PWR reactor (pure H₂O with additions of 2 wt.ppm LiOH and 1000 wt.ppm boric acid). The oxidation kinetics of the ZIRLO materials are shown in **Figure 4.2**.

Samples that just passed the first kinetic transition exhibit patchy corrosion which contains both black oxide and grey oxide, as shown in **Figure 4.3**. Characterization on both areas has been carried out to investigate the similarities and differences between them.

Oxides grown on RXA ZIRLO sheet have been the main focus of the work in this thesis.

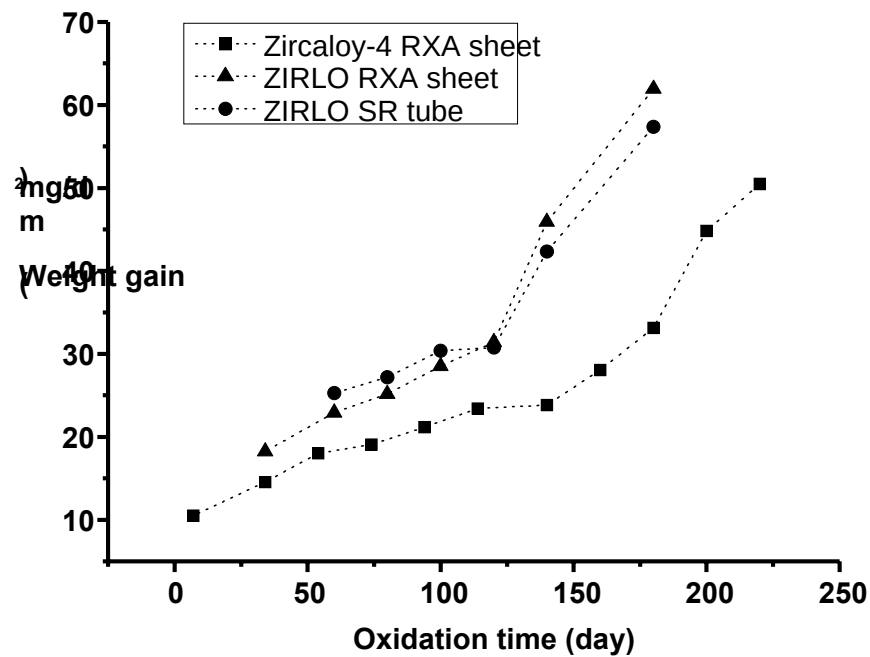


Figure 4.2 Oxidation kinetics from weight gain vs. oxidation time for ZIRLO RXA, ZIRLO SR and Zr-4 RXA. Data supplied by Jianfei Wei, Manchester University.



Figure 4.3 A patchy oxide formed on ZIRLO SR material after 140 days.

4.1.2 Oxides grown on Zircaloy-4

Oxides grown on Westinghouse Electric Company Zircaloy-4 from two different autoclave studies were analysed. Tubular material had been subjected to a final stage recrystallization heat treatment in argon at 620 °C for 2 hours before being subjected to autoclave exposure. The recrystallized tube specimens were subjected to corrosion testing for 90 days (2160 hrs) in 360 °C PWR primary water containing 2 wt.ppm Li and 1000 wt.ppm boric acid.

Sheet material had been processed with a similar thermal history. **Figure 4.4** shows the electrochemically etched Zircaloy-4 RXA sheet material. The autoclave testing on this material for up to 220 days was carried out in the same conditions as that for the ZIRLO material as described in **section 4.1.1**. Corrosion kinetics are also shown in **Figure 4.2**.

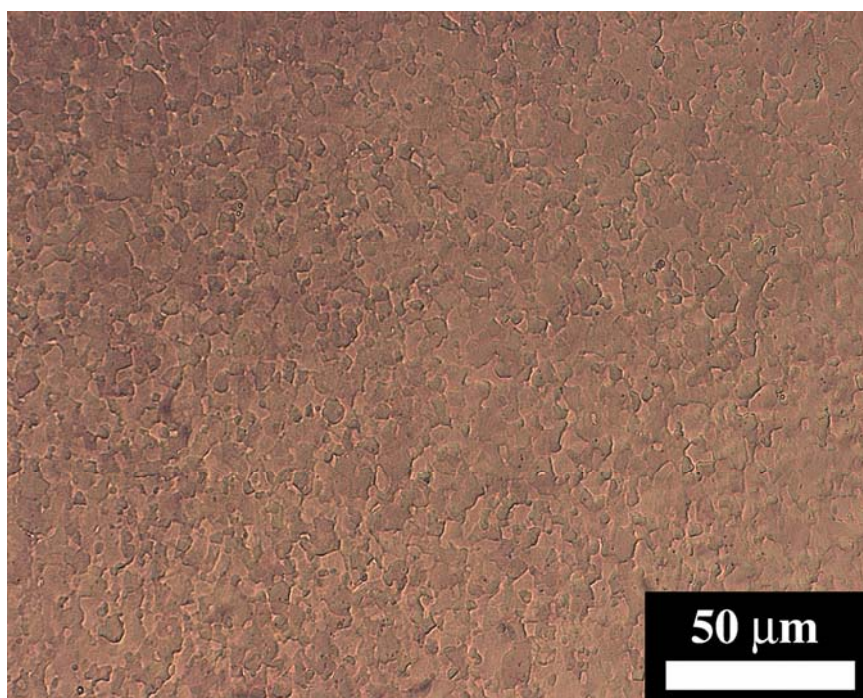


Figure 4.4 Electrochemically etched Zircaloy-4 RXA sheet material. Courtesy of Jianfei Wei, University of Manchester

It is seen from **Figure 4.2** that all three materials have only passed the first kinetic transition. In this work the stage before and after the first kinetic transition will be termed as “pre-transition” and “post-transition” respectively. The pre-transition kinetics for the RXA ZIRLO, SR ZIRLO and RXA Zircaloy-4 sheet can be fitted to power laws with an exponent of 0.3-0.43 by fitting the general empirical **Equation 1.1 (Table 4.2)**. The oxidation of Zircaloy-4 exhibits the typical near-cubic rate law, in agreement with previous published data [2, 3, 256]. A direct comparison on the rate exponent for ZIRLO cannot be achieved due to the absence of an exact fitting analysis in previous studies of ZIRLO oxidation, but a similar trend of decreased oxidation rate in the pre-transition stage has been shown [1, 53, 111, 257]. The determination of the post-transition kinetics has been constrained by the limited data available.

Table 4.2 Fitting of pre-transition oxidation kinetics for ZIRLO RXA, ZIRLO SR and Zircaloy-4 RXA sheet materials.

Materials	Fitting equation: (Weight gain) = $a \cdot (\text{oxidation time})^b$		
	a	b	Confidence R^2
ZIRLO RXA	3.88 ± 0.45	0.43 ± 0.03	0.9908
ZIRLO SR	7.34 ± 1.73	0.30 ± 0.05	0.9453
Zircaloy-4 RXA (sheet)	4.36 ± 0.54	0.35 ± 0.03	0.97788

The two ZIRLO alloys in different shapes and with different final heat treatments show very similar kinetics. This is in agreement with other studies showing that the final annealing process does not influence the uniform corrosion property significantly [109], while the intermediate annealing that determines the characteristics of intermetallic precipitates after hot rolling is important [258]. Ha et.al [259] also showed for Zr alloys with a high Nb content that the final Zr microstructure did not greatly affect the corrosion resistance. In this work Zircaloy-4 has a better performance than ZIRLO both before and after the first kinetic transition. Although this would not be expected from the literature, where ZIRLO usually exhibits a lower corrosion rate than Zircaloy-4 in long term corrosion, it has been shown that before a second transition (breakaway) the oxidation of Zircaloy-4 is slower than that of ZIRLO when oxidized in steam at 672K and 700K [53].

4.1.3 Other samples

Study of oxides of the following different zirconium alloys is also included when appropriate:

1. Zr-Nb-Ti test alloy. This alloy has a weight composition of Zr-0.98Nb-0.05Fe-0.21Ti and was processed as a 350 g test ingot and deformed to strip. The processing route was similar to that of the ZIRLO used in this study. After corrosion in primary water at 360 °C for only 1 day, the sample had already reached a weight gain of 1189 mg/dm², equivalent to an average oxide thickness of ~ 80 microns. Therefore the corrosion rate experienced by this material was 10⁵ times greater than that seen in ZIRLO samples.

This large difference in corrosion performance is attributed to the addition of 0.21 wt.% titanium. After the first kinetic transition as seen for the ZIRLO and Zircaloy-4 samples (**section 4.1.1 and 4.1.2**), the post-transition kinetics could show several weight gain cycles which mimic the pre-transition stage before eventually showing a linear behaviour, as summarized in **Figure 1.5**. At even longer time it is also reported that a “second transition” can happen at an oxide thickness of $\sim 30\mu\text{m}$, where the linear kinetics can change to a “stage 2 kinetics”, which is still linear but with a higher rate constant, that finally leads to rapid deterioration of the material in service [46]. Therefore in this work, this Zr-Nb-Ti oxide was termed to be a “post-second transition oxide”. This should not be confused with an oxide that may be in a second cycle of the cyclic stage after the first kinetic transition, although none of the Zircaloy-4 and ZIRLO oxides (c.f. **Section 4.1.1 and 4.1.2**) studied in this work belongs to the latter type.

2. Two Zircaloy-2 sheet materials in α -annealed condition and β -quenched condition respectively were provided by Westinghouse Electric Company. The α -annealed Zircaloy-2 had been oxidized in an autoclave at 415°C for 660 days and has a weight gain of 487.2 mg/dm^2 equivalent to an average oxide thickness of ~ 32 microns. The water chemistry of the autoclave was similar to that used for ZIRLO and Zircaloy-4 materials. The β -quenched Zircaloy-2 had been oxidized in the same conditions for 660 days and has a weight gain of 466.9 mg/dm^2 equivalent to an average oxide thickness of ~ 31 microns. These two oxides were considered to represent the later stage of the post-transition period with a higher oxidation rate than either the ZIRLO or the Zircaloy-4 oxides.

4.2 Instruments

Technical details of the main instruments used in this work are summarized here.

FIB: Focused ion beam (FIB) instruments used for transmission electron microscopy (TEM) sample preparation were an FEI FIB 200 instrument (Ga incident beam with 30 kV range and beam current from 50 -5000 pA) and a Zeiss NVision 40 dual-beam FIB instrument (2-30kV Ga⁺ incident beam energy with currents of 80-1000 pA). The Zeiss NVision 40 was also used for 3D FIB sectioning and imaging.

TEM: A Phillips CM20 running at 200kV equipped with an Oxford Instruments EDX detector, a Jeol 4000HR, and a Jeol 3000F microscope operated at 297 kV and equipped with a Gatan image filter (GIF) were used for most of the TEM work. Some of the TEM results were acquired with a JEOL JEM-2100 operated at 200kV at the University of Warwick, and a VG HB 501 microscope with a Cs corrector operated at 100kV at SuperSTEM, Daresbury.

5 Characterization of zirconium oxide

This chapter describes basic TEM characterization of oxide morphology and oxide phase analysis on oxides grown on ZIRLO and other materials in different stages of the oxidation process. Particular attention has been paid to the careful investigation of oxide nano-porosities using Fresnel imaging, which will lead to the proposal of a possible mechanism for the kinetic transition. Some preliminary characterization of second phase particles in the metal and the oxide, and hydrides in the metal near the metal-oxide interface, is also included in this chapter.

5.1 Oxide morphology

5.1.1 Observations

2-6 good TEM specimens for each oxide sample have been investigated, which has resulted in thousands of images in total taken in this work. Only a small number of images have been selected to represent typical observations for the studied samples.

5.1.1.1 ZIRLO RXA oxides

Figure 5.1 shows typical TEM bright field images of the ZIRLO recrystallized (RXA) sheet oxides formed in an autoclave at 360°C after 34, 60, 120 and 140 days, showing the morphology of the whole oxide. The first 4 samples are pre-transition oxide and the 140 days sample is grey oxide from a sample just past the transition in the kinetic curve that contains patches of both black and grey oxide (c.f. **Figure 4.2**).

Table 5.1 lists the oxide thickness of ZIRLO oxides measured by TEM, which is reasonably in agreement with the thickness calculated from the weight gain data. The 120 days oxide, which sits around the transition point in the kinetic curve, shows a big variation in oxide thickness. The black oxide from the 140 days sample has smaller thickness than the grey oxide.

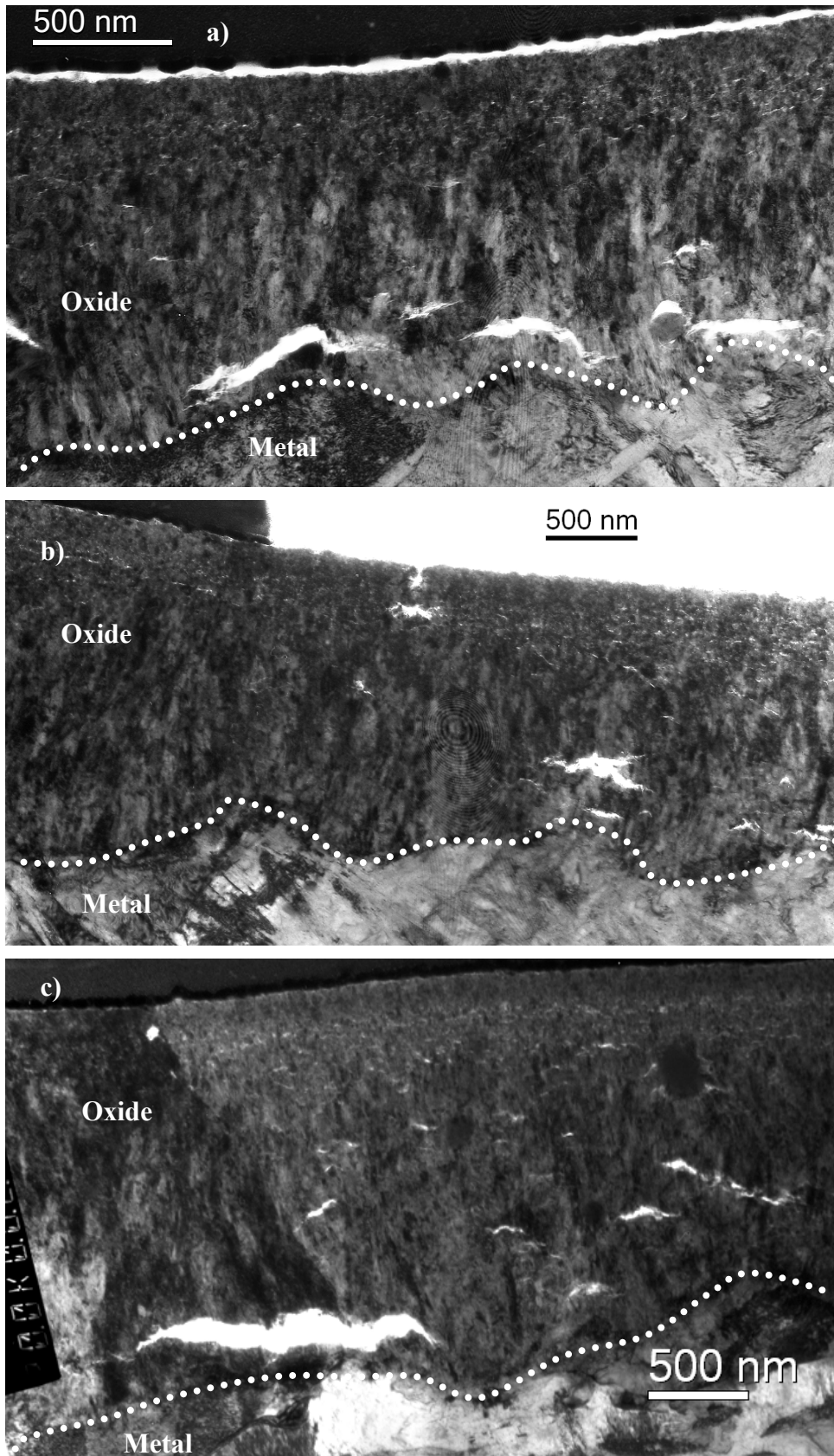


Figure 5.1 Oxide morphology of recrystallized ZIRLO oxides formed after different oxidation times: a) 34 days oxide; b) 60 days oxide; c) 100 days oxide; d) 120 days oxide (shown with 2 connected images) e) black oxide of 140 days sample; f) grey oxide of 140 days sample.(Figures continued on the next page.)

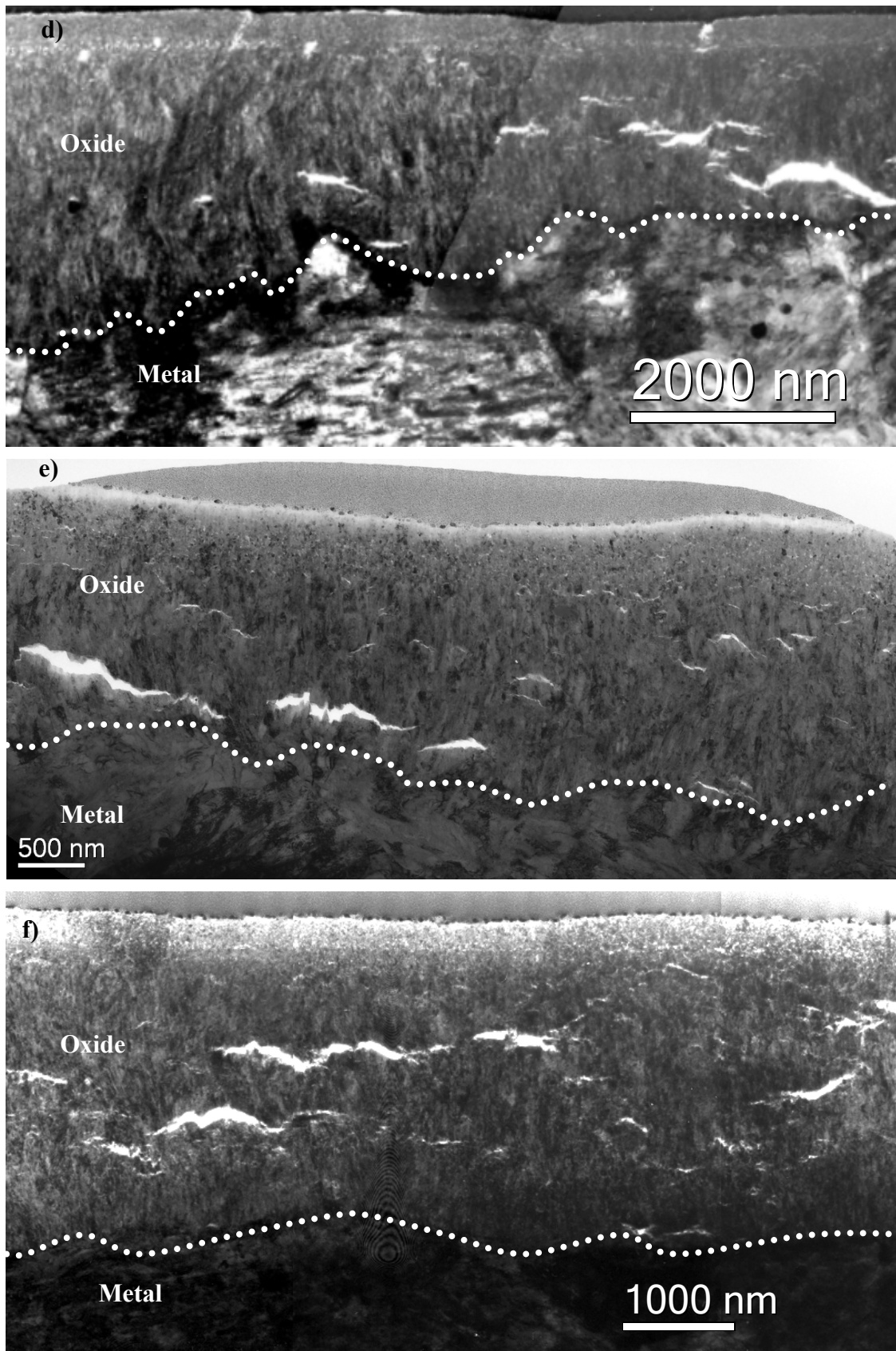


Figure 5.1 Continued: Oxide morphology of recrystallized ZIRLO oxides formed after different oxidation times: d) 120 days oxide (shown with 2 connected images) e) black oxide of 140 days sample; f) grey oxide of 140 days sample.

Table 5.1 Oxide thickness of ZIRLO RXA samples

ZIRLO RXA Oxide samples (oxidation time)	Average thickness calculated from weight gain (μm)	Thickness measured by TEM (μm)
34 days	1.2	1-1.4
60 days	1.5	1.3-1.8
100 days	1.9	1.6-2.1
120 days	2.1	2.0-3.3
140 days (black oxide)	3.1	1.4-2.3
140 days (grey oxide)		2.8-3.3

The oxide morphology is generally very similar for all the samples. It exhibits a columnar grain structure predominately at the innermost and middle part of the scale. The columnar grains always grow along a direction roughly perpendicular to the metal-oxide interface. The continuity of the columnar grains is interrupted by equiaxed grains, which are seen between columnar grain regions along the growth direction (**Figure 5.2**). Towards the outer oxide surface a region containing mainly quasi-equiaxed grains appears (**Figure 5.3**). The grains are similar in size in all samples, about 14-40 nm wide and 135-230 nm long for the columnar grains, and about 10-30 nm in diameter for the equiaxed grains.

Detailed investigation reveals subtle differences between samples with different oxidation times. The thickness of the outer equiaxed layer appears to increase with increasing oxidation time, from about 208 nm for the 34 days sample to about 410 nm for the 140 days grey oxide. In the middle of the grey oxide on the 140 days sample, starting 600-700 nm away from the metal-oxide interface, we can see a higher density of equiaxed grains than in the earlier oxide samples (**Figure 5.4**).

Cracks were seen in all the oxides studied, with an inhomogeneous distribution (**Figure 5.1**). They can be roughly grouped into two types in terms of size. The first are small cracks with lengths below ~ 150 nm, the shortest can look like pores. This type of crack is usually associated

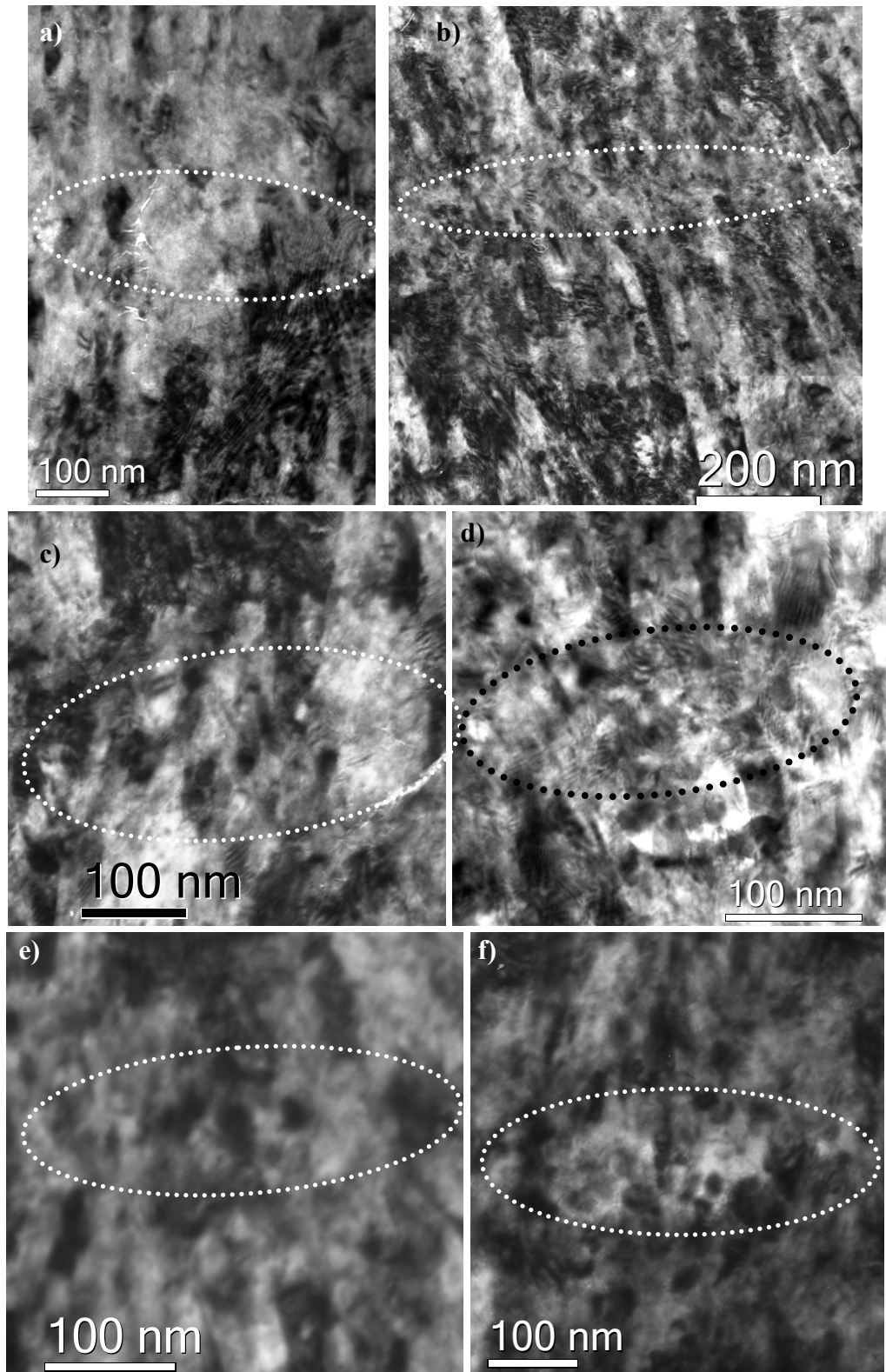


Figure 5.2 Examples of equiaxed grain structure (circled) in between columnar grain regions. a) ZIRLO RXA 100 days oxide, b) ZIRLO RXA 120 days sample c) higher magnification image in the ZIRLO RXA 120 days oxide; d) higher magnification images in the black oxide of ZIRLO SR 140 days sample; e) and f) higher magnification image in the grey oxide of ZIRLO SR 140 days sample.

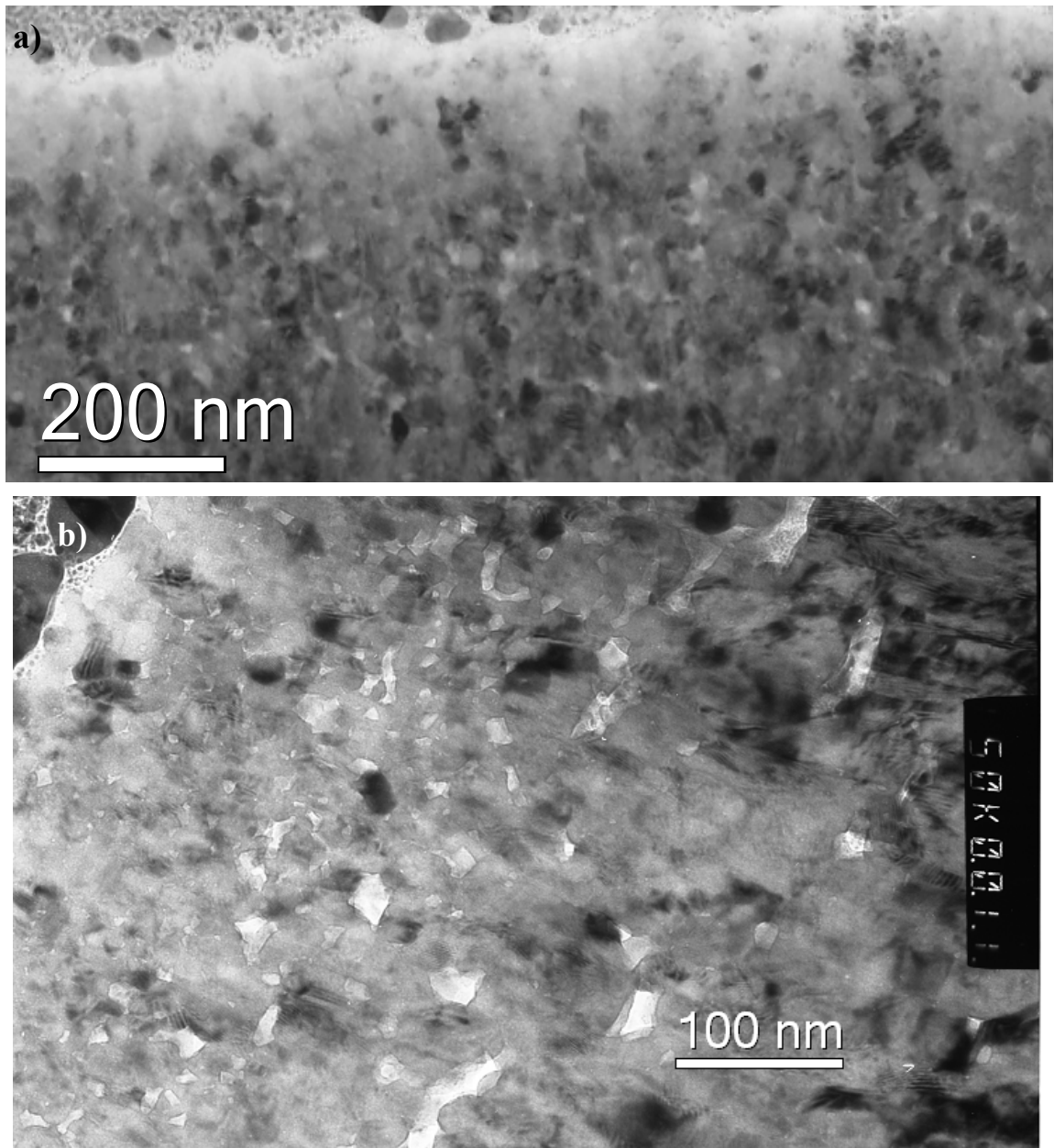


Figure 5.3 Equiaxed grain region in the outer part of the oxide in the a) ZIRLO RX 60 days sample and b) ZIRLO RX 100 days sample

with the equiaxed grains, therefore dominates in the outer part of the oxide, such as shown in both images in **Figures 5.3a** and **5.5a**, or in equiaxed region in the inner part of the oxide such as shown in **Figure 5.5b**. The second type of cracks are larger, normally exceeding ~300 nm in length and often as long as 500-1000 nm. They don't necessarily propagate through the equiaxed grain region and can cut cross well-developed columnar grains (**Figure 5.5c and d**).

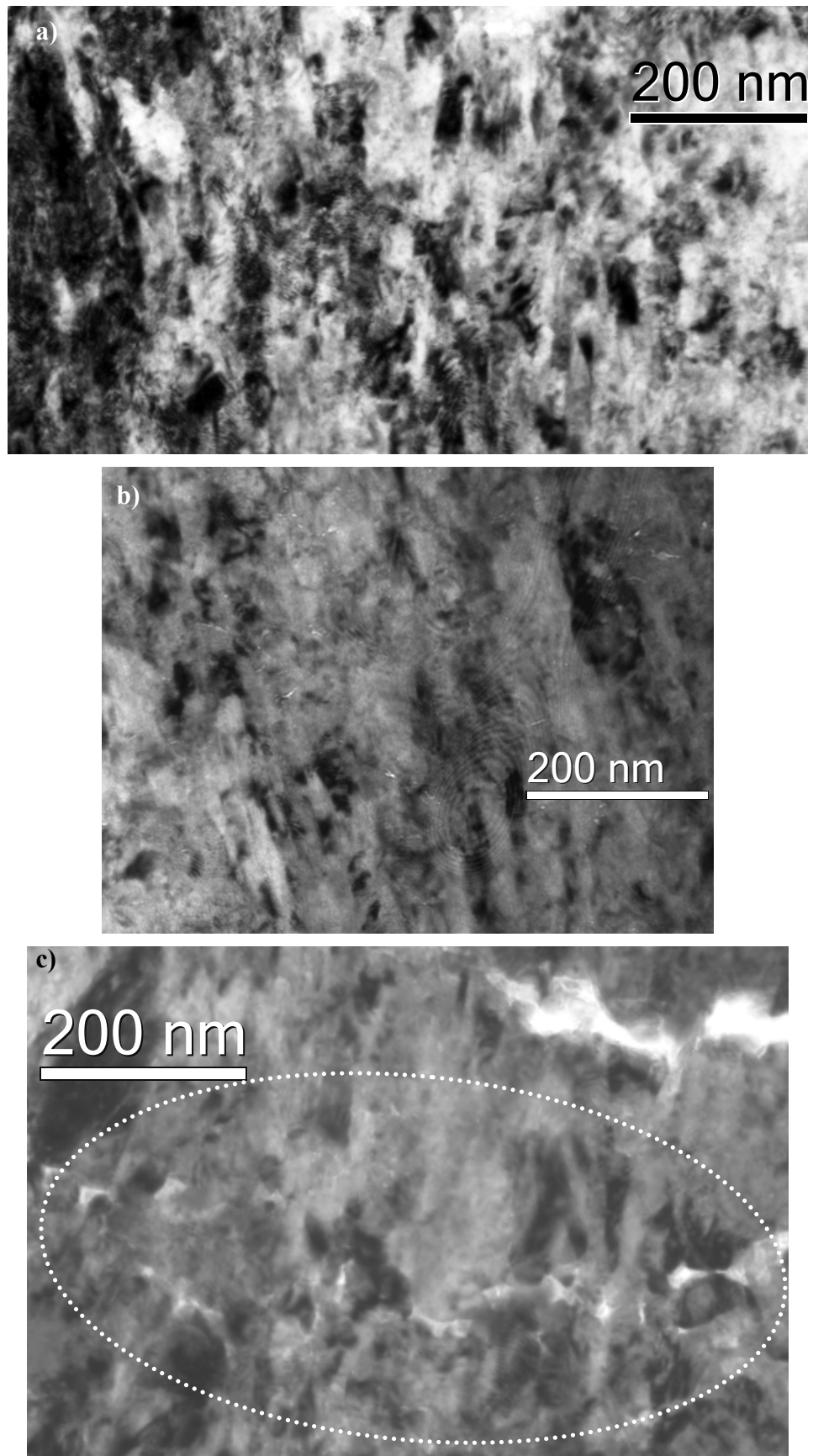


Figure 5.4 ZIRLO RXA oxides all at ~ 600 nm away from the metal-oxide interface, showing the oxide is denser with lower density of equiaxed grains in a) 34 days oxide and b) 100 days oxide but more porous with higher density of equiaxed grains (circled) in c) grey oxide of the 140 days sample.

It appears that this type of crack is concentrated either ~ 900 nm or ~ 1.7 μm away from the top surface, and the crack density increases with increasing oxide thickness. More detailed characterization of cracks in a bigger oxide volume by 3D reconstruction from FIB sequential sectioning and imaging will be reported in **Chapter 7**.

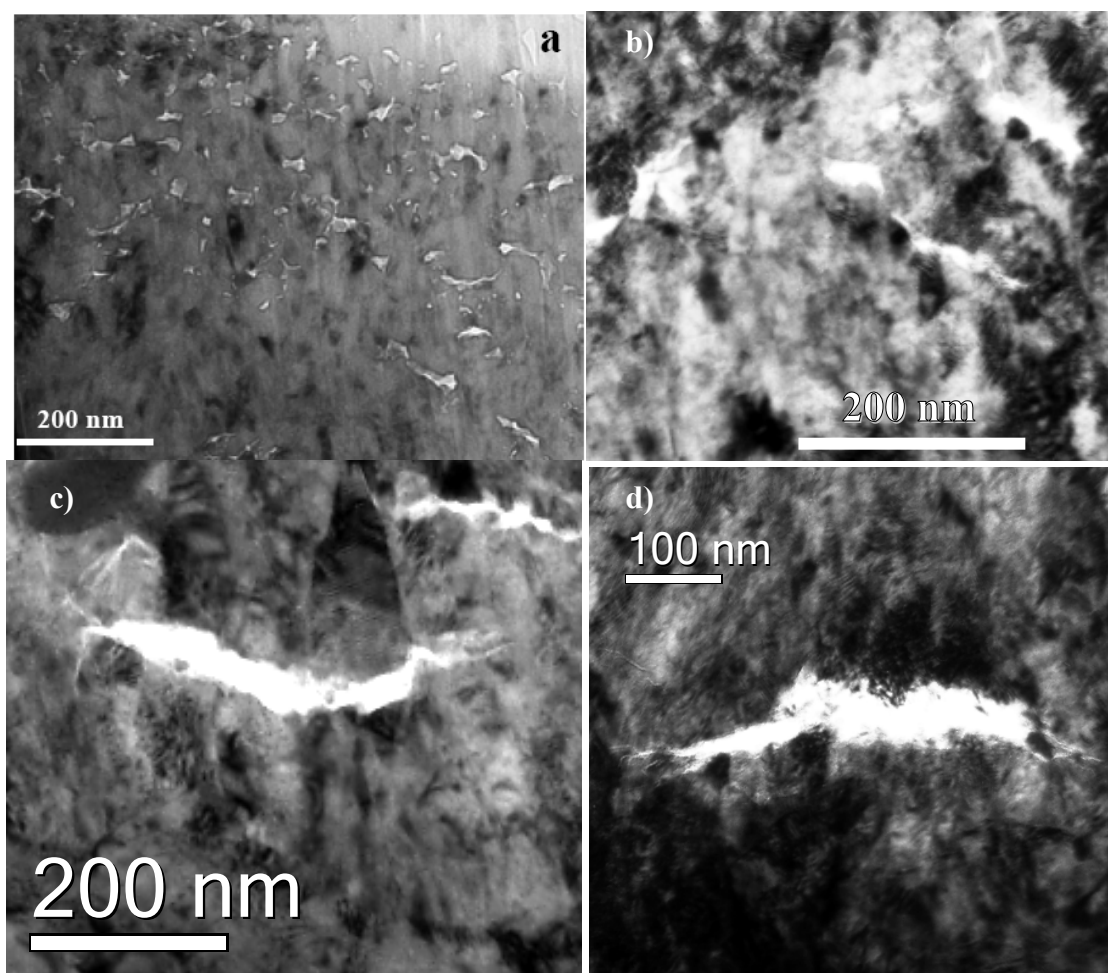


Figure 5.5 Small cracks associated with equiaxed grains in a) the outer part of the oxide grown on a Zircaloy-4 tube at 360 °C for 90 days and b) in the inner part of the 34 days ZIRLO RXA oxide. Bigger cracks are seen to propagate through the columnar grains in c) the black oxide of 34 days ZIRLO RXA sample and d) the 120 days ZIRLO RXA oxide. Oxide growth direction is from the top to the bottom.

5.1.1.2 Other oxide samples

Figure 5.6 shows BF images of oxides grown on Zircaloy-4 RXA after 7 days (pre-transition, ~ 700 nm oxide scale), 34 days (pre-transition, ~ 1 μm oxide scale) and 180 days (post transition, 2.7-3.5 μm oxide scale) under the same conditions as the ZIRLO RXA samples, compared with the grey oxide grown on ZIRLO SR after 140 days (post transition, $\sim$

3.2 μm oxide scale). Across these samples, differences in sample geometry, history of heat treatment or alloy composition don't result in significant differences in the oxide morphology. The middle of the post transition 180 days oxide on Zircaloy-4 has a better-developed columnar structure with fewer big cracks than the post-transition grey oxide of the ZIRLO RXA 140 days sample. Big cracks are mainly seen $\sim 2\ \mu\text{m}$ away from the top surface. The Zircaloy-4 RXA 7 days sample (the only ZIRLO or Zircaloy-4 sample available at such a short oxidation time) exhibits some features that were not observed in any later oxides. The outermost oxide contains a high density of columnar grains and some equiaxed grains at the very top, and has fewer cracks and pores compared to other samples (**Figure 5.7a**). In addition, no big cracks longer than $\sim 300\ \text{nm}$ (second type of cracks) such as those in **Figure 5.1** were found in this sample. This is also confirmed by SEM images of a FIB cross-sectioned sample, as shown in **Figure 5.7b**.

More obvious differences in oxide morphology can be found in much thicker oxides. **Figure 5.8** shows the oxide morphology near the metal-oxide interface for the $\sim 32\ \mu\text{m}$ later post-transition oxide grown on α -annealed Zircaloy-2, the $\sim 31\ \mu\text{m}$ oxide grown on β -quenched Zircaloy-2 and the $\sim 80\ \mu\text{m}$ oxide grown on Zr-Ti-Ni alloy that has very poor corrosion resistance. The first two samples show a higher fraction of equiaxed structure, and the Zr-Ti-Ni oxide contains very high density of cracks which interrupt severely the development of any columnar structures.

5.1.2 Discussion

FIB techniques have enabled the preparation of TEM specimens with a large homogeneous electron transparent area so that the whole oxide layer can be studied continuously in the same sample. This has enabled a much more detailed and reliable comparison of microstructures in

different oxides than normally reported in the literature. These FIB samples are also good enough for much more sophisticated chemical analysis as will be reported in Chapter 6.

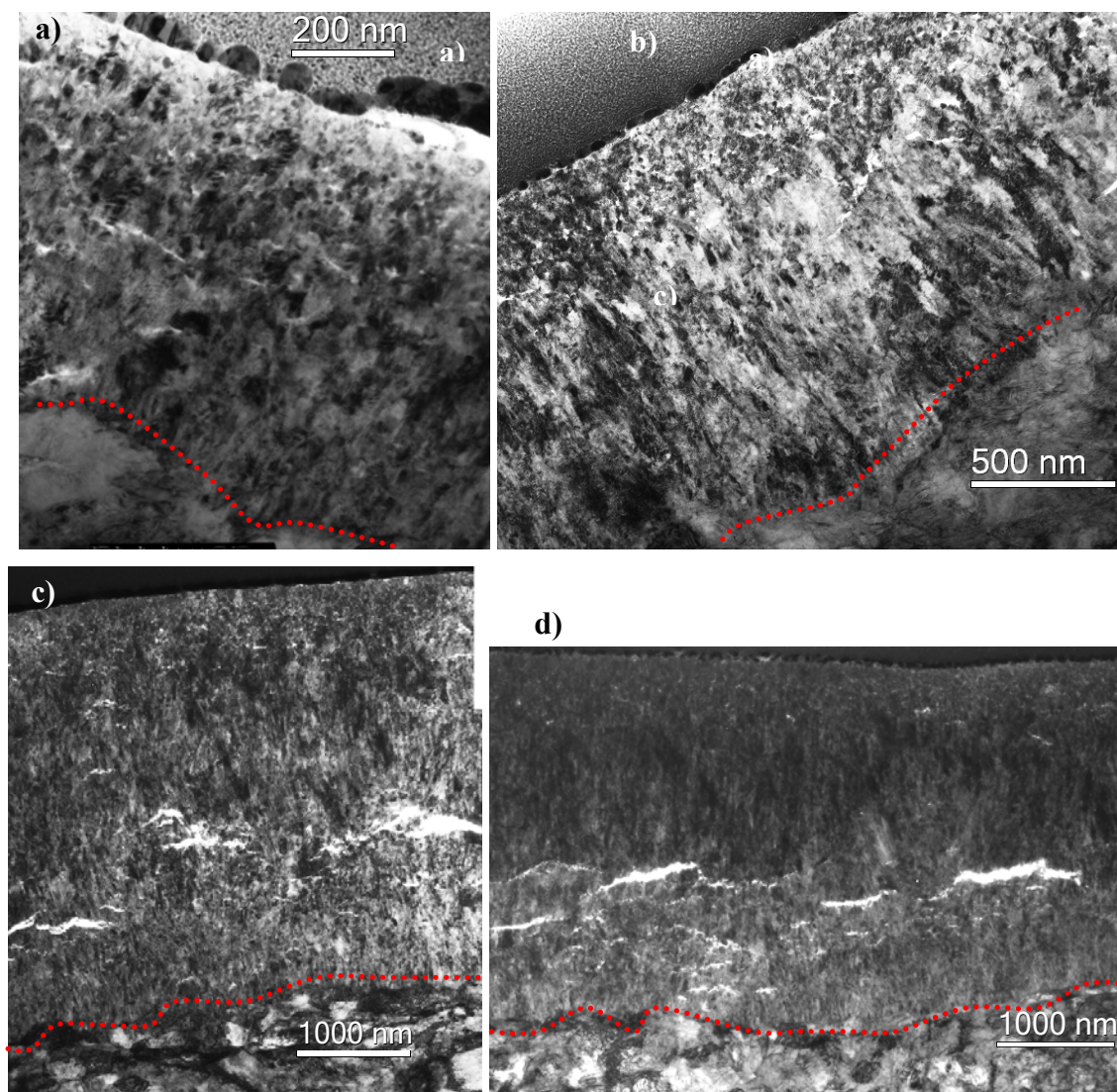


Figure 5.6 Oxide morphology of a) the 7 days Zircaloy-4 oxide, b) the 34 days Zircaloy-4 oxide, c) the grey oxide of 140 days ZIRLO SR sample, and d) the 180 days Zircaloy-4 oxide. The metal-oxide interfaces are indicated and the oxides are on the top.

The oxidation of zirconium is known to occur by inward diffusion of oxygen ions through the oxide layer and the new oxide forms at the metal-oxide interface, therefore the oxide morphology observed in **Figures 5.1** and **5.6** suggests the formation of an equiaxed grain structure first, followed by columnar grains which grows 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, e.g. [80, 124, 125, 138]. However, this equiaxed layer seems to be very thin initially, as seen in the Zircaloy-4 RXA oxide formed after a short period of 7 days (**Figure 5.7**). The increase in the thickness of the equiaxed structure dominated region at the outer oxide in longer oxidized samples indicates that a columnar to equiaxed transformation might have happened.

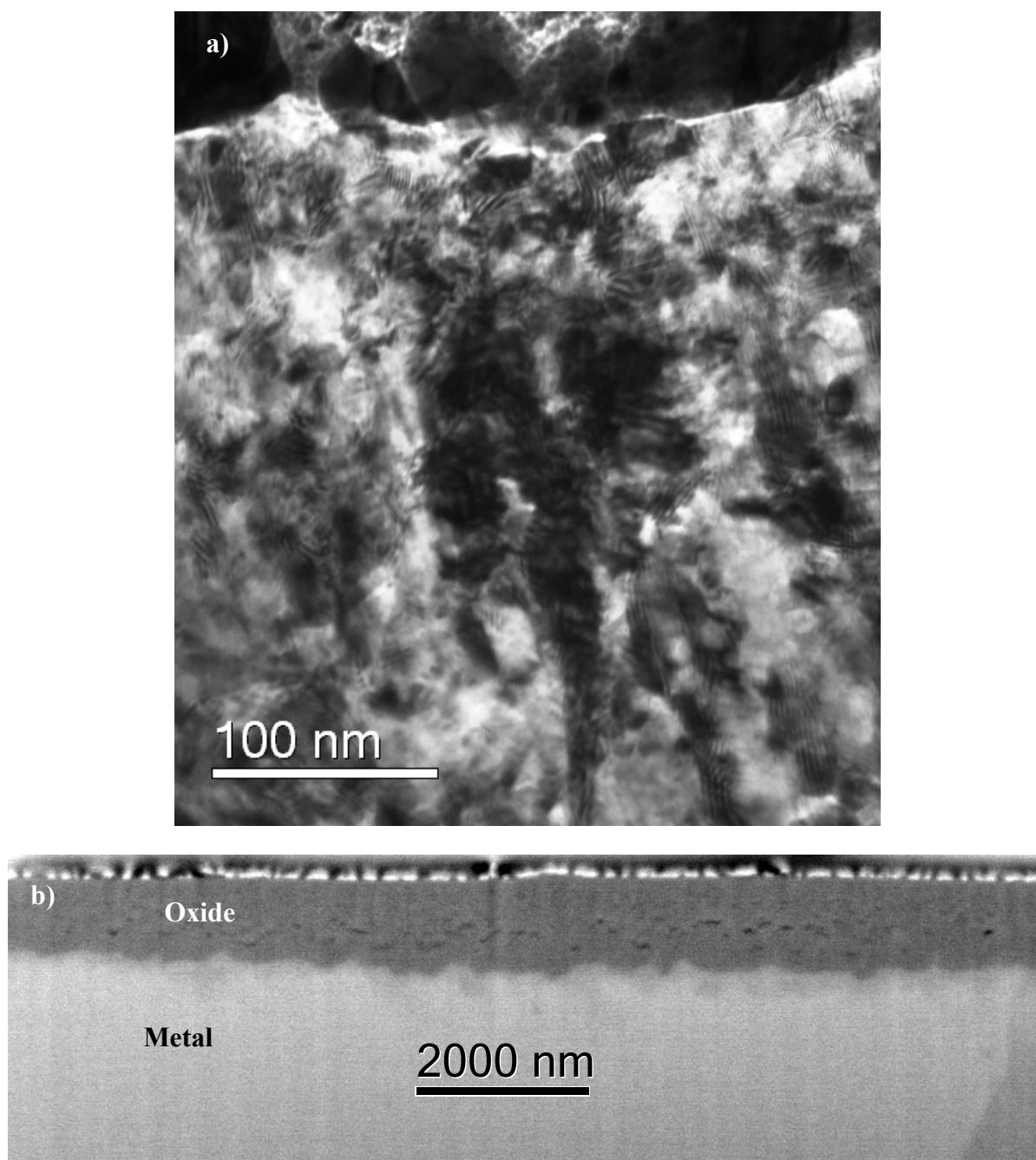


Figure 5.7 a) Details of the top oxide in the Zircaloy-4 RXA 7days sample. b) SEM image of the FIB cross-sectioned oxide showing no cracks longer than ~300nm.

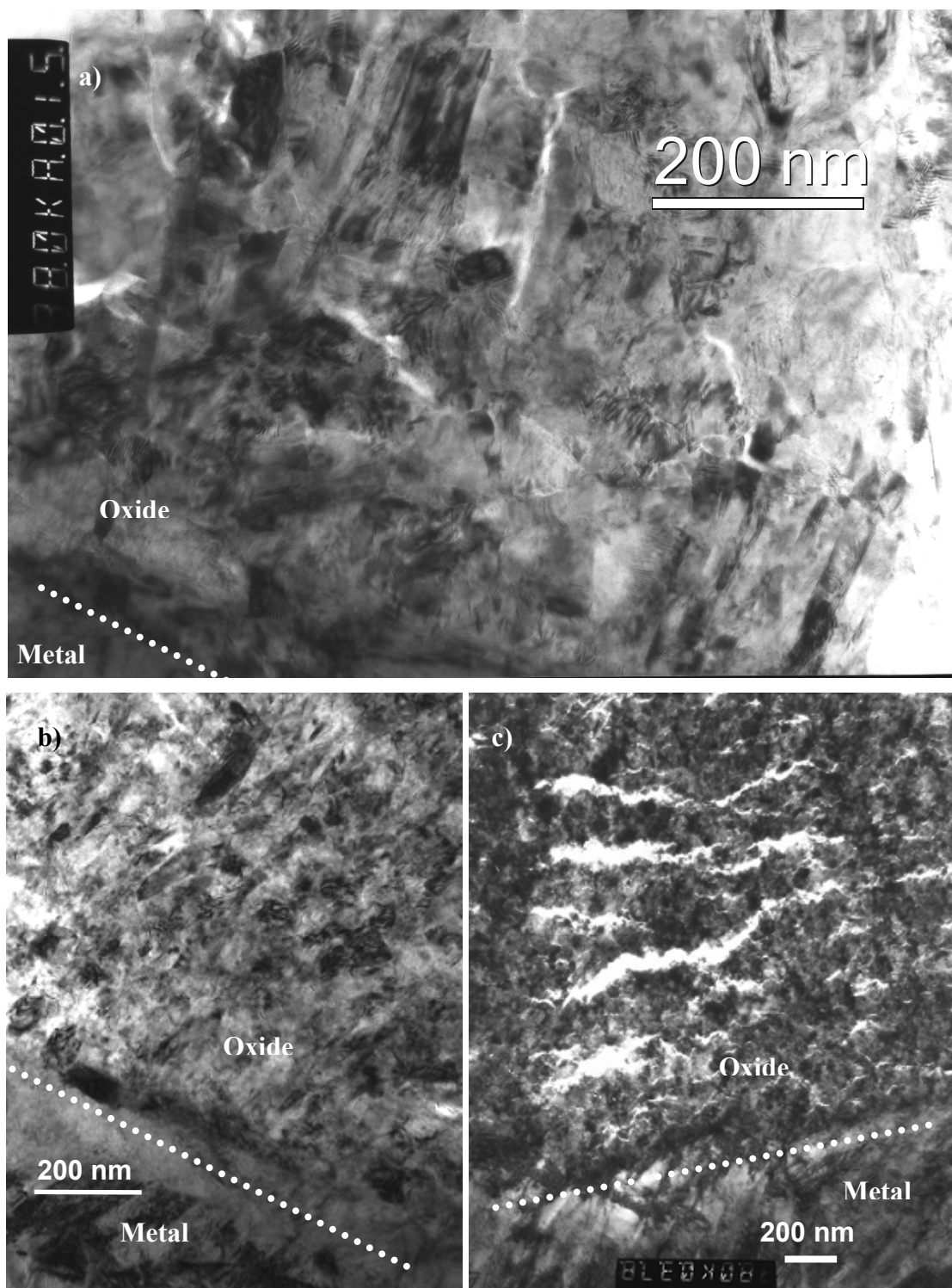


Figure 5.8 Oxide morphology near the metal-oxide interface of a) the ~32 μm oxide grown on α -annealed Zircaloy-2, b) the ~31 μm oxide grown on β quenched Zircaloy-2, both showing a mixture of columnar grains and equiaxed grains, and c) the ~80 μm oxide grown on Zr-Ti-Ni alloy showing predominantly equiaxed grains with a very high crack density.

Similar observation of the transformation from columnar to equiaxed grains has also been reported by Anada et al. [93] for a Zircaloy-4 oxide corroded in a 633K water autoclave. The transformation is probably due to a gradual tetragonal to monoclinic phase transformation

within the outer part of the oxide, which can be supported by previous studies where a decrease in tetragonal oxide content and an increase in the monoclinic oxide content at the oxide surface was found by grazing XRD measurements [156], and a lower tetragonal fraction has been indicated by TEM at the oxide surface for thicker oxides [122]. The compressive stress in the oxide has been shown to decrease towards the outer surface [260]. When the oxide thickens, the stress at a particular depth in the oxide would be expected to decrease accordingly, and as a result the tetragonal oxide initially stabilized by the stress at that position may transform to monoclinic oxide.

The Zircaloy-4, which shows a lower oxidation rate, has a better developed columnar structure and fewer cracks in the oxide compared to ZIRLO. Similarly, the thick oxides grown on α -annealed or β -quenched Zircaloy-2, which are in the later post-transition stage and have higher oxidation rates, show a higher density of equiaxed grains. The $\sim 80\text{ }\mu\text{m}$ oxide grown on Zr-Ti-Ni alloy, which is expected to be in the post-second transition stage, shows even poorer columnar structure. These observations suggest that a columnar grain structure is beneficial for reducing the oxidation rate, in agreement with previous studies [123].

This advantage of the columnar structure might be related to its stronger intergranular cohesion, which could have the effect of reducing crack propagation. Cracks are usually seen to be associated with equiaxed grains rather than columnar grains, in good agreement with previous studies [25, 69, 125]. This correlation, however, seems to be more obvious for smaller defects that fall into our first type of cracks (**Figure 5.5a and b**), and is not always true for the second group of bigger cracks (**Figure 5.5c and d**), implying they might form by different mechanisms. The observation that the bigger cracks are mainly located at particular distances of $\sim 900\text{ nm}$ and $\sim 1.7\text{ }\mu\text{m}$ away from the oxide surface suggests that they are not formed until the oxide thickens to $\sim 1\text{ }\mu\text{m}$, which might be a thickness at which a critical stress is built up to initiate the cracks.

It has been proposed that the big cracks, especially in the pre-transition oxide, are artifacts produced by the TEM specimen preparation process [19, 25]. However, for the same sample we have observed cracks similar in location and size in the SEM images while FIB cross-sectioning the bulk material, which indicates that they are more likely to be real features in the oxide. An example of the SEM image of the ZIRLO RXA 34 days sample in **Figure 5.9** shows very similar crack features to those that shown in the TEM image in **Figure 5.1a** (reproduced in **Figure 5.9** for ease of comparison).

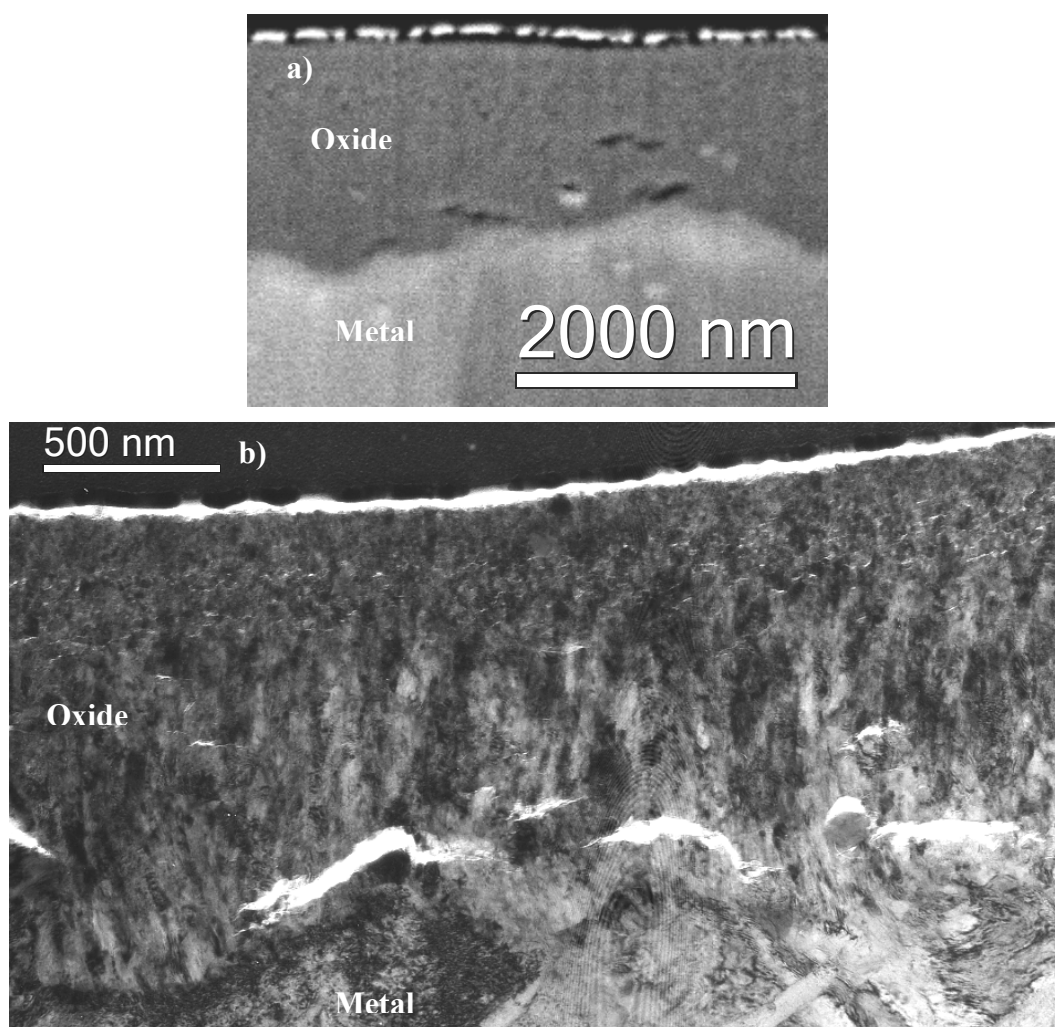


Figure 5.9 a) A SEM image of the ZIRLO RXA 34 days oxide. b) Reproduced from Figure 5.1 a

The big cracks in Zircaloy-4 oxide appeared to be developed later than those in ZIRLO oxide, as they were found to be at a greater distance of $\sim 2 \mu\text{m}$ from the oxide surface. This is correlated with a lower oxidation rate for Zircaloy-4 than ZIRLO. It is noticeable that the

extremely fast oxidizing Zr-Nb-Ti has a high density of cracks with a very short periodicity of ~220 nm. All these observations agree with previous studies that higher corrosion rates are associated with more frequent cracking [137, 138]. However, as will be discussed in Chapter 7, we cannot necessarily conclude that the enhanced oxidation rate is a direct result of more severe cracking. For instance, it is also noticed that a higher density of bigger cracks is associated with regions of thinner oxide scale, as obviously seen on the right hand side of the 120 day ZIRLO RXA oxide in **Figure 5.1d**, implying these big cracks serve as obstacles for the migration of corroding species (or current flow) during oxidation.

5.2 Oxide phases and texture

5.2.1 Observations

Selected area diffraction (SAD) was carried out in the oxide scale to analyze the characteristic phases and texture, and a selection of the diffraction patterns are given here. The diameter of the selected area aperture is about 830 nm. **Figure 5.10** shows indexed SAD patterns from the middle part of two pre-transition oxides on the Zircaloy-4 RXA tube 90 days sample and the ZIRLO RXA 100 days sample. **Figure 5.11** shows typical SAD patterns taken from different locations in two post-transition oxides; the grey oxide of the ZIRLO SR 140 days sample and the Zircaloy-4 RXA sheet 180 days oxide. In addition, intensity profiles across selected locations in some diffraction pattern where monoclinic (-111), (111) and tetragonal (101) reflections can be identified are shown. The intensities of the reflection spots across different diffraction patterns are not calibrated, and therefore are only comparable within each profile. **Figure 5.12** shows a typical SAD pattern from the oxide near the metal-oxide interface in the Zr-Nb-Ti oxide.

BF images of particular tetragonal grains near the metal-oxide interface of the oxide grown on the Zircaloy-4 RXA tube and on the Zr-Ti-Ni test alloy are shown in **Figure 5.13**. The

micro-diffraction patterns taken from these two grains confirm that they have a tetragonal structure. **Figure 5.14** shows HRTEM images from the Zircaloy-4 RXA tube oxide and the black oxide of the 140 days ZIRLO RXA sample, showing ~10 nm tetragonal grains present in the middle of the oxide layer. Tetragonal grains with a columnar morphology, but with a small aspect ratio, were occasionally found. An example is shown in **Figure 5.15**.

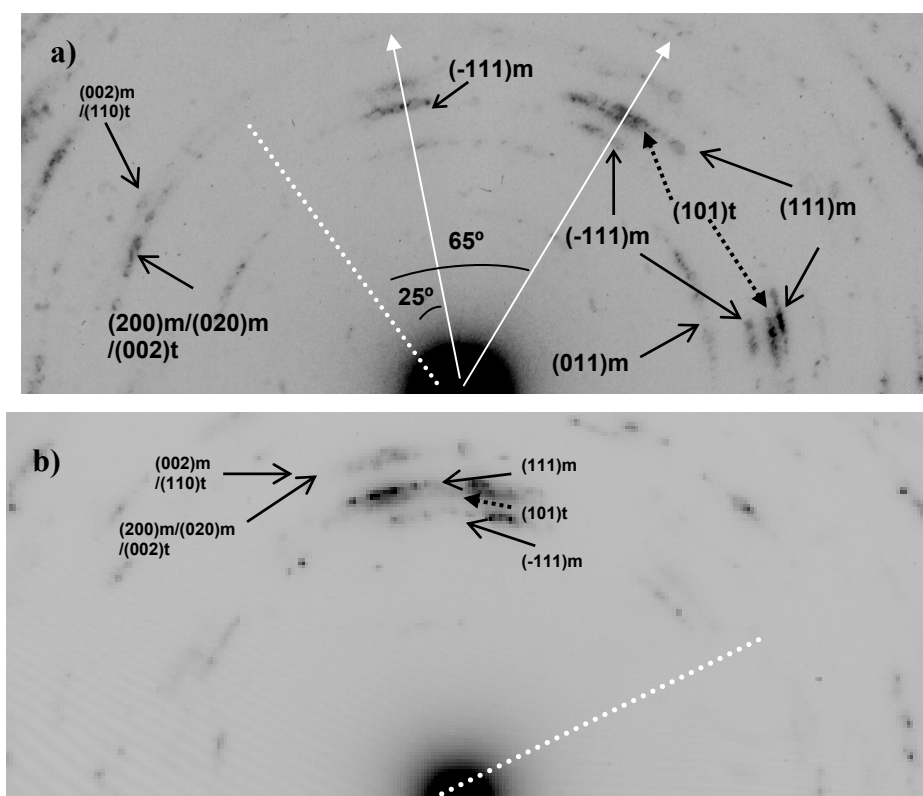


Figure 5.10 Selected area electron diffraction patterns of the middle part of two pre-transition oxides. a) Zircaloy-4 tube 90 days oxide; b) ZIRLO RXA 100 days oxide. Dotted lines show the direction of the normal to the metal-oxide interface.

Information about oxide texture was also gained from HRTEM. **Figure 5.16a-b** shows the HRTEM image and corresponding FFT diffraction patterns taken from columnar grains in the grey oxide of the 140 days ZIRLO RXA sample. In a) the (020) and (-111) planes of monoclinic oxides were indexed with the measured spacing to be 0.526 ± 0.007 nm and 0.316 ± 0.007 nm respectively. It was found that the $(020)_m$ planes are orientated almost parallel to the oxide growth direction (i.e. the $(020)_m$ pole perpendicular to the growth direction). In b) the (020) and (002) planes were indexed with the measured spacing to be

0.527±0.012 nm and 0.532±0.012 nm. It shows in addition to the orientation found in a) that the (002)_m planes are orientated almost perpendicular to the oxide growth direction (i.e. the (002)_m

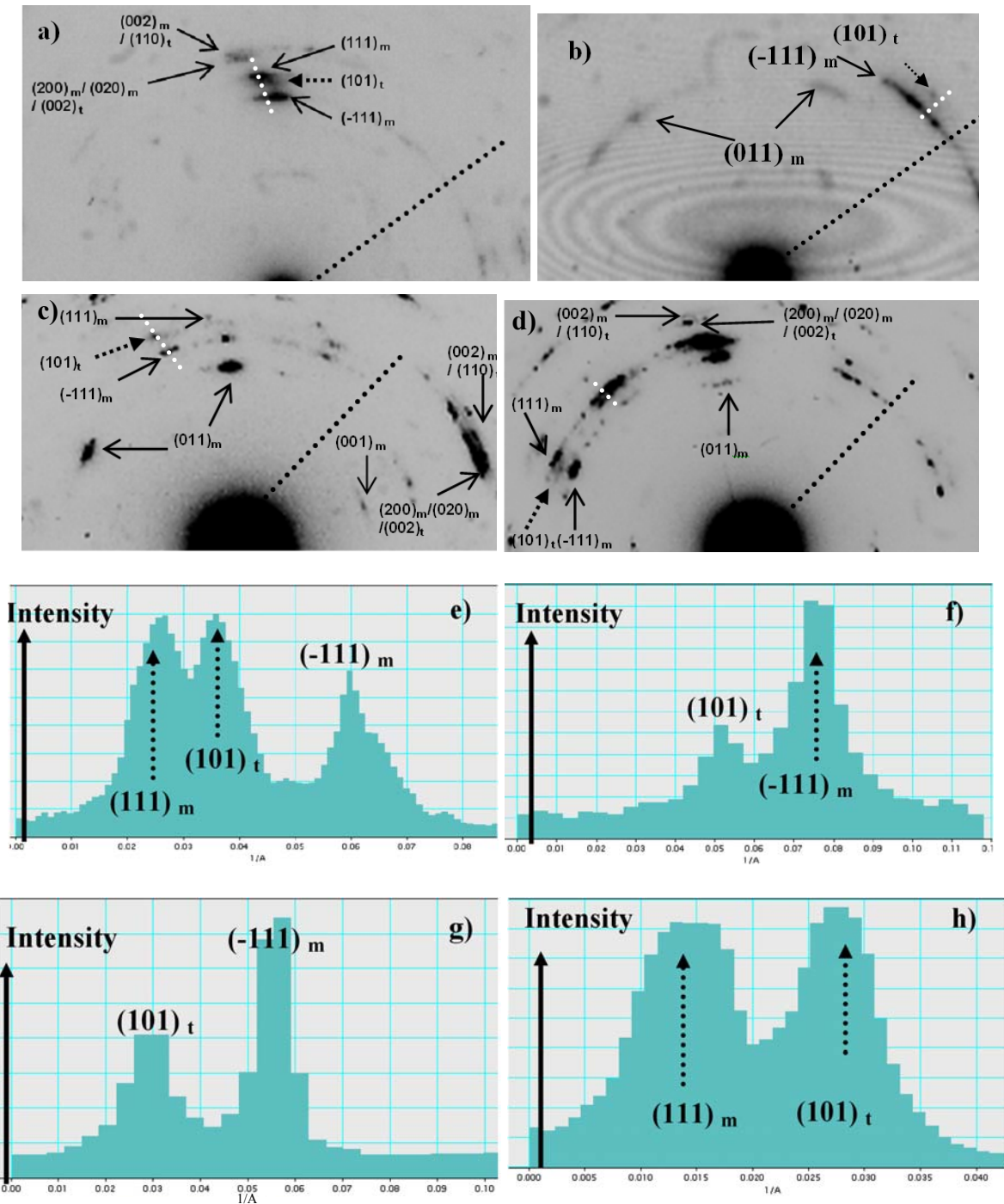


Figure 5.11 Selected area electron diffraction patterns at different locations of two post-transition oxides. a) and b) are patterns taken from the inner and the outer part of the black oxide of the ZIRLO SR 140 days sample respectively; c) and d) are patterns taken from the inner and the outer part of the Zircaloy-4 RXA sheet 180 days oxide respectively. Black dotted lines show the direction of the normal to the metal-oxide interface. e)-h) show the intensity profiles across the white dotted lines indicated in the diffraction patterns a)-d), demonstrating the identification of (101)_t reflections.

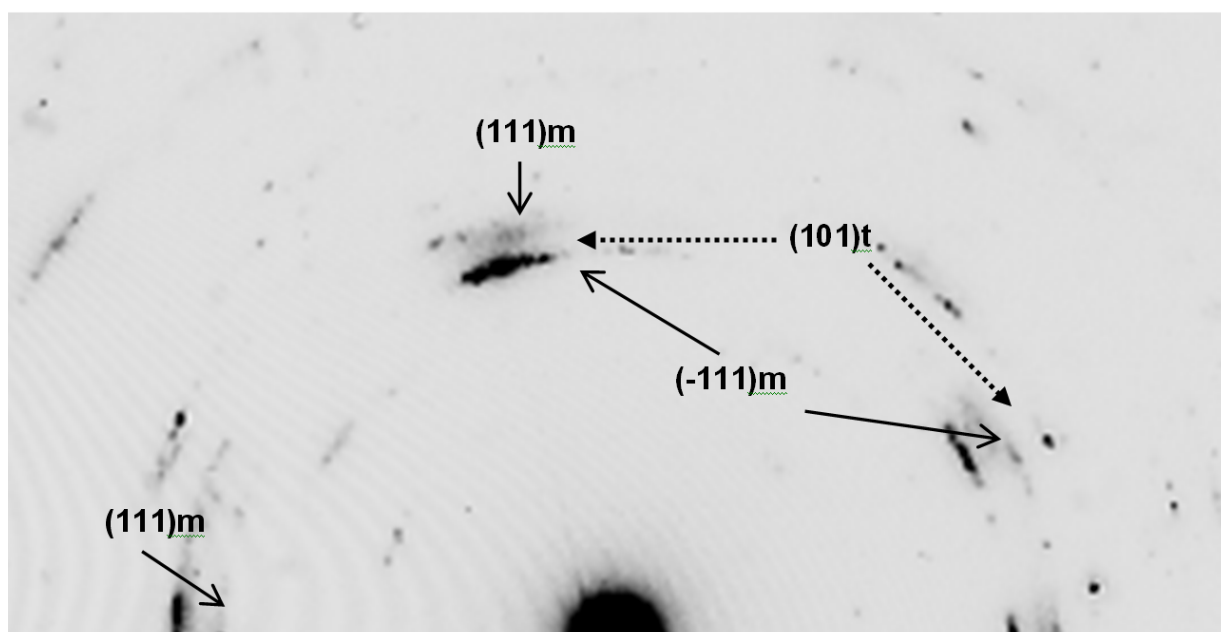


Figure 5.12 Selected area electron diffraction patterns of the oxide near the metal-oxide interface in the Zr-Nb-Ti oxide.

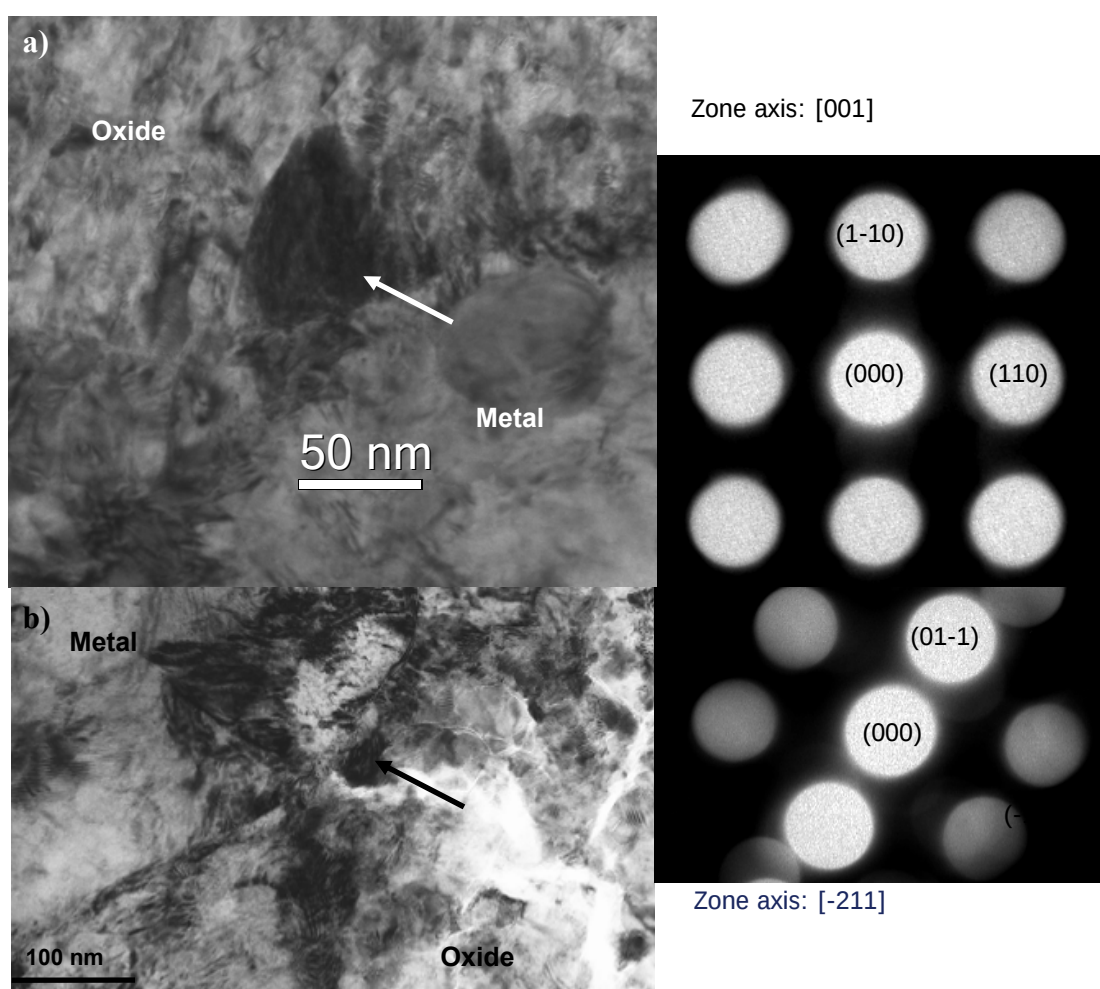


Figure 5.13 a) BF image of a ~50 nm tetragonal grain near the metal-oxide interface of the oxide grown on the ZIRLO SR 60 days sample. b) BF image of a ~30 nm tetragonal grain near the metal-oxide interface of the oxide grown on the Zr-Ti-Ni test alloy. The micro-diffraction patterns taken from these grains confirm that they have the tetragonal oxide structure.

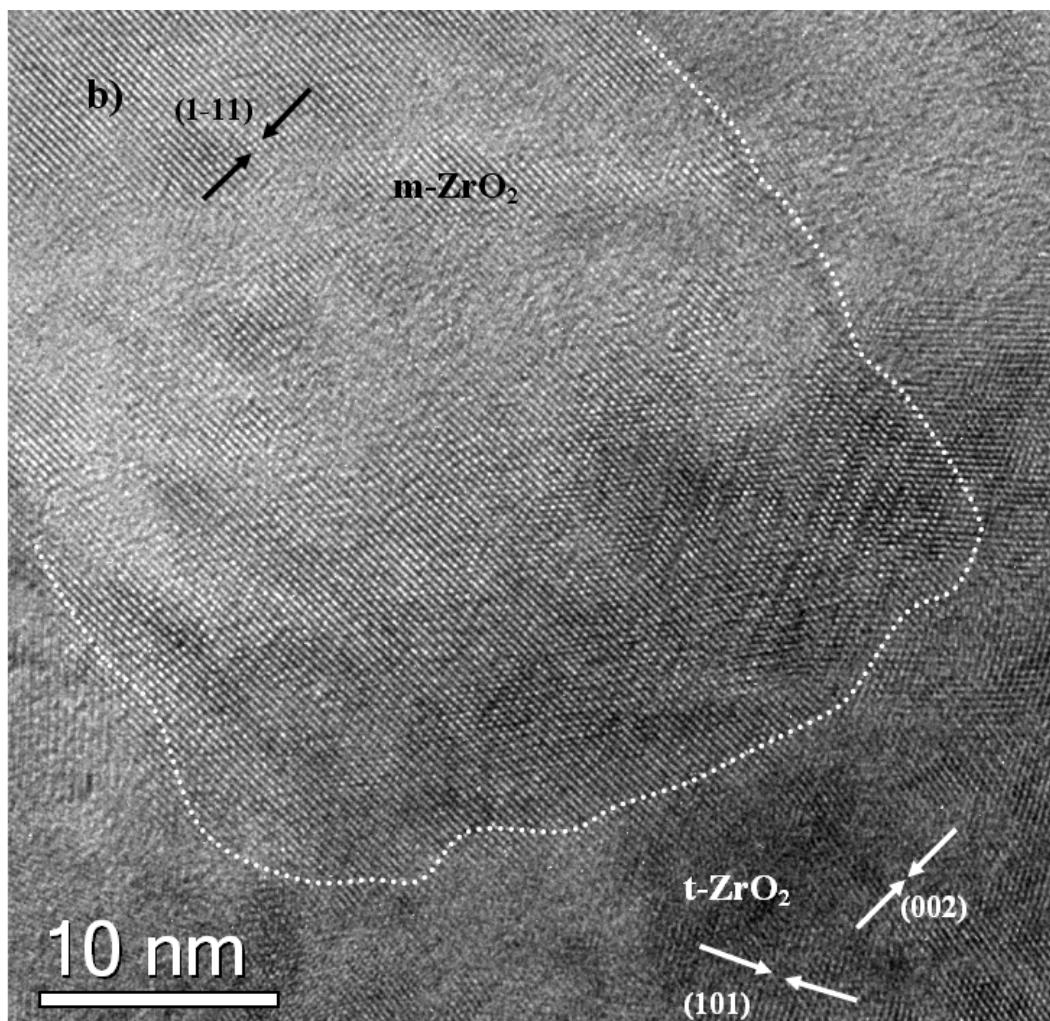
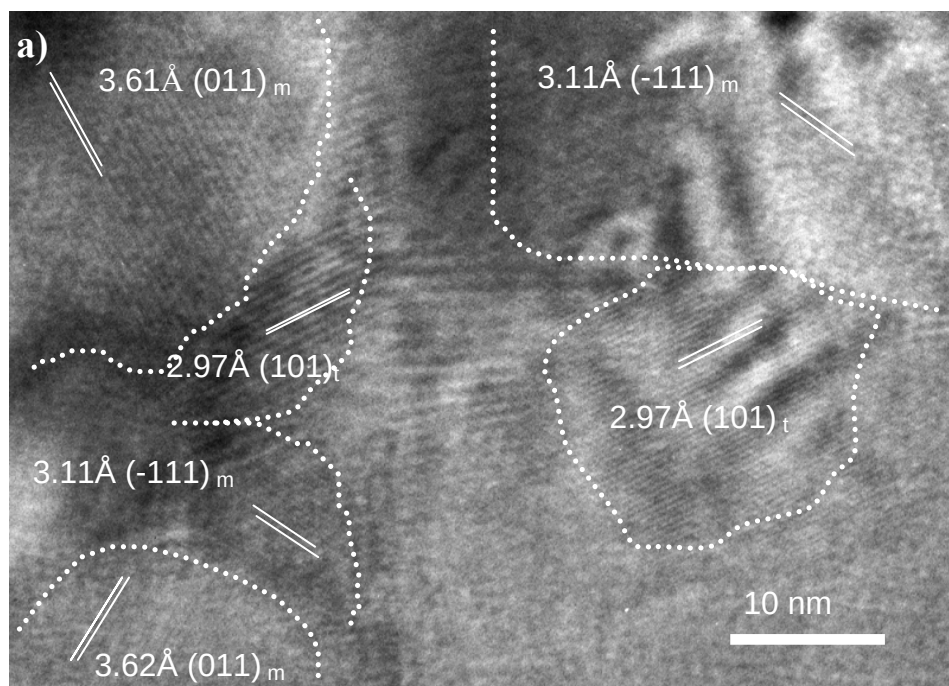


Figure 5.14 a) HRTEM image of Zircaloy-4 RXA tube oxide showing ~10-20 nm tetragonal particles in between the monoclinic oxide grains. b) HRTEM image of the black oxide of 140 days ZIRLO RXA sample showing tetragonal grains at the end of the columnar grains.

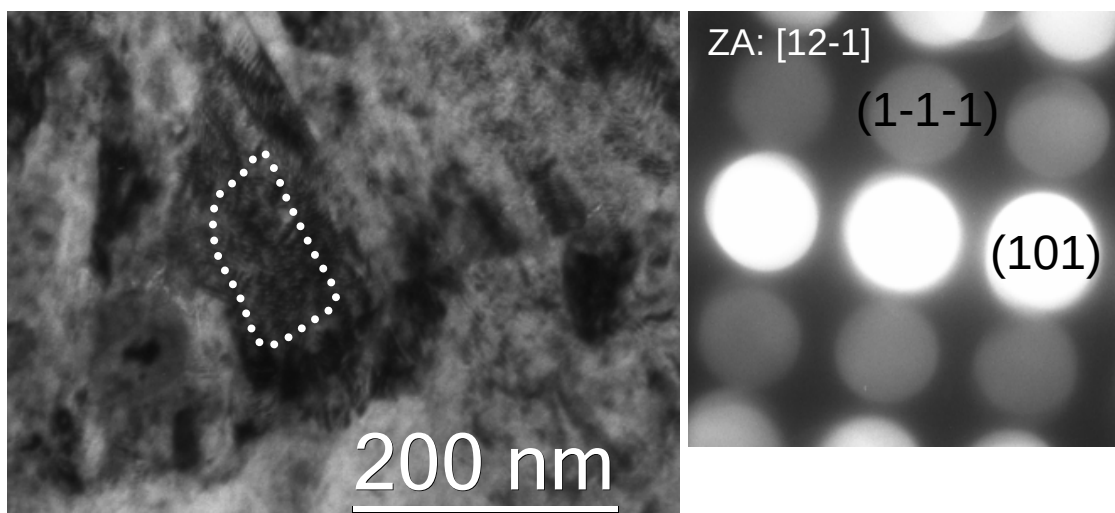


Figure 5.15 BF image of a columnar tetragonal grain (marked) near the metal-oxide interface of the oxide grown on the ZIRLO RXA for 34 days. The micro-diffraction pattern is also shown.

pole parallel to the growth direction), which is also indicated in the μ -diffraction of a monoclinic grain (**Figure 5.16c**).

5.2.2 Discussion

All diffraction patterns from the oxide scale mainly contain reflections from monoclinic zirconium oxide. **Table 5.2** lists the largest d spacings of the monoclinic oxide and tetragonal oxide which were used to analyze the diffraction pattern. It can be seen that almost all tetragonal oxide reflections except the $(101)_t$ reflection overlap with monoclinic oxide ones considering the associated error in this kind of analysis (**c.f Table 1 in Appendix A**). Weak $(101)_t$ reflection were seen in both pre- and post-transition oxides, indicating the presence of a small amount of tetragonal oxide. The same reflection was also observed in the oxide close to the metal-oxide interface in the post-second transition Zr-Nb-Ti oxide. Two examples of the BF images of tetragonal grains have been given in **Figures 5.13** and **5.14**.

A strong variation of intensity along the diffraction arcs was observed in all patterns, which indicates that the oxide is strongly textured. The strongest intensity of the $(-111)_m$ poles was found within the range of orientations 25° - 60° away from the oxide surface normal, and the strongest intensity of $(111)_m$ is within 45° - 65° . Most of the reflections from the tetragonal oxide

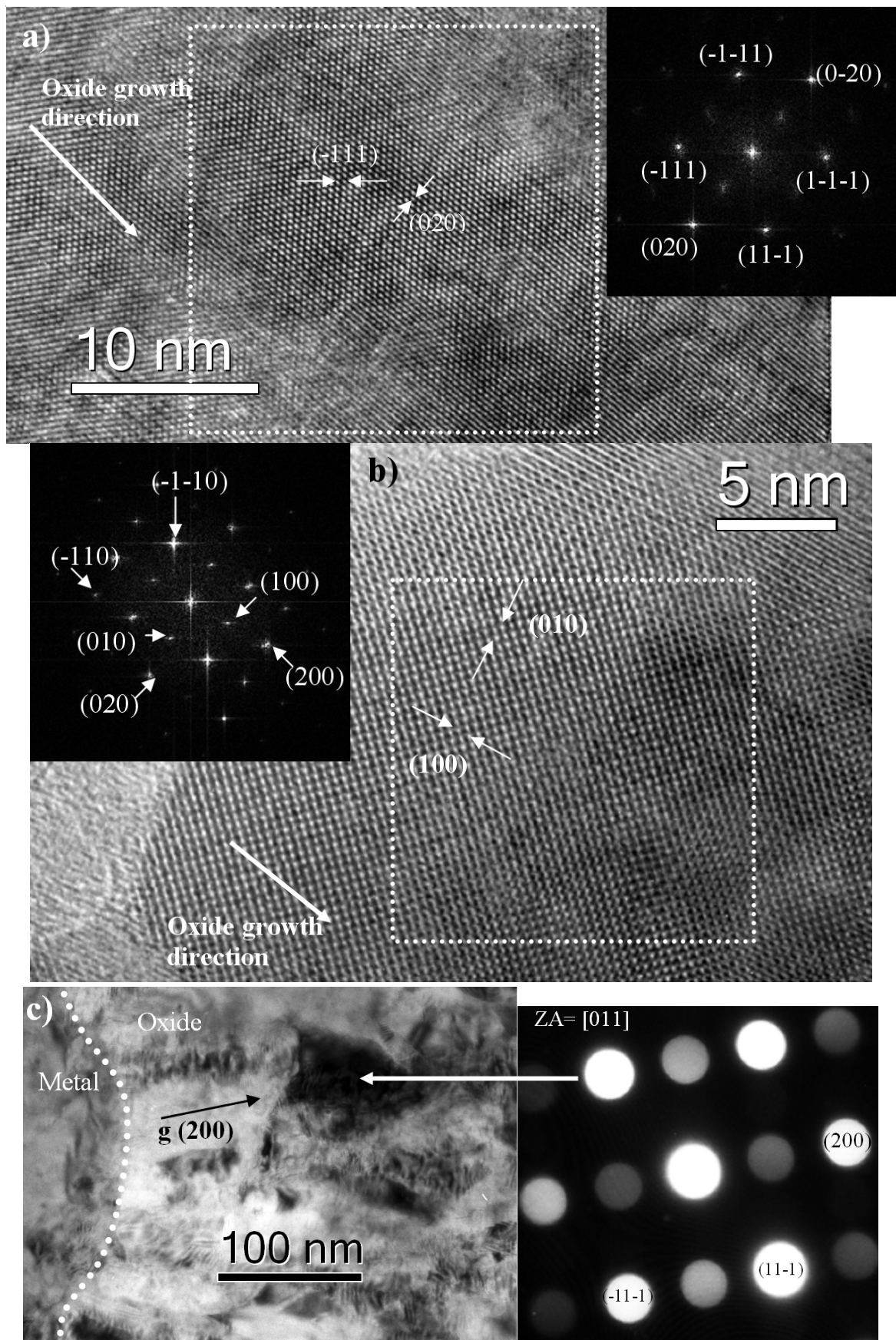


Figure 5.16 a) and b) HRTEM images of columnar grains in the grey oxide of 140 days ZIRLO RXA sample. The insets are FFT diffractograms from the regions indicated with the white boxes. c) A BF image of a monoclinic grain together with the indexed μ -diffraction pattern of this grain.

Table 5.2 List of reflections of monoclinic and tetragonal oxide and their relative intensities in X-ray diffraction. The data is from established powder diffraction files for monoclinic (37-1484) and tetragonal ZrO₂ (42-1164). Lattice parameter for monoclinic are $a = 5.31 \text{ \AA}$; $b = 5.21 \text{ \AA}$; $c = 5.14 \text{ \AA}$; $\alpha = \gamma = 90.00^\circ$; $\beta = 99.22^\circ$, and for tetragonal structure are $a = 3.649 \text{ \AA}$; $b = 3.64 \text{ \AA}$; $c = 5.27 \text{ \AA}$; $\alpha = \beta = \gamma = 90.00^\circ$

Monoclinic			Tetragonal		
hkl	d (Å)	I (%)	hkl	d (Å)	I (%)
110	3.69765	14.0			
011	3.63907	10.0			
-111	3.16470	100.0	101	2.99500	100.0
111	2.84063	68.0			
200	2.62268	21.0	002	2.63500	39.0
020	2.60618	11.0	110	2.57400	34.0
002	2.53992	13.0			
220	1.84810	18.0	112	1.84100	34.0

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 the metastable tetragonal oxide was confirmed by the clear identification of (101)_t reflections between (-111)_m and (111)_m reflections, such as seen in **Figure 5.10**. 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, suggesting the textures are related. This kind of texture is qualitatively in agreement with previous TEM observations [137] and synchrotron XRD results [261].

The (002)_m reflection overlaps with possible (110)_t reflections, but (001)_m is more separated from other possible reflections (c.f. **Table 5.2**, **Figure 5.11**). As a result, it was possible to be confident that the monoclinic (002) poles are orientated nearly parallel ($\pm \sim 20^\circ$) to the oxide growth direction, which is in agreement with [260] and indicates that the main texture of the oxide is most likely to be (10-4) or (10-6) as reported and predicted in [197] for minimizing

stresses from oxide growth. The $(200)_m$ and $(020)_m$ monoclinic reflections overlap with $(020)_t$, and are too close to be resolved reliably in electron diffraction, but can be distinguished in favourable cases by HRTEM and micro-diffraction, where the grain is orientated in zone axis and other crystal planes from the same grain in addition to $\{200\}_m$ are in the Bragg-diffraction orientation. When these conditions were achieved, it was found that the $(020)_m$ pole is orientated almost perpendicular to the oxide growth direction, i.e. these planes are orientated almost parallel to the growth direction (**Figure 5.16a**). Based on the above information and the monoclinic crystal structure, the monoclinic (200) poles should be orientated roughly perpendicular to the growth direction, as indicated in **Figure 5.16b** and confirmed by micro-diffraction of a monoclinic grain (**Figure 5.16c**). This is in agreement with reported synchrotron XRD observations [135].

The monoclinic reflections appear to be more diffuse in the outer oxide than in the inner oxide (**Figure 5.11**), indicating the oxide texture is less well-defined towards the oxide surface. This is similar to the observation reported by Foord and Newcomb [122]. The less textured part is also coincident with the transformation to a more equiaxed structure in the outer part. This suggests a greater misalignment between the equiaxed grains than the columnar grains, which may contribute to the higher density of cracks in the equiaxed region.

The tetragonal phase fraction in the oxide has been reported by several groups to be highest near the metal-oxide interface decreasing towards the outer oxide surface [153, 154, 158]. This is expected if the tetragonal oxide is stabilized by stresses. Motta et al. [135] have reported from synchrotron XRD study that the tetragonal and monoclinic oxide peak intensity showed periodic variations in the oxide layer along the growth direction, and suggested that the tetragonal layer consists of equiaxed grains and the monoclinic layer had a columnar grain structure. But in this work the intensity of the $(101)_t$ reflections does not appear to depend on the position in the oxide when SAD patterns from different locations in the oxide are

compared (**Figure 5.11**). Also, although tetragonal oxide was generally in the form of small equiaxed grains (**Figures 5.13 and 5.14**) and columnar grains were predominantly monoclinic, it was also very common to find equiaxed grains with a monoclinic structure, and occasionally tetragonal columnar grains have been detected. A possible explanation for the disparity between the current observation and other studies might be a tetragonal to monoclinic phase transformation that could happen when the stresses in the oxide are released during TEM specimen preparation. A fairly high density of twin grain boundaries have been found in the monoclinic oxide grains, which could be associated with transformation from the tetragonal phase [262]. Two examples are given in **Figure 5.17**. Therefore the trace of tetragonal phase remaining all through the oxides is probably stabilized by other mechanisms such as small grain size [215] or defects induced by the dopant alloying elements [222]. The size of tetragonal oxide grains has been found to be indeed as small as ~5-30 nm in most of this work (**Figures 5.13 and 5.14**) and other studies [125, 138].

5.3 Oxide nano-porosity

Small cracks with length below ~150 nm (the first type of cracks mentioned in **section 5.1**) and nanometer size pores have been investigated in more detail at different locations in the oxide. Defocused Fresnel imaging was used particularly to study the latter kind of porosity.

5.3.1 Pre-transition oxides

When Fresnel contrast was employed, very small pores 1-3 nm in size were detected in the metal-oxide interface region in the pre-transition oxide samples investigated, including the 60, 100 days ZIRLO RXA oxides and 34 days Zircaloy-4 RXA sheet oxide. A series of through-focal images in **Figure 5.18** shows the effectiveness of Fresnel contrast imaging at revealing fine pores. The pores are invisible when the image is in focus, but become bright dots surrounded by dark fringes when the defocus value (Δf) is -600 nm and dark dots surrounded

by bright fringes when Δf is +600nm. It can be seen that these pores are present in large numbers but seem to be wholly isolated from each other. Another example of similar porosity is

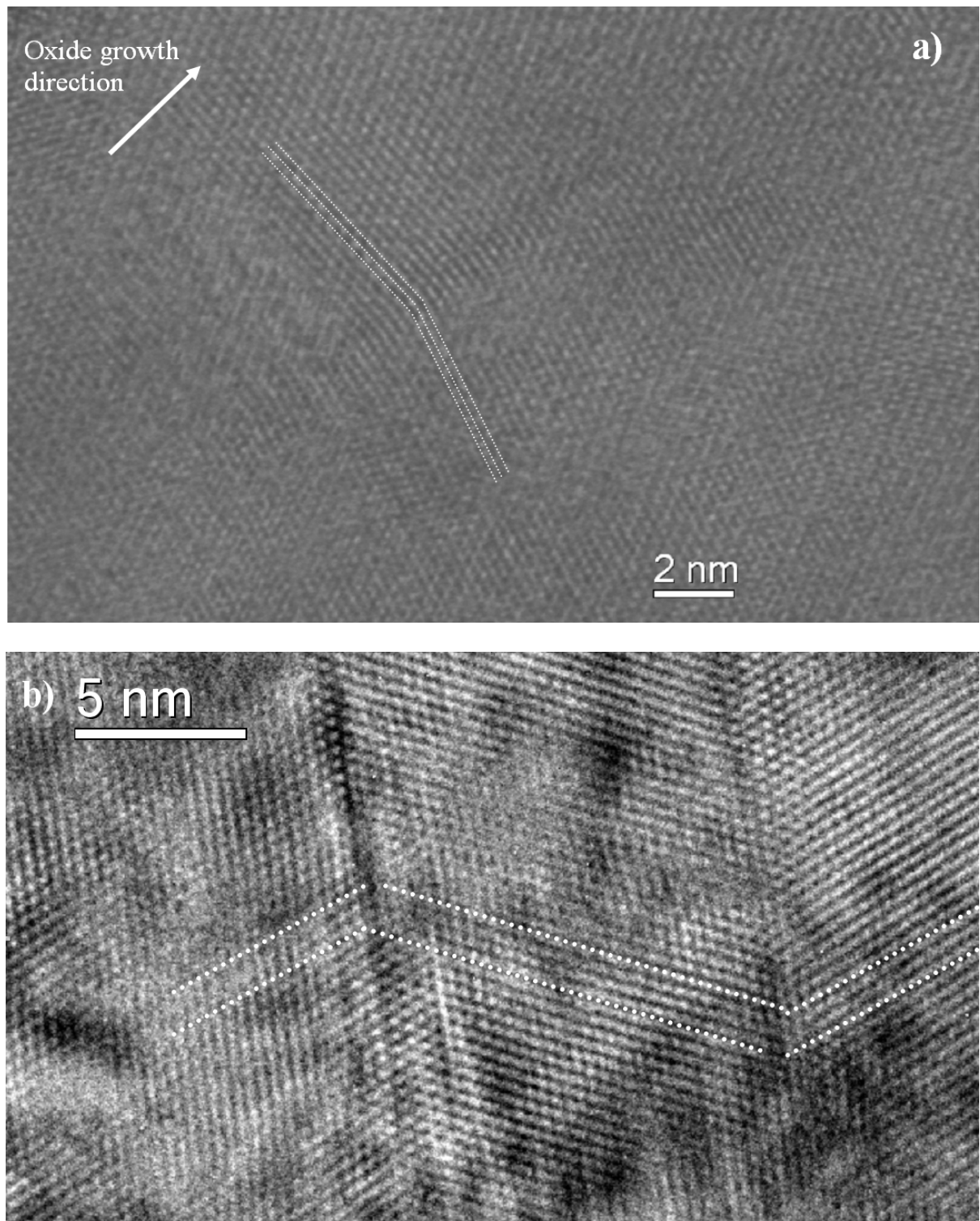


Figure 5.17 HRTEM images showing twin boundary structures in monoclinic oxide grains taken from a) the middle part of the grey oxide of the 140 days ZIRLO RXA sample and b) the oxide near the metal-oxide interface of the 90 days Zircaloy-4 RXA tube sample.

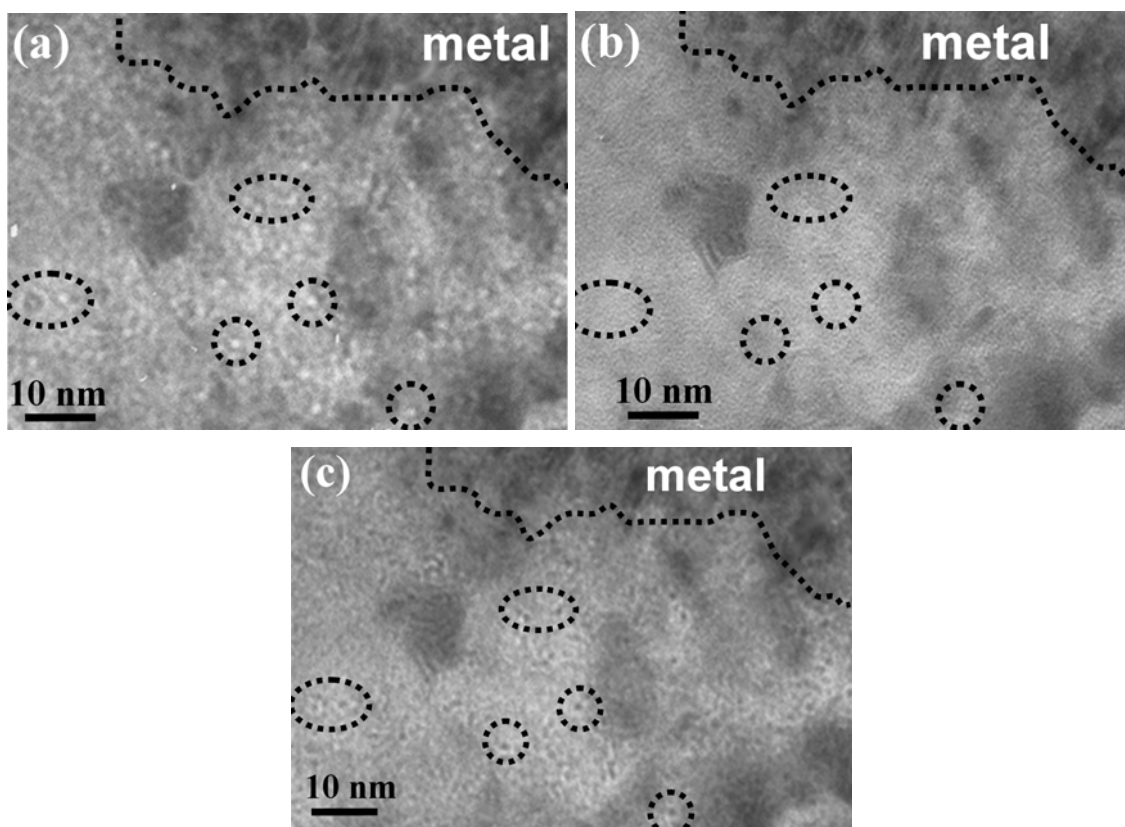


Figure 5.18 Through-focal imaging of fine pores (circled) at the metal-oxide interface of Zircaloy-4 RXA tube oxide. The pores are invisible in (b) the in-focus image ($\Delta f = 0$ nm), but show Fresnel contrast in (a) the under-focus image ($\Delta f = -600$ nm) and in (c) the over-focus image ($\Delta f = +600$ nm). The dashed line on the top indicates the metal-oxide interface.

given in **Figure 5.19a**. Similarly sized pores were also seen decorating discontinuously the columnar grain boundaries, **Figure 5.19b**. Flake-like pores were also found at the top of the oxide columns, elongated in the direction parallel to the oxide/metal interface (**Figure 5.19c**).

Further away from the metal-oxide interface, it was observed that the nano-pores became fully connected at grain boundaries along the oxide growth direction (vertical connected porosity). **Figure 5.20** shows two examples at ~ 600 nm away from the metal-oxide interface for the 60 days ZIRLO RXA oxide and $\sim 1\mu\text{m}$ away for the 100 days sample. This type of porosity appeared to increase in density with increasing distance from the interface in each sample, but in general is only observed at a few grain boundaries in the whole oxide apart from the very top 300-500 nm of the oxide where equiaxed grains associated with high porosity are present. When the 60 and 100 days ZIRLO RXA oxides were compared, the overall density of vertical connected porosity appeared to be higher for the latter sample. A

schematic representation of the oxide porosity observed for the pre-transition oxides is shown in **Figure 5.21a**.

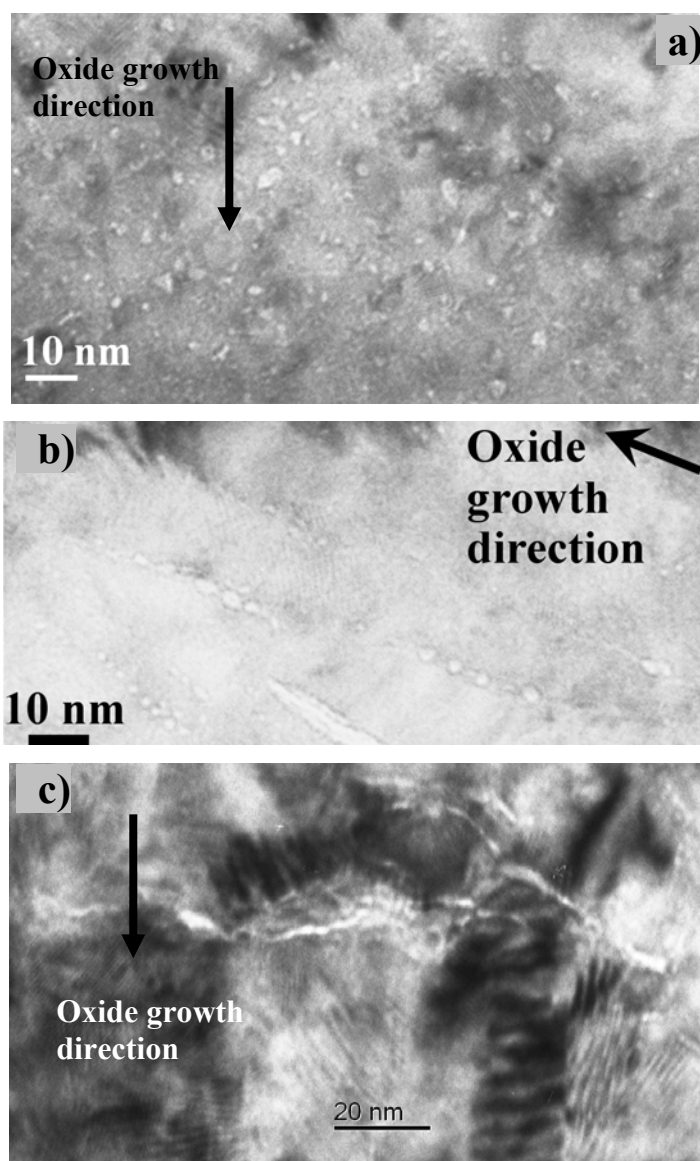


Figure 5.19 Examples of characteristic porosities observed in the oxide near the metal-oxide interface by imaging with under-focus Fresnel contrast. a) shows fine isolated pores in the Zircaloy-4 RXA tube oxide; (b) shows disconnected pores along a boundary between columnar monoclinic grains near the oxide/metal interface in the 60 days ZIRLO RXA oxide. c) shows flake-like pores at the top of the oxide columns elongated in the direction parallel to the oxide/metal interface in the 100 days ZIRLO RXA oxide.

5.3.2 Post-transition oxide

Figure 5.22 shows a series of under-focus Fresnel images taken at increasing distances away from the metal-oxide interface for the post-transition grey oxide of the 140 days ZIRLO RXA sample. It was found that the characteristics of the porosity in the oxide near the metal-oxide

interface were similar to those observed in the pre-transition oxides. Connected porosity along the oxide growth direction was again seen further away from the interface. In contrast to the pre-transition oxides, the density of this vertical connected porosity increases significantly at a

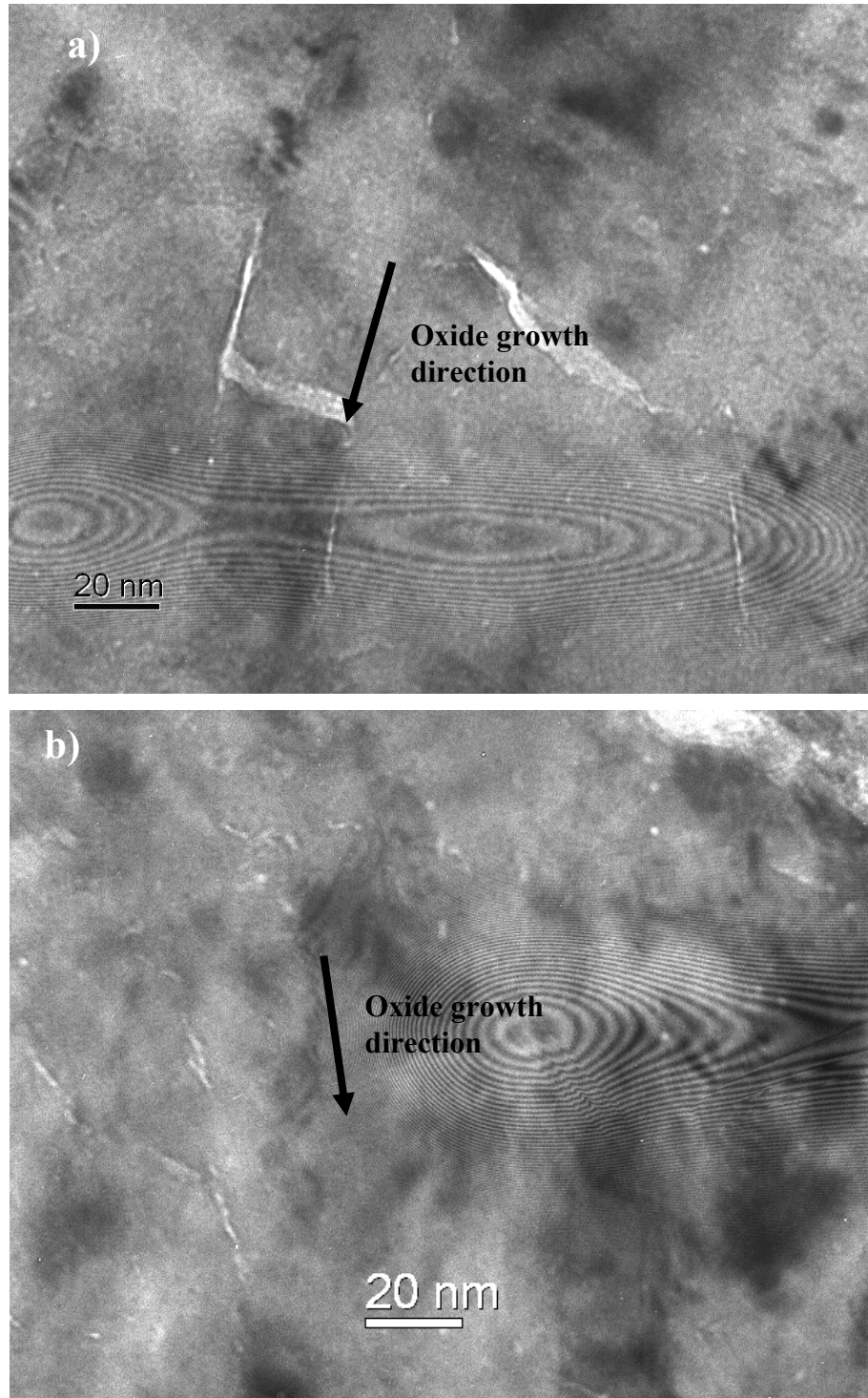


Figure 5.20 Connected porosity along oxide growth direction observed in two ZIRLO RXA pre-transition oxides. a) ~600 nm away from the metal-oxide interface of the 60 days sample, b) ~1 μ m away from the metal-oxide interface of the 100 days sample.

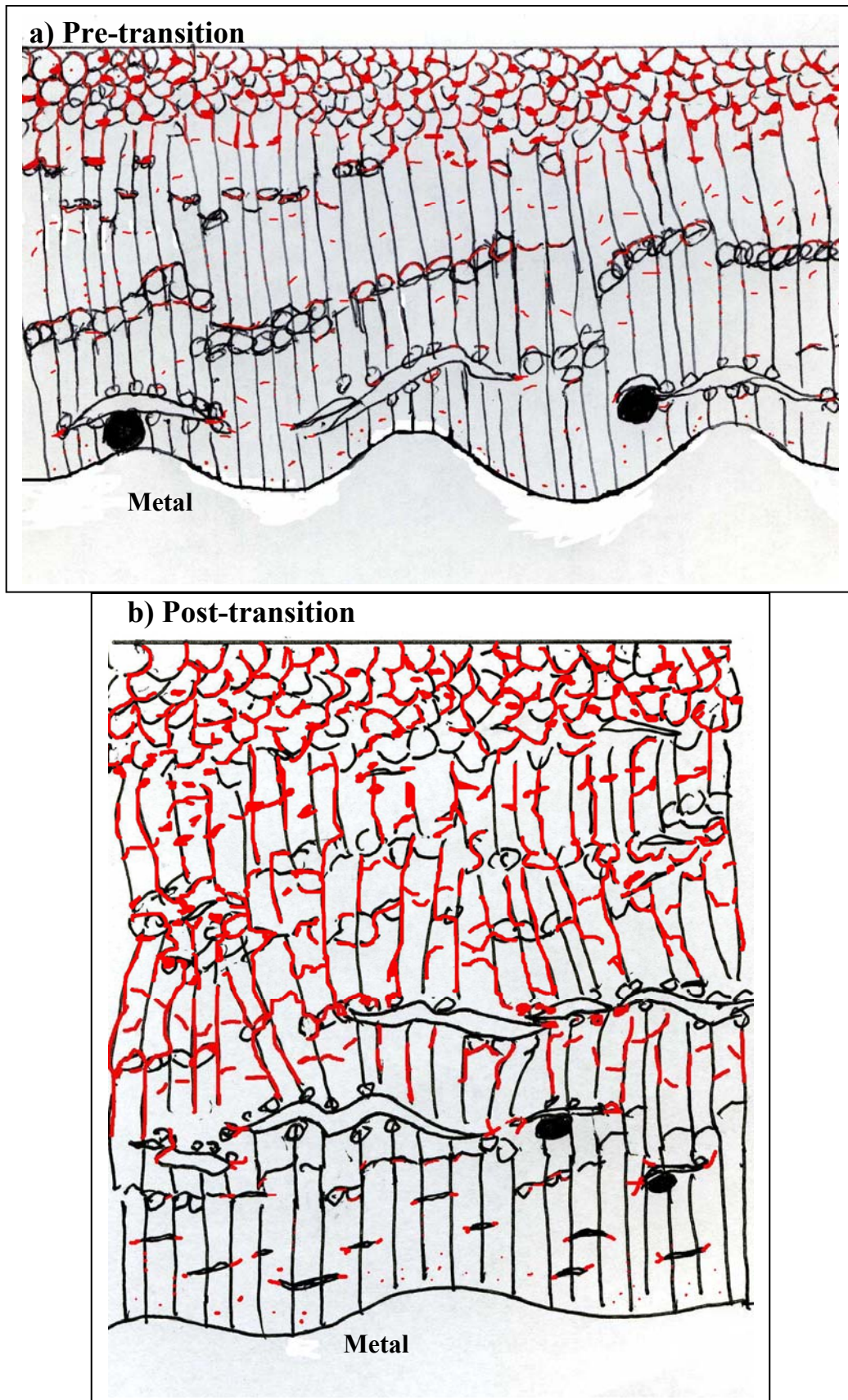
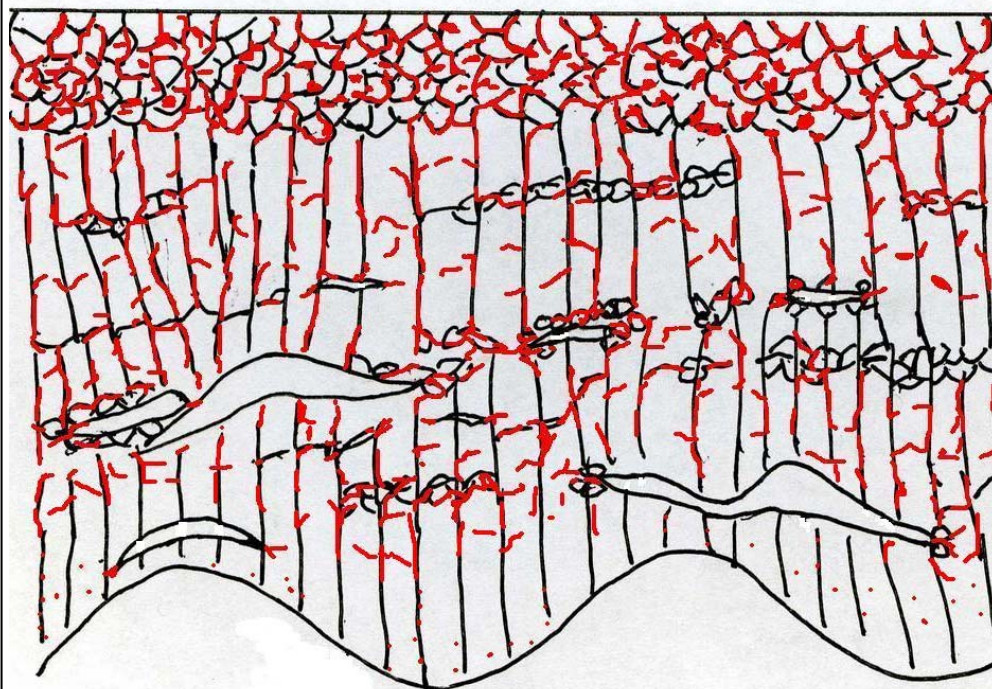


Figure 5.21 Schematic representations of oxide nano-porosity in oxides at different oxidation stages. Red dots represent isolated nano-pores and red lines represent connected nano-pores. (Figures continued on the next page.)

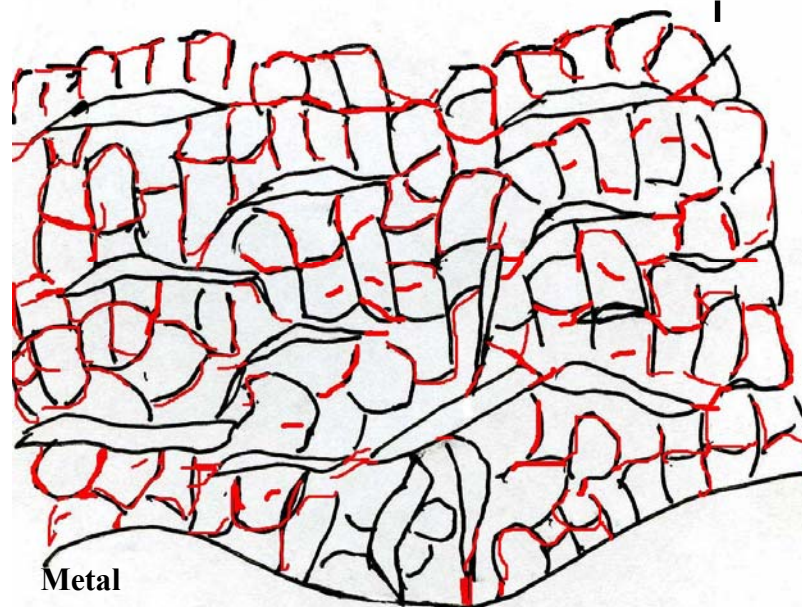
c) Around transition



Metal

d) Post-second transition (Zr-Nb-Ti)

Towards oxide surface ↑



Metal

Figure 5.21 Continued. Schematic representations of oxide nano-porosity in oxides at different oxidation stages. Red dots represent isolated nano-pores and red lines represent connected nano-pores.

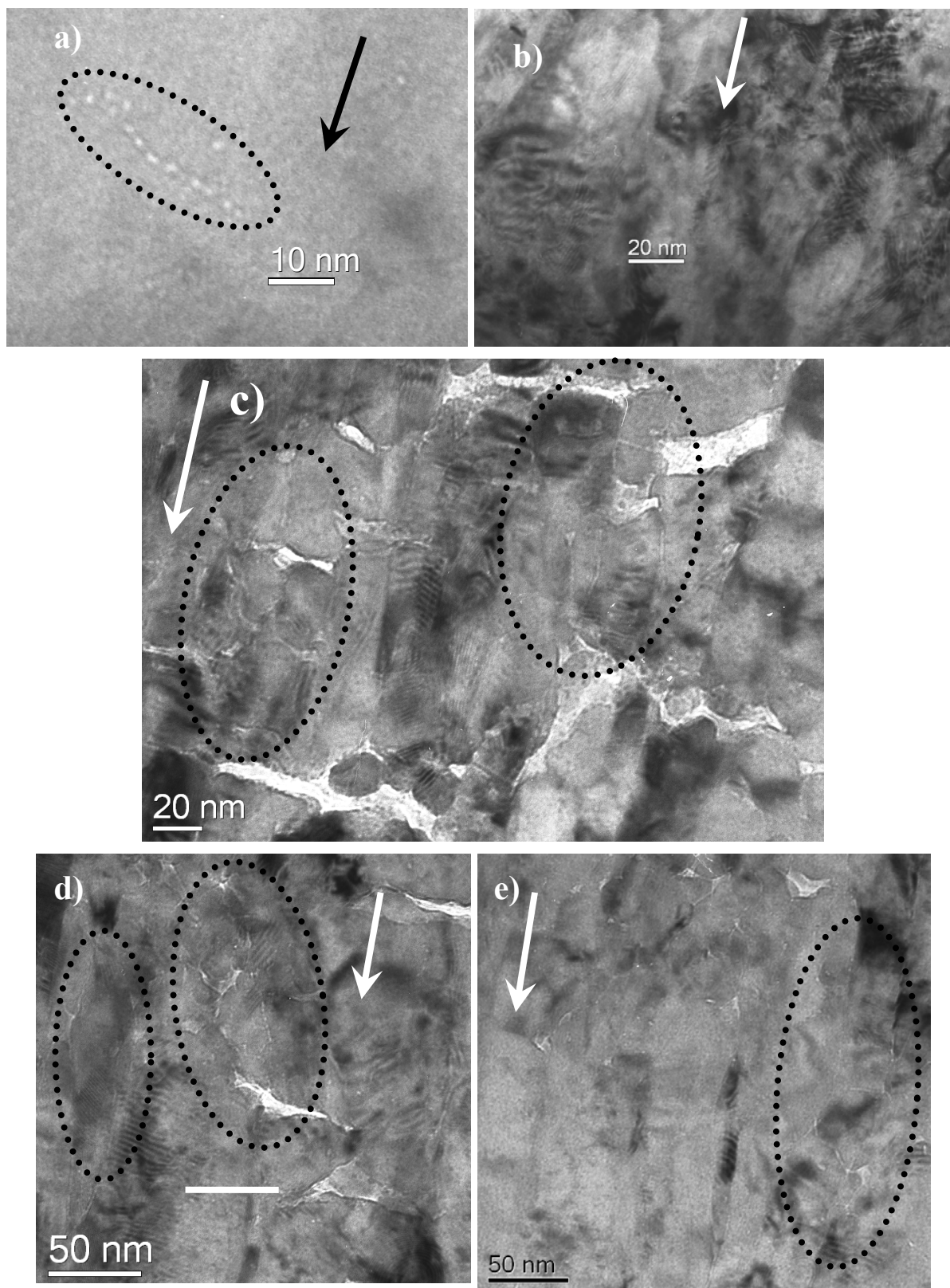
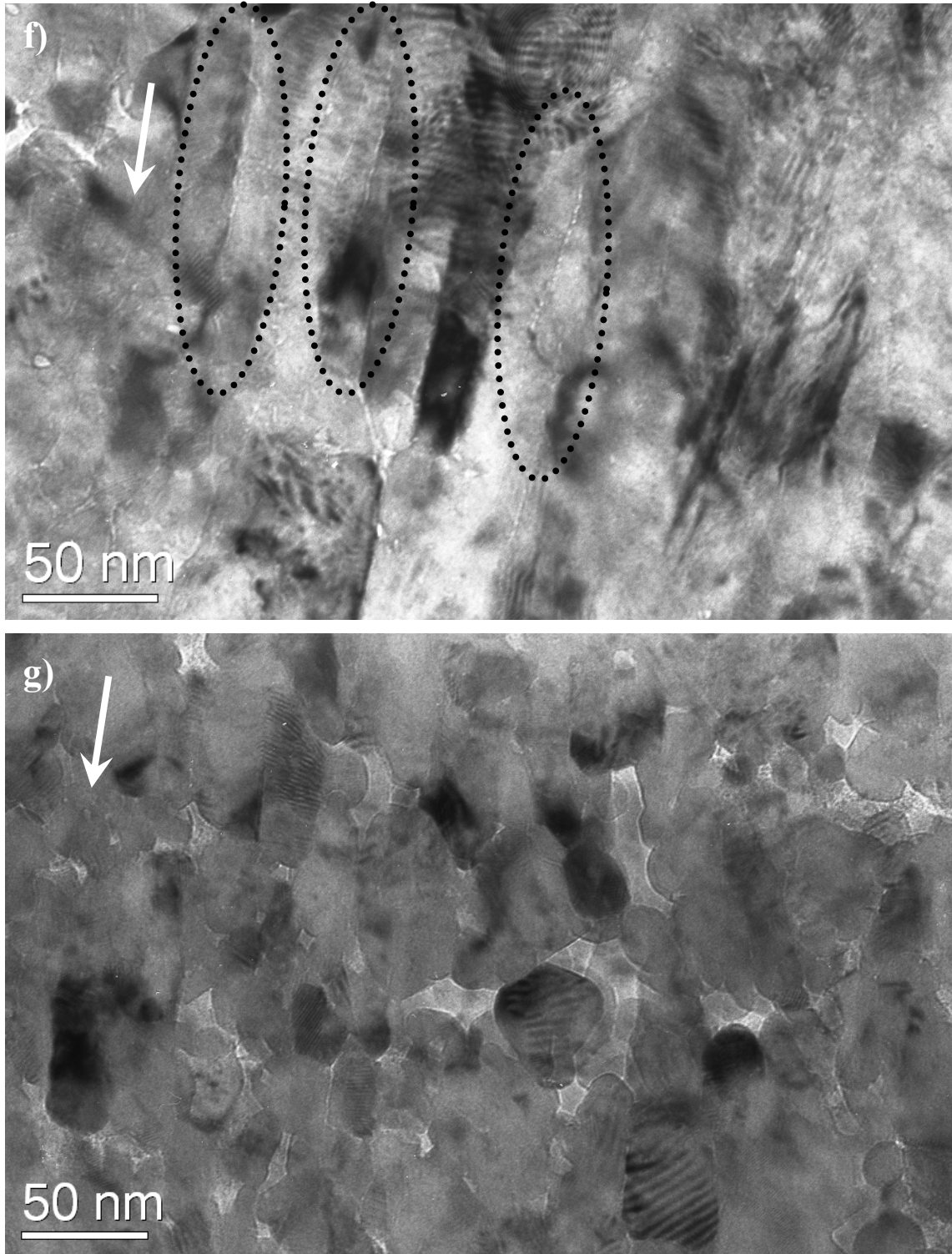


Figure 5.22 Oxide porosity at increasing distance away from the metal-oxide interface in the grey oxide of the 140 days ZIRLO RXA sample. Arrows indicate the oxide growth direction. a) adjacent to the interface showing an array of nano-pores along the direction perpendicular to the oxide growth direction (circled); b) 200 nm showing no nano-porosity; c) 450 nm; d) 650nm, e) 1μm, f) 1.6μm, g) 3 μm away (top oxide) from the interface. From d) ~650 nm, nano-porosity along the oxide growth direction (some of them are circled in the images) becomes common enough to form an interconnected porosity with pores parallel to the metal-oxide interface. (Figures continued on the next page).



characteristic distance away from the interface, which is ~ 700 nm for this sample. At this point and beyond, the probability of finding connected vertical pores along a grain boundary is

at least 5 times higher than that in the inner oxide. As a result, a network of fully interconnected porosity is formed aided by the connected pores and cracks perpendicular to the growth direction that are already present in the inner oxide. As a result, a highly porous outer oxide can be identified on the top of a less porous inner layer, as schematically shown in **Figure 5.21b**.

A similar trend was observed for another post-transition oxide grown on the Zircaloy-4 RXA sheet after 180 days, but the inner layer which didn't exhibit extensive vertical connected porosity appears to extend as much as $\sim 1\text{ }\mu\text{m}$ away from the interface, further than for the 140 days ZIRLO RXA oxide. The $\sim 32\text{ }\mu\text{m}$ thick Zircaloy-2 oxide was found to be generally porous, containing extensive vertical connected pores throughout the scale.

5.3.3 Sample around transition

As mentioned in section 5.1.1, the 120 days ZIRLO oxide, which sits around the transition point in the kinetic curve, has a big variation in oxide thickness. The 120 days specimen prepared for porosity investigation has a thinner scale region $\sim 2.0\text{ }\mu\text{m}$ thick with more horizontal cracks and a thicker region of $\sim 3.3\text{ }\mu\text{m}$ with fewer cracks. By linking to the weight gain curve in **Figure 4.2** and considering the variable oxide thickness of different regions, it is reasonable to assume that the thinner oxide region in the 120 days sample is just before the onset stage of the transition.

It was found that in the thinner oxide of the 120 days sample, there was strong evidence of connected porosity along the oxide growth direction only $\sim 300\text{-}400\text{ nm}$ away from the interface (**Figure 5.23**), much closer than that observed for other pre-transition oxides. This situation is also schematically shown in **Figure 5.21c**. In the thicker oxide on this same sample this distance from the interface before interconnected porosity could be observed was larger.

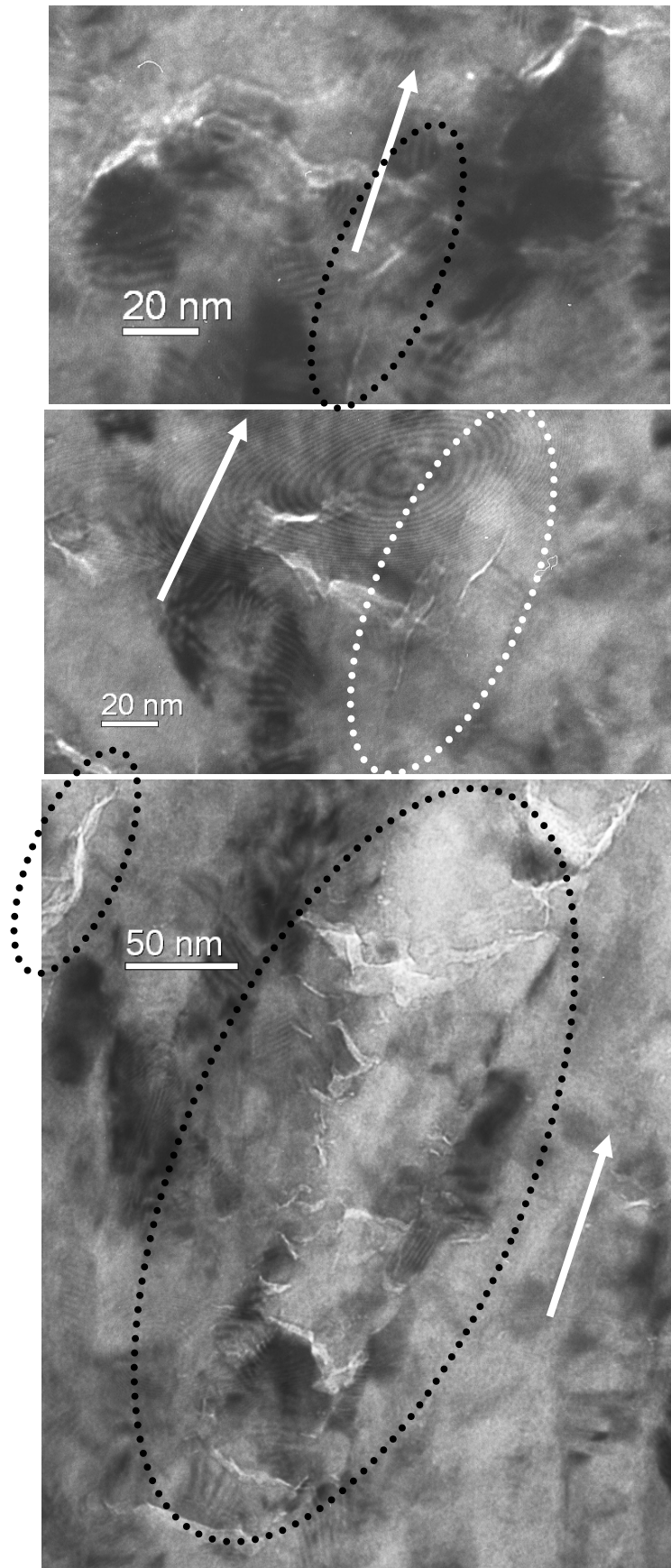


Figure 5.23 Extensive nano-porosity connected along the oxide growth direction (circled) observed ~300-500 nm away from the metal-oxide interface in the 120 days ZIRLO oxide. Arrows indicate the oxide growth direction.

5.3.4 Post-second transition oxide

The investigation of the post-second-transition $\sim 80\ \mu\text{m}$ Zr-Nb-Ti oxide reveals high porosity throughout the oxide. Severe interconnected grain boundary porosity similar to that shown in [64] was observed throughout the oxide up to the metal-oxide interface, **Figure 5.24a**, with wide vertical cracks right down to the oxidizing metal surface, **Figure 5.24b**. **Figure 5.21d** shows the schematic representation of the oxide porosity observed for this sample.

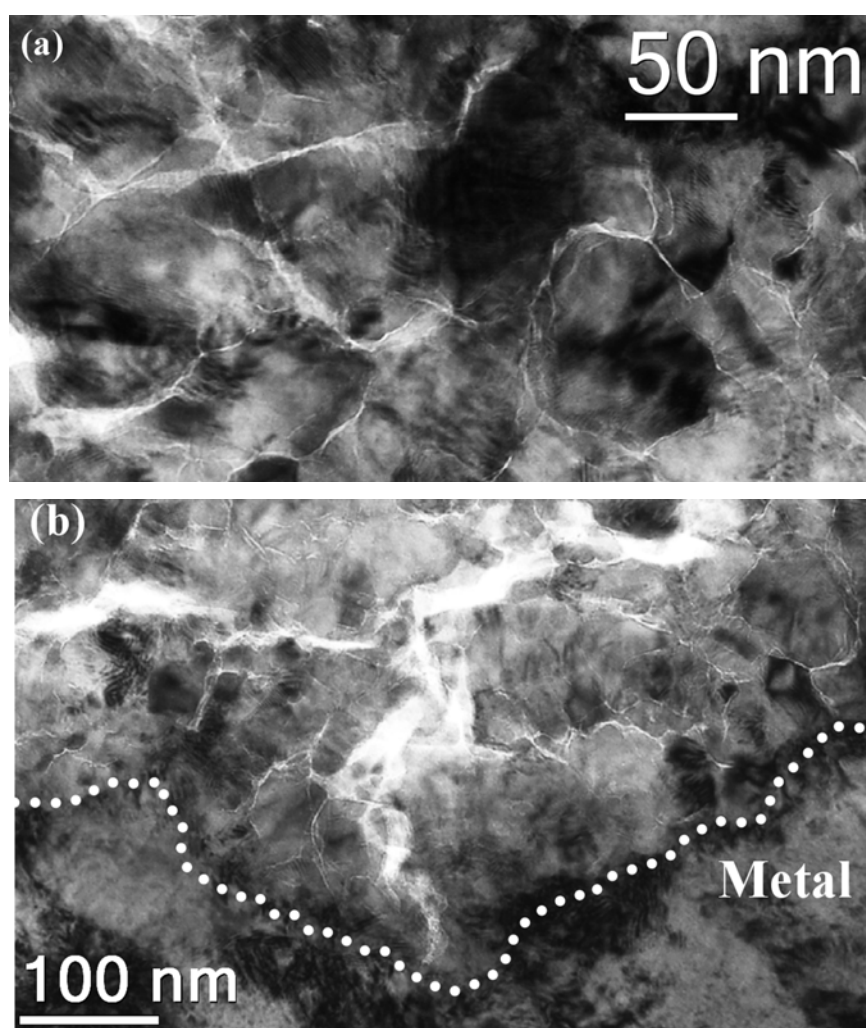


Figure 5.24 Bright field Fresnel phase contrast images of the post-second transition Zr-Nb-Ti oxide. (a) A region adjacent to the metal-oxide interface, showing fully interconnected porosity along equiaxed grain boundaries. (b) oxide at the metal-oxide interface (indicated by the dashed line) showing large vertical cracks down to the interface as well as grain boundary porosity.

5.3.5 Correlations between nano-porosity and cracks

Cracks here are defined as openings that have considerably larger width (at least 15-30 nm) compared to the 1-5 nm wide nano-pores.

Small cracks parallel to the metal-oxide interface seem to be connected with nano-porosities such that the crack branches into connected nano-pores at the tip, as shown in **Figure 5.25a**. However, the presence of larger cracks does not necessarily alter the general nano-porosity in that region. In other words, a region containing a big crack does not have to be porous at the 1-5 nm scale. An example is given in **Figure 5.25b** for an oxide region adjacent to the metal-oxide interface of the 34 days ZIRLO oxide sample where a big crack is present but the oxide is still dense in terms of being mostly free of interconnected nano-pores along the growth direction.

5.3.6 Discussion

The rather abrupt transition from an approximately cubic rate law of oxide thickening (pre-transition) to the linear (or cyclic) kinetic (post-transition) is believed by some authors to be a strong indication that porosity must have developed in the previously protective oxide [2]. Discontinuous arrays of pores aligned along the columnar monoclinic grain boundaries as seen in **Figure 5.19b** have been reported by Kubo and Uno [86]. Flake-like pores at the top of the oxide columns shown in **Figure 5.19c** were also similar to those observed in other studies [64, 146]. However, the observations reported here have shown that many different crack/nano-porosity types can be observed in a single oxide. Garzarolli *et al.* [119] have deduced from BET isotherms that the average pore size in the oxides of stress-relieved Zircaloy-4 produced by oxidation in 350°C water could be as small as 3 nm. I have now shown directly for the first time that even smaller isolated pores are present close to the metal-oxide interface in aqueous oxides. It is worth noting that the Fresnel contrast features

characteristic of isolated pores shown in **Figure 5.19** are absent in the metal region close to the oxide/metal interface, demonstrating that the phase contrast seen is not an artefact produced by the FIB sample preparation [241].

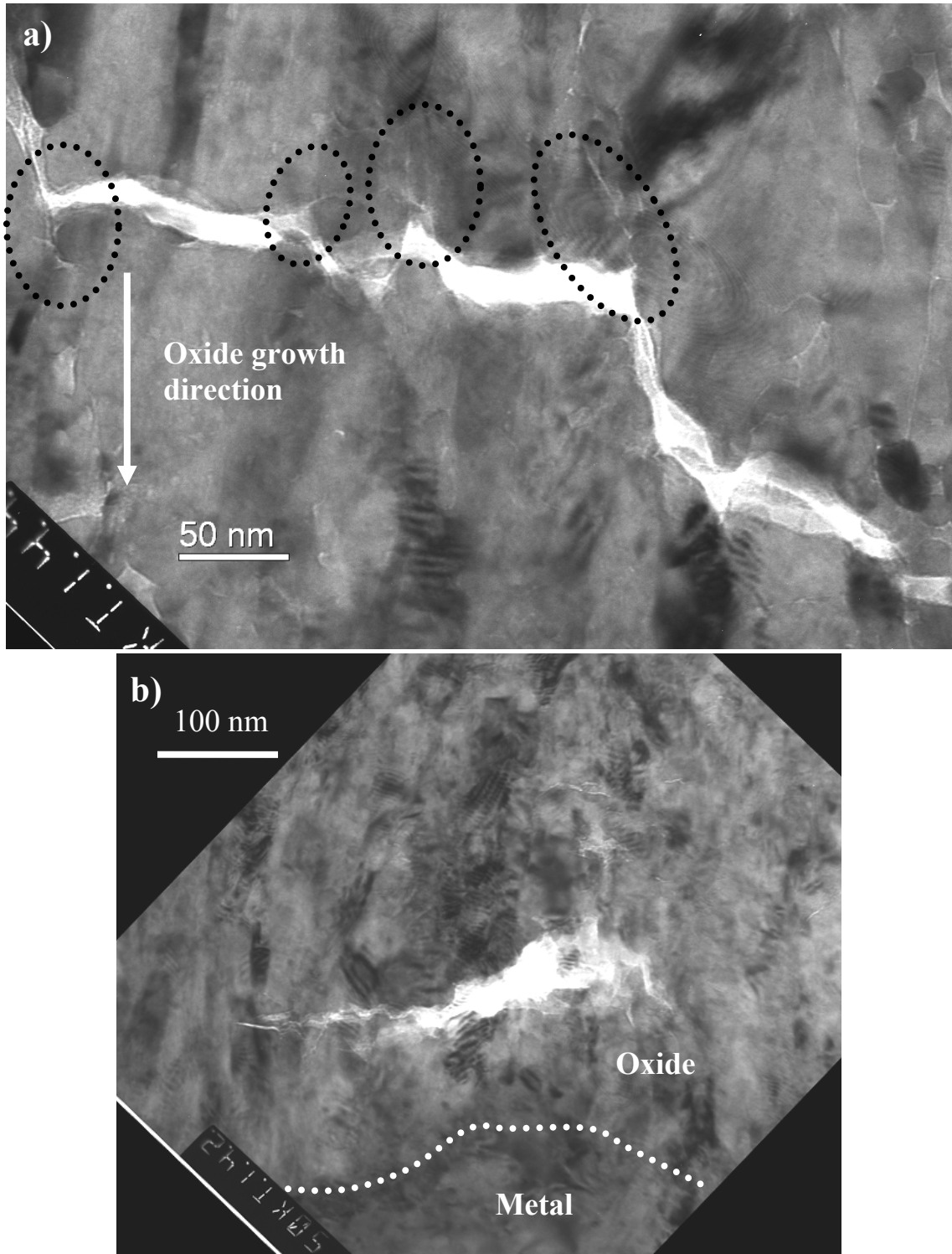


Figure 5.25 a) Cracks parallel to the metal-oxide interface branch into connected nano-pores at their tip positions (highlighted by circles). b) An oxide region adjacent to the metal-oxide interface, where a big crack is present but the oxide is still dense in terms of being free of interconnected nano-pores along the growth direction.

Further away from the metal-oxide interface, it was found these small pores start to connect both along and perpendicular to the oxide growth direction, forming the easy diffusion paths for oxidizing species to the oxide/metal interface region anticipated by Cox [2]. This model of the development of the pore structure at different stages of aqueous corrosion is reinforced by the observation that the width of the connected pathways such as shown in **Figure 5.22f** is close to the size of the isolated pores in **Figure 5.19**. Therefore I suggest that it is the gradual accumulation of small pores along grain boundaries between the columnar monoclinic grains which is the critical mechanism for forming a continuous path for oxidising species to penetrate closer to or right down to the reacting metal surface.

In the absence of vertical cracks, if an oxide contains only isolated pores and/or pores connected perpendicular to the oxide growth direction (and/or very low density of pores connected along the oxide growth direction), it can be regarded as protective since it is difficult for oxidizing species to be transported through the oxide down to the metal-oxide interface for the oxidation reaction. This is the case in the pre-transition oxides that were still far from the kinetic transition. It was found in these samples that the density of nano-pores connected along the growth direction was very low apart from in the top region of equiaxed oxide, making the oxide overall protective, as schematically shown in **Figure 5.21a**. On the other hand, for the oxide around the onset of the kinetic transition it appeared that the density of nano-pores connected along the oxide growth direction has increased at distances closer to the metal-oxide interface compared to earlier pre-transition oxides, implying a reduced protective oxide thickness that could lead to an increasing oxidation rate and a transition in oxidation rate (**Figure 5.21b**). After the transition, a new layer of fresh, dense oxide forms beneath the early oxide full of connected porosities. As a result, a very porous outer oxide layer was found on top of an inner dense layer (**Figure 5.21c**). In the post-second transition Zr-Nb-Ti oxide, no dense protective oxide was found. The porosity is so severe that it has

become connected into a network of transport pathways along every grain boundary down to the metal-oxide interface (**Figure 5.21d**), as observed in steam-grown oxides further from the oxide/metal interface by Warr *et al.* [64]. It should be noted that the vertical connected nanopores are drawn almost along every vertical grain boundary in the cartoons in **Figure 5.21**, but this exaggerates the real observations in these oxides, except for the Zr-Nb-Ti sample.

An estimation of the width of the dense protective oxide layer in oxides grown on ZIRLO for different times is shown in **Figure 5.26a**. It is noted that the estimation of this width may have large errors due to the very small area investigated by TEM. However the general trend of the evolution of the protective oxide thickness is in good agreement with the in-situ electrochemical impedance spectroscopy (EIS) measurements on oxides grown on the same ZIRLO material (**Figure 5.26b**, courtesy of Peng Wang, Manchester University), i.e. the protective oxide thickness grows gradually in the pre-transition stage (capacitance decreasing) but becomes much thinner (abrupt increase in capacitance) around the kinetic transition and then starts to grow again.

Kumar *et al.* [263] argued that for oxides growing by anion transport, voids can initiate by coalescence of vacancies generated in the alloy by the Kirkendall effect when rejected solute diffuses away from the oxide/metal interface faster than matrix atoms diffuse towards it. This can be a mechanism giving rise to pores in Zr alloys where anion in-diffusion dominates the oxide growth rate [2], and it is relevant that both Sn and Ti diffuse much faster than Zr [264]. The vacancies can condense to form pores then become embedded in the growing oxide as observed. The pores would preferentially condense at grain boundaries due to a lowered surface energy, and gradually become connected when more and more pores are formed at an individual grain boundary with time.

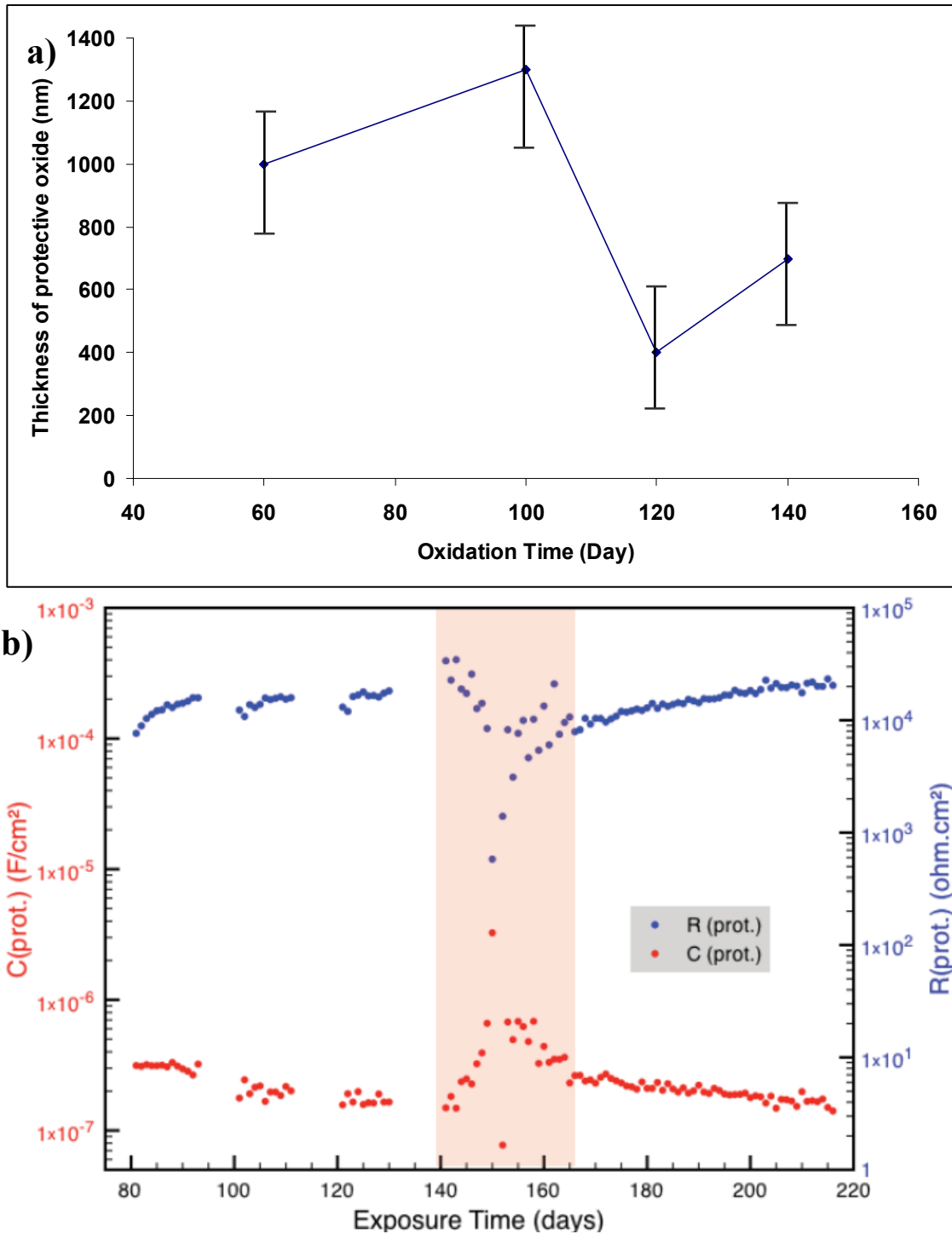


Figure 5.26 a) Estimation of the thickness of the protective oxide layer characterized from TEM work for oxides grown on ZIRLO for different times. b) In-situ EIS measurement of the capacitance and the resistance of the oxides grown on ZIRLO for different time (Peng Wang, Manchester University).

However, it is noted that extensive grain boundary porosity is also seen in oxides grown on pure Zr [64] where this Kirkendall mechanism cannot operate. Another possibility is the creep of the oxide under the compressive stresses parallel to the metal-oxide interface, as suggested by Kofstad [265]. The compressive stresses introduce strains along the oxide growth direction,

which are difficult to accommodate by dislocation glide in the polycrystalline oxide as too few slip systems are likely to be active at the typical oxidation temperatures. Therefore creep has to be a possible mechanism to provide the required strain. As a result of a materials transport accompanying creep, voids may be formed between the sides of the grains (**Figure 5.27a and b**), which can only be relieved by a grain boundary sliding, as shown in **Figure 5.27c**. If the grain boundary sliding is slower than the creep process, for instance due to the segregation of foreign atoms in the grain boundaries or an impingement on quadruple points of the grain boundary network, then the voids and porosity can remain and develop.

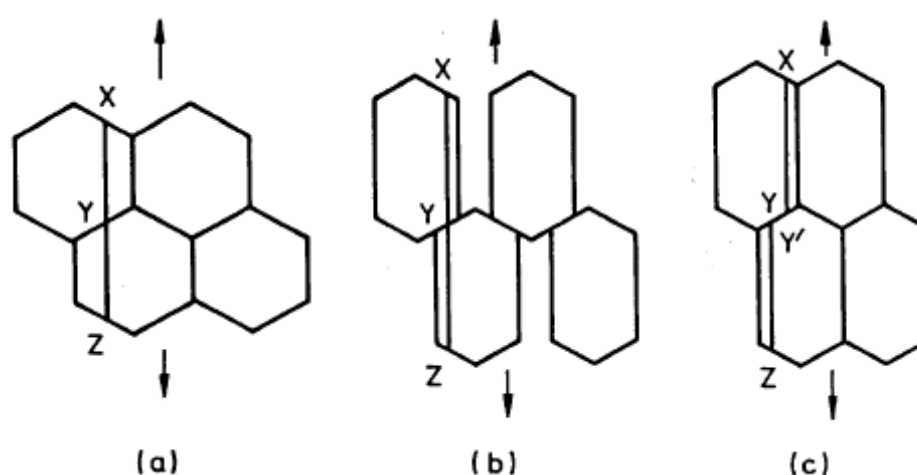


Figure 5.27 Schematics of deformation of grains by creep: a) grains subjected to longitudinal strains; b) creep of the grains create voids between the sides of the grains, which can only be relieved by a grain boundary sliding shown in c). [266]

Cracks of different sizes have been shown in all the investigated samples. They are often reported in zirconium alloy oxides [19, 25, 89, 123, 138], and are often correlated with accelerated onset of transition [25, 101, 123] or a higher corrosion rate [89, 127]. However, they are usually orientated parallel to the oxide/metal interface, which should make them obstacles for oxidizing species rather than easy diffusion paths. The 120 days ZIRLO RXA oxide serves an example for this point (as also will be shown clearly from the 3D microstructure characterization in **Chapter 7**). The oxide in this sample is thickest in the part containing fewer horizontal cracks. The investigation of porosity near the horizontal cracks also revealed that they were not necessarily associated with an overall higher porosity in the

nearby oxide. Therefore, it can be suggested that horizontal cracks are only effective at increasing the rate of oxidation when they are connected to the outer surface via continuous porosity along the oxide growth direction. This could be a scenario for the thinner oxide scale part of the 120 days ZIRLO RXA sample, where a higher densities of both horizontal cracks and vertical connected porosity extending very close to the metal-oxide interface were observed, suggesting that a rapid oxide growth period will occur once the porosity reaches the metal-oxide interface. By comparison, the vertical connected porosity was further away from the interface for the thicker scale region, where rapid post-transition growth has created new columnar oxide without interconnected grain boundary porosity.

Vertical cracks, which were only seen at the oxide/metal interface in the Zr-Nb-Ti oxide with abnormally rapid oxidation (**Figure 5.24**), can enhance the transport of the oxidizing species. It seems likely that the grain boundary porosity along the vertical direction serves as easy nucleation sites for vertical cracks, which then form with the larger lateral ones a continuous network from the free surface down to the oxide/metal interface.

5.4 Second phase particles

5.4.1 Observations

5.4.1.1 Nb containing alloys

Table 5.3 and **Table 5.4** show the characterization of second phase intermetallic particles in the metal matrix of ZIRLO and Zr-Nb-Ti samples, with their size, crystal structure and composition. The composition was measured by EDX and the crystal structure was identified by micro-diffraction. Two main types of intermetallic particles were found in the metal matrix. One has a BCC β -Nb crystal structure ($a = \sim 0.33$ nm) with almost no Fe and the other one is Zr-Nb-Fe(-Cr) type with the hexagonal Zr(Fe,Nb)_2 structure ($a = \sim 0.54$ nm and $c = \sim 0.88$ nm)

and a significant Fe content of ~20 at.%. TEM images of some example particles in the Zr-Nb-Ti alloy are shown in **Figure 5.28**.

The relative error associated with EDX composition measurement is around 10%, and it is noted that the composition measured by EDX is also strongly influenced by the surrounding metal matrix, i.e. an overestimation of Zr content is expected, especially for small precipitates, for examples precipitates # 3 and # 4 in **Table 5.3** and # 4 and # 5 in **Table 5.4**. The Nb/Fe ratio in all the measured precipitates lies in the range ~1.5 - 2.1. 3D atom-probe analysis (D. Hudson, Oxford Materials), where matrix interference can be avoided, has measured a more accurate atomic composition of a Zr-Fe-Nb type precipitate to be 38.96%Zr-33.48%Nb-25.3%Fe-2.08%Cr-0.17%O-0.01%Sn with Nb/Fe ratio of ~1.3 in ZIRLO and 36.63%Zr-38.5%Nb-19.22%Fe-2.65%Ti-2.44%Cr-0.46%O-0.09%Ni with Nb/Fe ratio of ~2 in the Zr-Nb-Ti alloy.

Table 5.3 Intermetallics in the metal matrix of ZIRLO

	Crystal structure type identified by diffraction	Composition measured by EDX (at. % $\pm$ 0.1 at. %)	Size (nm)
1	Hexagonal Zr(Fe,Nb) ₂	Zr(28.9)-Nb(17.5)-Fe(14.8)-Cr(1.26)	~100
2	Hexagonal Zr(Fe,Nb) ₂	Zr(38.0)-Nb(40.2)-Fe(20.3)-Cr(1.6)	170
3	Hexagonal Zr(Fe,Nb) ₂	Zr(71.7)-Nb(18.3)-Fe(9.3)-Cr(0.6)	~60
4	Hexagonal Zr(Fe,Nb) ₂	Zr(43.8)-Nb(35.2)-Fe(19.8)-Cr(1.2)	~130
5	BCC β -Nb	Zr (69.9)-Nb (30.1)	~45
6	BCC β -Nb	Zr (68.9)-Nb (31.1)	~40
7	Hexagonal Zr(Fe,Nb) ₂	Zr(38.0)-Nb(40.9)-Fe(19.9)-Cr(1.2)	~200
8	Hexagonal Zr(Fe,Nb) ₂	Zr(38.5)-Nb(36.7)-Fe(23.0)-Cr(1.9)	~140

Figure 5.29 shows crystalline SPPs in oxides near the metal-oxide interface (60 days ZIRLO RXA oxide) and about 1 μ m away from the interface (120 days ZIRLO RXA oxide),

indicating a delayed oxidation of these precipitates compared to the Zr matrix. Micro-diffraction and EDX analysis confirm that they are both β -Nb particles (28.9%Zr-69.6%Nb-1.5%Cr and 63.3%Zr-36.7% Nb in atomic concentration respectively). It can also be seen that these SPPs exhibit crescent shaped cracks on the side away from the metal-oxide interface. An amorphous SPP containing mainly Nb and a trace of Fe (62.5%O-15.3%Zr-21.9%Nb-0.3%Fe in atomic concentration) was seen $\sim 1 \mu\text{m}$ away from the metal-oxide interface in the 34 days RXA ZIRLO oxide (**Figure 5.30**). This level of Fe content is within the range that could result from Fe in the microscope column.

Table 5.4 Intermetallics in the metal matrix of the Zr-Nb-Ti test alloy

	Crystal structure type identified by diffraction	Composition measured by EDX (at. %)	Size (nm)
1	BCC β -Nb	Zr (47.5)-Nb (51.9) - Ti (0.5)	40
2	Hex. Zr(Fe,Nb)_2	Not measured	70
3	BCC β -Nb	Zr(48.6)-Nb(49.3)-Fe(0.6)-Ti(1.0)-Cr(0.5)	40
4	Hexagonal Zr(Fe,Nb)_2	Zr(51.6)-Nb(27.7)-Fe(18.5)-Cr(1.1)	50
5	Hexagonal Zr(Fe,Nb)_2	Zr (52.3)-Nb (29.3)-Fe (14.1)-Ti (2.4)-Cr (1.8)	70
6	Hexagonal Zr(Fe,Nb)_2	Not measured	60
7	Hexagonal Zr(Fe,Nb)_2	Not measured	100

Figure 5.31 shows four SPPs in oxides on different ZIRLO specimens at $\sim 470 \text{ nm}$, $\sim 800 \text{ nm}$ and $\sim 2 \mu\text{m}$ away from the metal-oxide interface. Apart from the one at the metal-oxide interface which changed contrast upon tilting, the appearance and associated diffraction patterns of the other three proved that they had become amorphous. The precipitate/oxide interface is sharp in b) but appears more diffuse in c) and d). A similar amorphous SPP to that shown in b) was also found as close as $\sim 270 \text{ nm}$ to the interface in the 34 days oxide sample. These amorphous precipitates usually have a size $> 100 \text{ nm}$ and were found by EDX analysis to

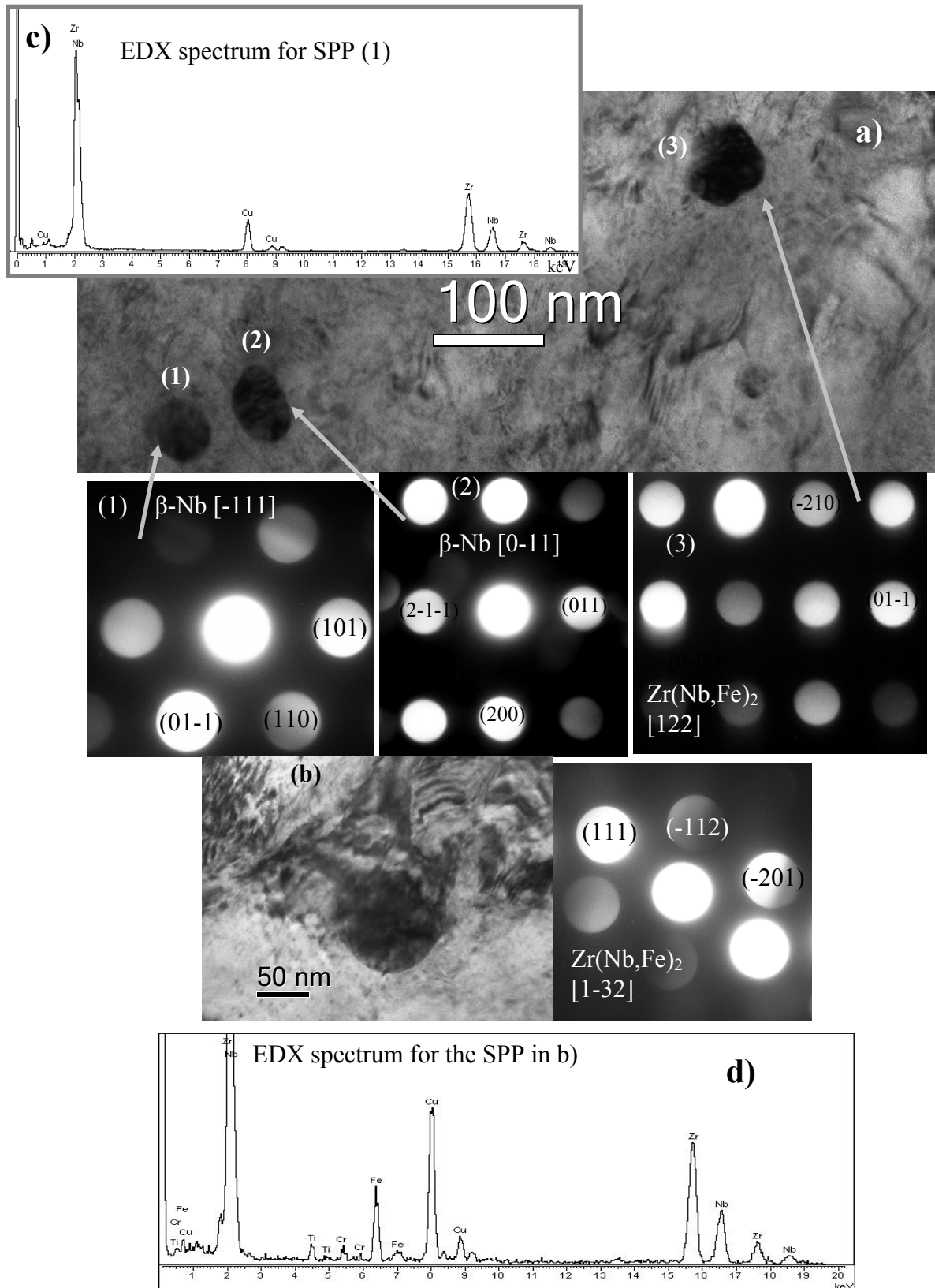


Figure 5.28 Examples of intermetallic second phase particles in the metal matrix of the Zr-Nb-Ti oxide sample. a) BF image showing three SPPs and their micro-diffraction patterns. The first two ~ 50 nm particles have a BCC β -Nb structure and contain $\sim 50\%$ Nb; the third ~ 70 nm one has a hexagonal $\text{Zr}(\text{FeNb})_2$ structure and contains ~ 30 at.% Nb and ~ 15 at.% Fe. b) BF image of another SPP of ~ 100 nm with a hexagonal $\text{Zr}(\text{FeNb})_2$ structure indicated by micro-diffraction. c) and d) EDX spectra from the SPP (1) in a) and the SPP in b) are also shown.

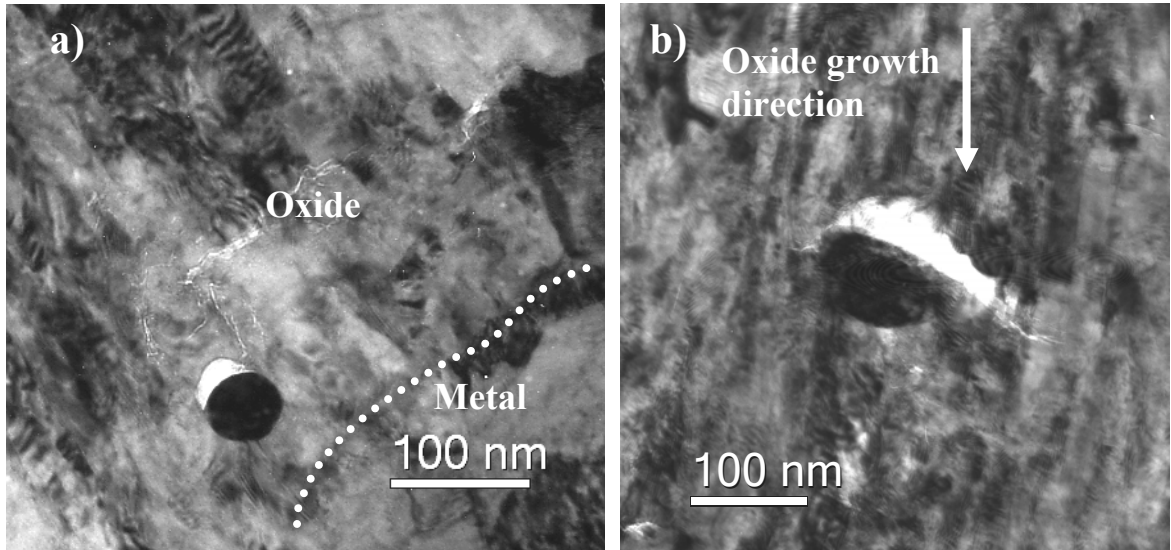


Figure 5.29 Crystalline SPPs found in the oxide a) close to the metal-oxide interface and b) $\sim 1\mu\text{m}$ away from the metal-oxide interface. a) is from the 60 days ZIRLO RXA oxide and b) is from the 120 days sample.

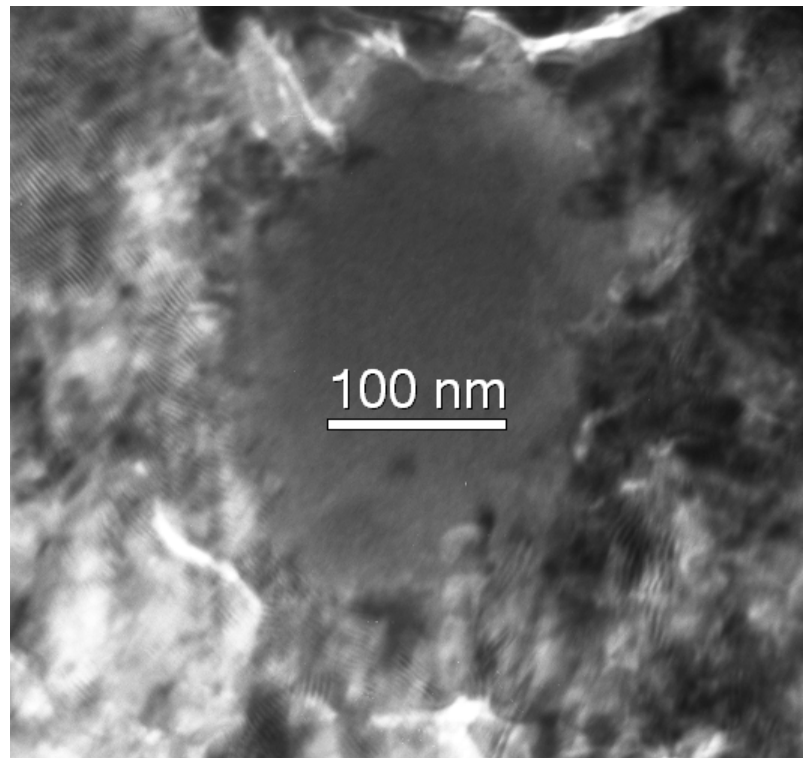


Figure 5.30 An amorphous SPP containing mainly Nb and a trace of Fe (62.5%O-15.3%Zr-21.9%Nb-0.3%Fe in atomic concentration) $\sim 1\mu\text{m}$ away from the metal-oxide interface in the 34 days RXA ZIRLO oxide.

be Zr-Nb-Fe particles containing a Fe content of ~ 14 at. %. Therefore compared with the Zr-Nb-Fe precipitates found in the metal, these amorphous Zr-Nb-Fe ones have a higher Nb/Fe ratio in the range of ~ 2.1 - 2.5 . The crescent-shaped cracks associated with crystalline SPPs were not present above the amorphous ones. HRTEM analysis found the presence of

tetragonal ZrO_2 near amorphous SPPs (**Figure 5.32**), which was not evident for the crystalline SPPs.

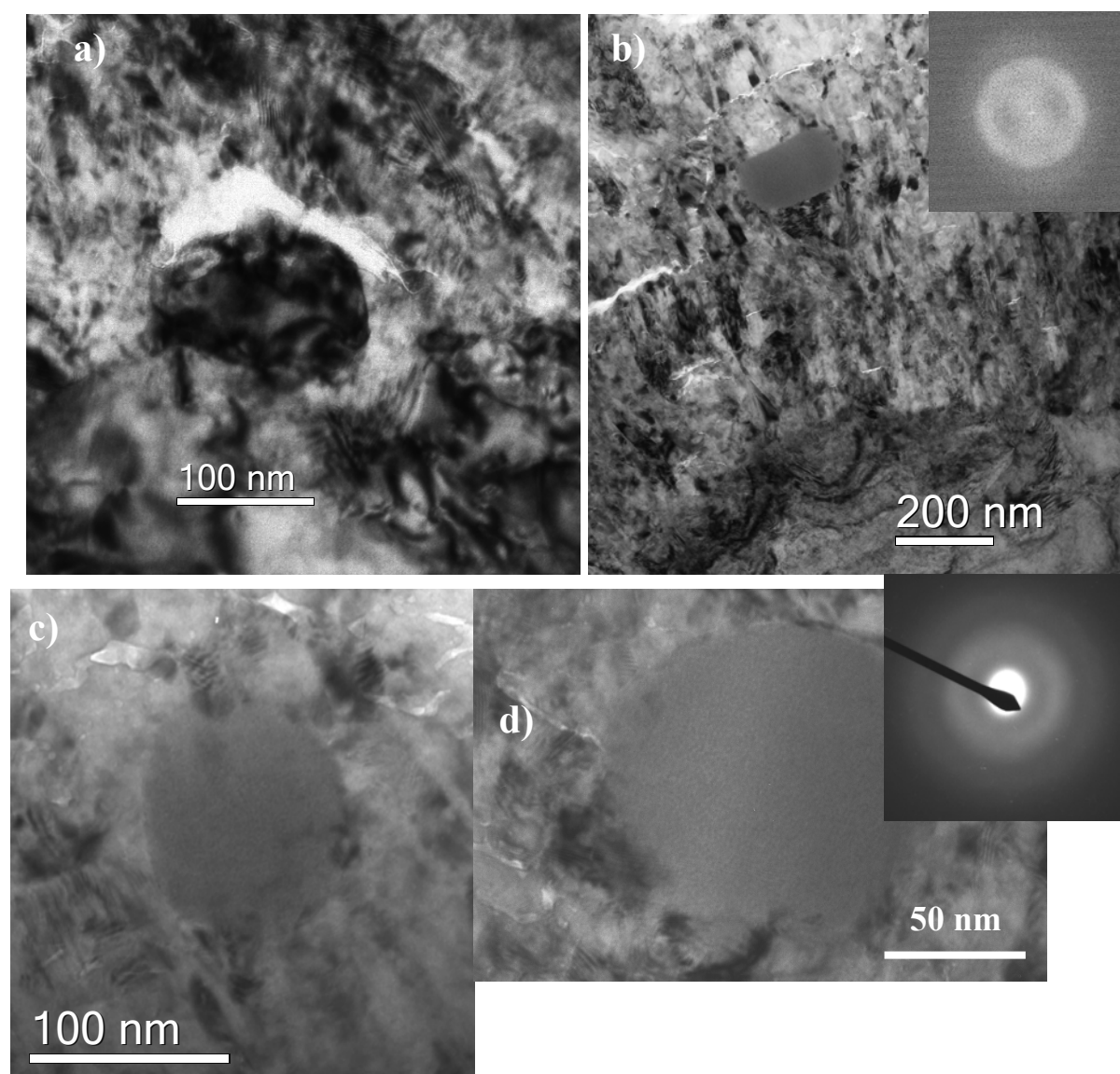


Figure 5.31 Zr-Nb-Fe type second phase particles in oxides on ZIRLO. a) Crystalline SPP at the metal-oxide interface. b), c) and d) amorphous SPPs at ~ 470 nm, ~ 800 nm and ~ 2 μm away from the metal-oxide interface. a) is from the 120 days ZIRLO RXA oxide, b) is from the 34 days ZIRLO RXA oxide, c) and d) are from the grey oxide of 140 days ZIRLO RXA sample.

Figure 5.33 shows an STEM bright field image and Fe, Nb elemental maps for the oxide grown on ZIRLO RXA after 120 days. SPPs containing only Nb have smaller average size than those containing both Nb and Fe. At about 1.5 μm away from the metal-oxide interface, no precipitates containing Fe could be identified presumably because they have preferentially oxidized and the Fe diffused into the oxide.

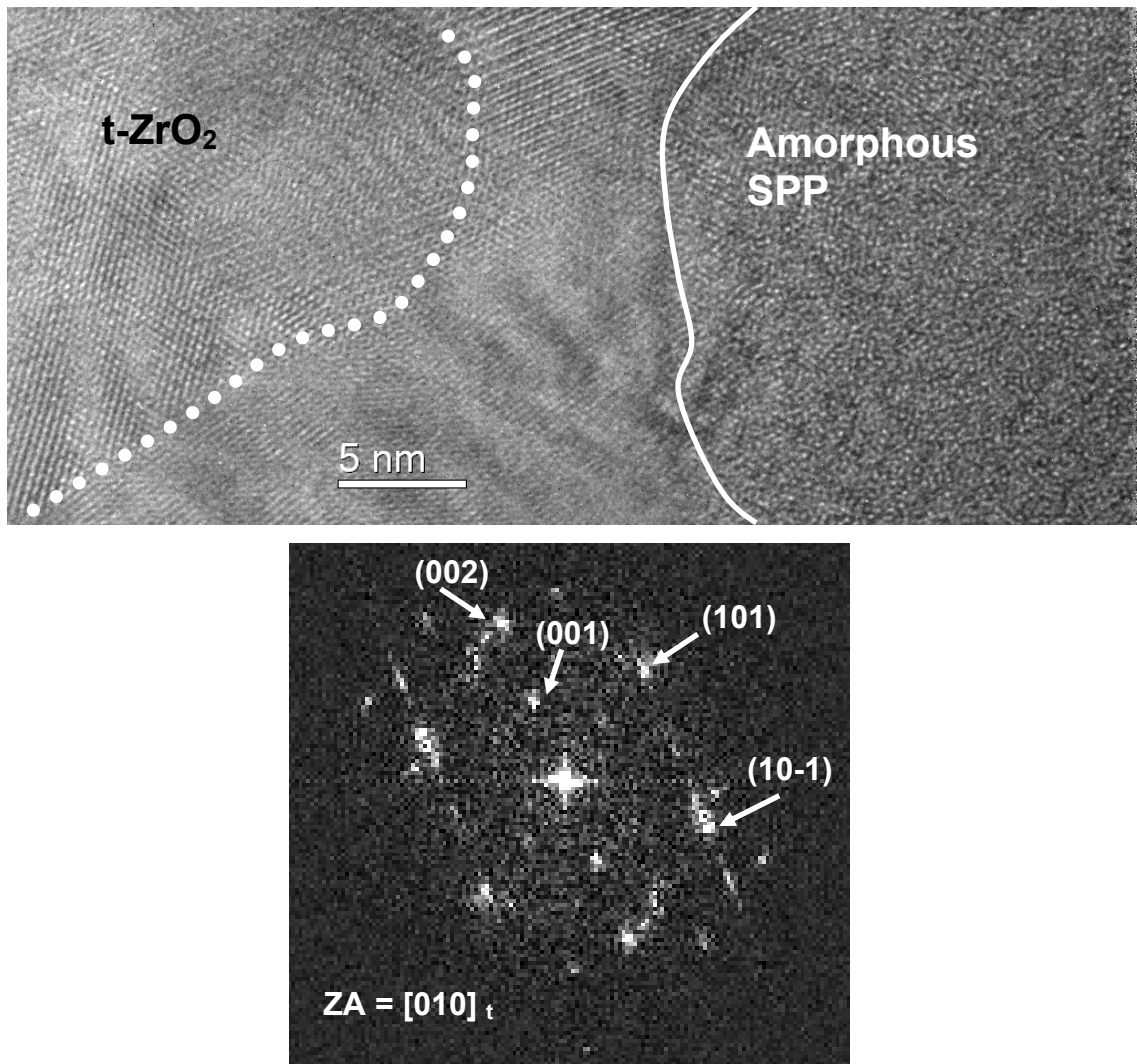


Figure 5.32 Top: HRTEM image showing the presence of $t\text{-ZrO}_2$ near an amorphous SPP in the grey oxide of the 140 days RXA ZIRLO oxide. Bottom: Indexed diffractogram from the $t\text{-ZrO}_2$ grain region.

5.4.1.2 Zircaloy-4

Most of the characterized intermetallic precipitates in the Zircaloy-4 metal matrix were found to have the hexagonal Laves $\text{Zr}(\text{Fe,Cr})_2$ structure. The Fe/Cr ratio was found to be ~1.5-~1.9. An example of these SPPs in the metal is shown in **Figure 5.34a**.

Figure 5.34b shows a crystalline SPP in the oxide adjacent to the metal-oxide interface together with a micro-diffraction pattern. **Figure 5.34c** shows an amorphous SPP in the oxide ~2 μm away from the metal-oxide interface.

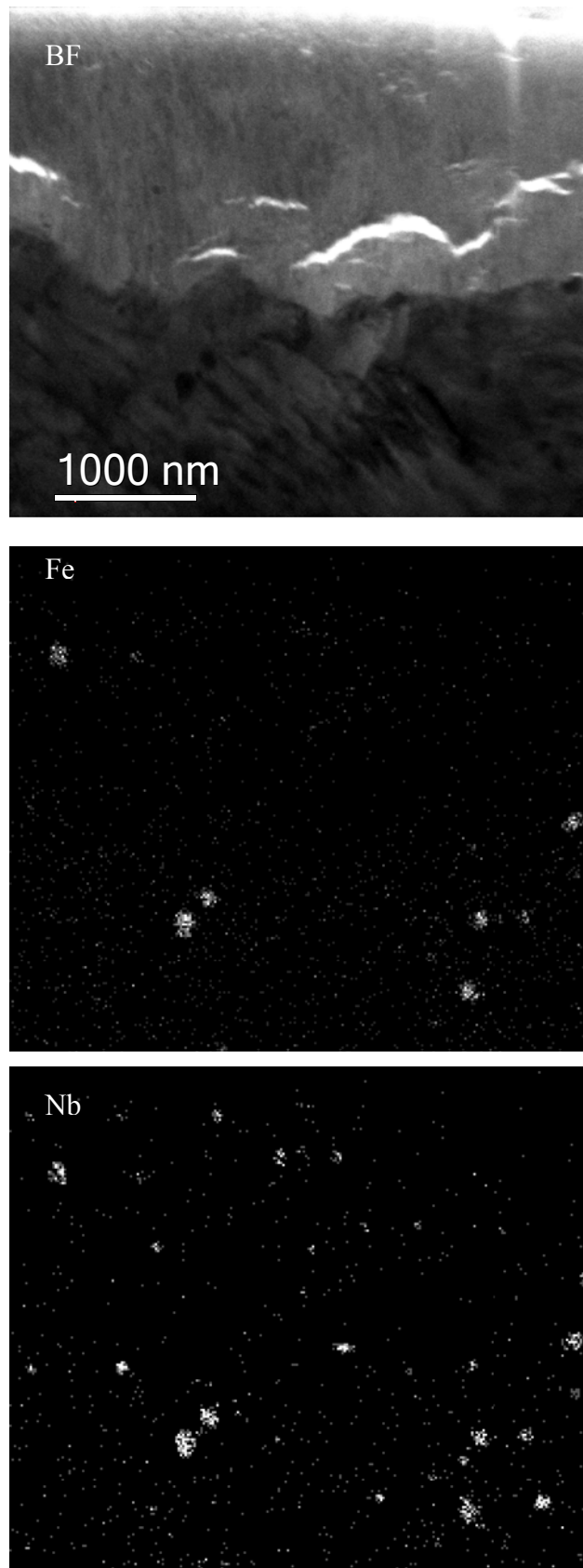


Figure 5.33 STEM-EDX bright field image and Fe, Nb maps of 120 days ZIRLO RXA oxide sample containing both the oxide and part of the metal. SPPs containing only Nb have a smaller size than these containing both Fe and Nb.

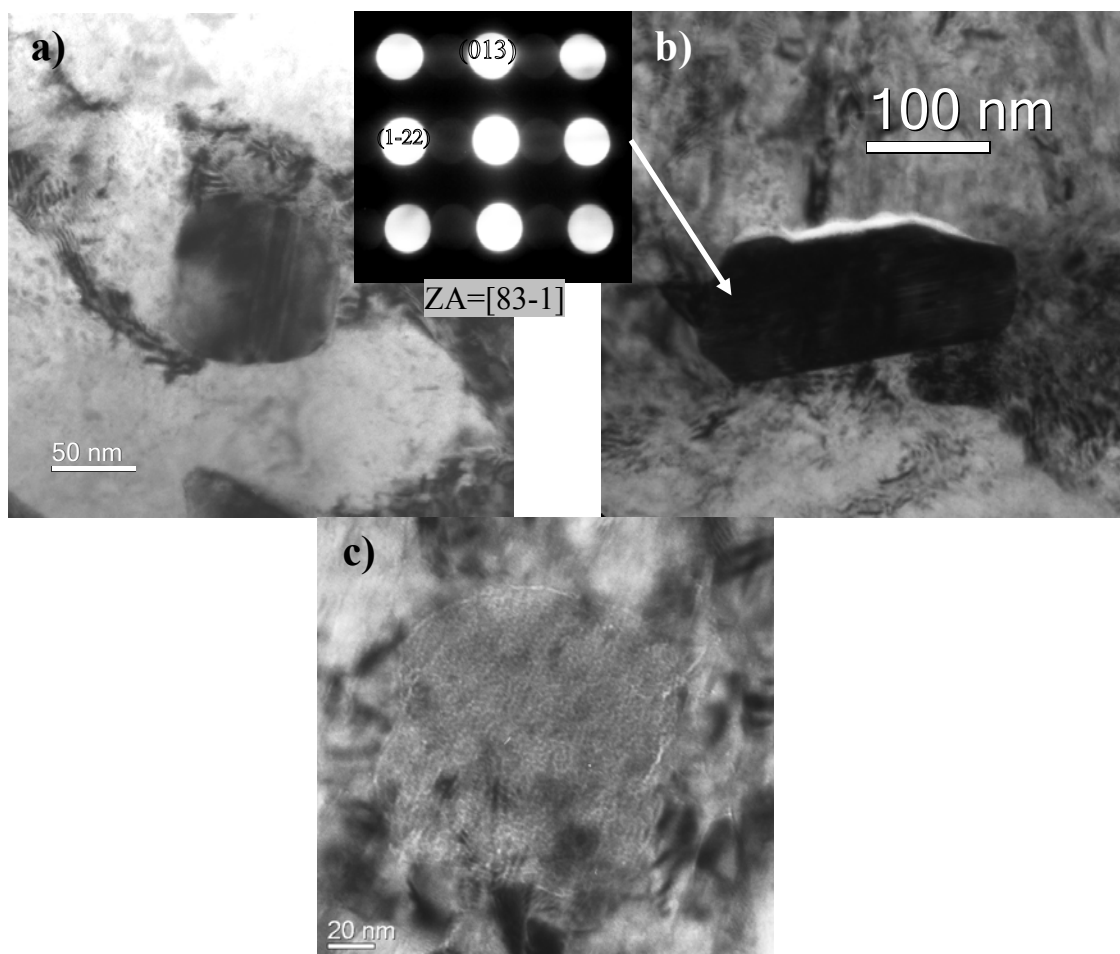


Figure 5.34 SPPs in a) the metal matrix of Zircaloy-4 RXA tube, b) the oxide adjacent to the metal-oxide interface in the 34 days Zircaloy-4 RXA sheet sample and c) the oxide $\sim 2\mu\text{m}$ away from the metal-oxide interface in the 180 days Zircaloy-4 RXA sheet oxide.

Figure 5.35a shows a STEM bright field image and Fe, Cr elemental maps from an oxide grown on Zircaloy-4 RXA sheet after 180 days. The intensity of Fe in the precipitates away from the metal-oxide interface decreases compared to the ones near the interface. The precipitate detected near the top of the oxide (circled in the EDX maps) was found to have a Fe/Cr ratio of ~ 0.5 . A bright field image of this precipitate is shown in **Figure 5.35b**. At the precipitate location, Fe and Cr were detected, but no well-defined precipitate morphology can be seen in the image. A similar Fe/Cr ratio was also found for a precipitate ~ 700 nm away from the metal-oxide interface.

Occasionally precipitates containing Fe and Ni were found in Zircaloy-4 samples and their structure matches BCT $\text{Zr}_2(\text{Fe},\text{Ni})$ ($a = \sim 0.650$ nm, $c = \sim 0.527$ nm). **Figure 5.36** shows an example of this type of precipitate in a STEM-HAADF image, with associated micro-

diffraction pattern and EDX line profile across the SPP. The presence of Ni is obvious. Occasional amorphous SPPs were found in the middle of oxides on the 180 days Zircaloy-4 RXA sheet, which EDX analysis showed contained Ni in addition to Fe, so the Ni containing SPPs also appeared to become amorphous more easily in the oxide layer than the Zr-Fe-Cr SPPs.

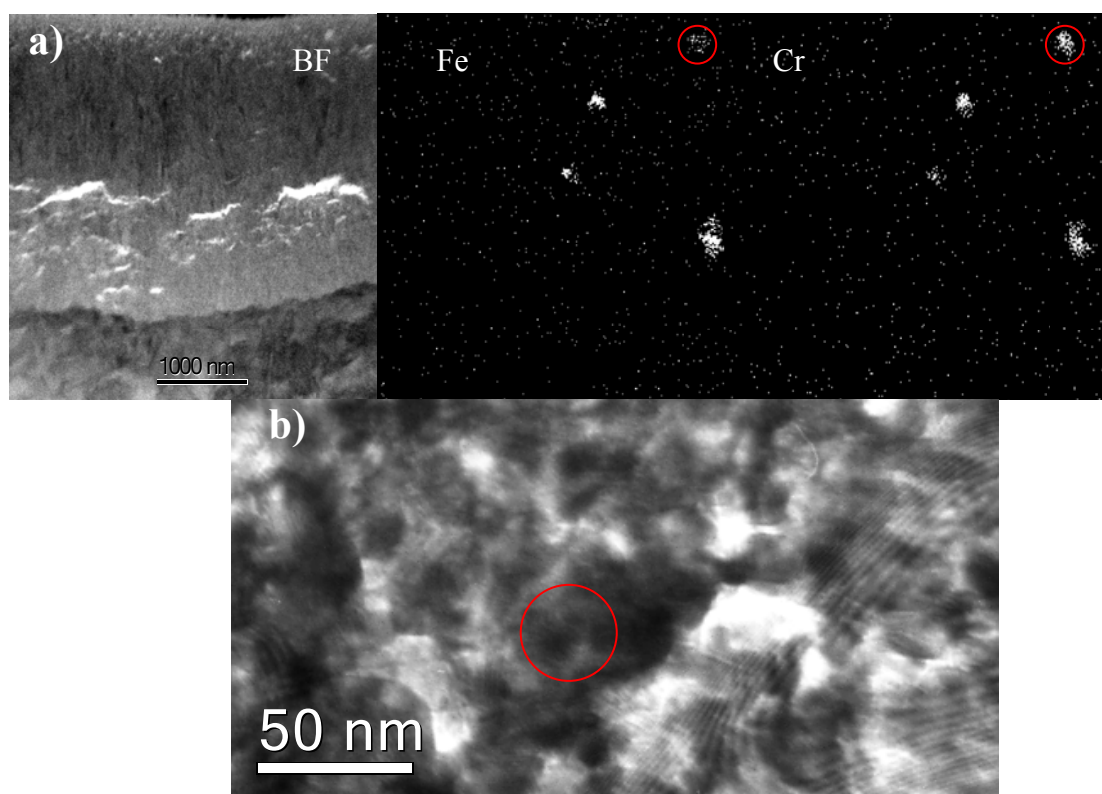


Figure 5.35 a) STEM-EDX bright field image and Fe, Cr map of 180 days Zircaloy-4 RXA sheet oxide sample containing both the oxide and part of the metal. The SPP (circled) close to the oxide top contains decreased Fe than those in the inner oxide. b) Bright field image of the SPP showing no well-defined shape. The location was confirmed by EDX.

5.4.2 Discussion

As a result of a low solubility in Zr, alloying elements such as Fe, Nb and Cr form intermetallic precipitates with Zr. In ZIRLO, Yilmazbayhan et al. [138] reported β -Nb precipitates while Sabol et al. [53] found Zr-Nb-Fe type precipitates with a hexagonal structure in addition to the β -Nb, in agreement with my observations. I found that the β -Nb precipitate can also contain low levels of Fe (~ 1 at %), which has not been reported before. The composition of the Zr-Nb-Fe SPPs found by EDX is approximately $\text{Zr}_{0.5}\text{Nb}_{0.3}\text{Fe}_{0.2}$,

similar to that reported in [53] except for the presence of up to ~2 at.% Cr found in the current work. 3D atom probe analysis has revealed more accurate compositions of $\text{Zr}_{0.39}\text{Nb}_{0.33}\text{Fe}_{0.25}\text{Cr}_{0.02}$, which agree reasonably well with the EDX measurements when a contribution from the Zr matrix is taken into account. Therefore, the composition of these SPPs is better described as $\text{Zr}(\text{Nb,Fe,Cr})_2$ as reported by Liu et al. [267] for a Zr-Sn-Nb-Fe-Cr alloy. The average size of the β -Nb SPPs appears to be smaller than the Zr-Fe-Nb ones as can be seen from **Table 5.4** and **Figure 5.33**, which also confirms previous observations [53]. The types of the precipitates found in the Zr-Nb-Ti test alloy are similar to those in ZIRLO.

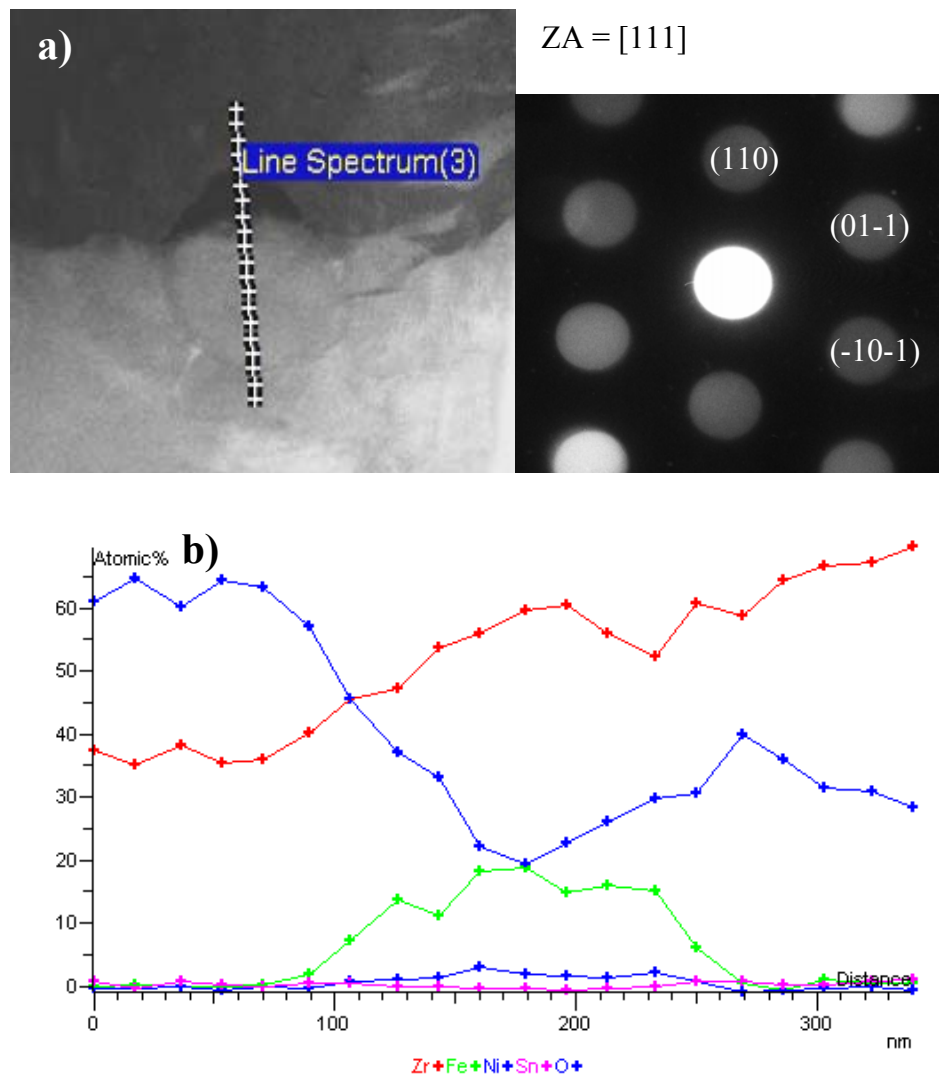


Figure 5.36 Top left: STEM-HAADF image of a second phase particle in the metal adjacent to the oxide/metal interface. Top right: micro-diffraction pattern taken from the SPP showing a BCT $\text{Zr}_2(\text{Fe,Nb})$ structure. Bottom: line profile of Zr, Fe, Ni content along the line across the SPP.

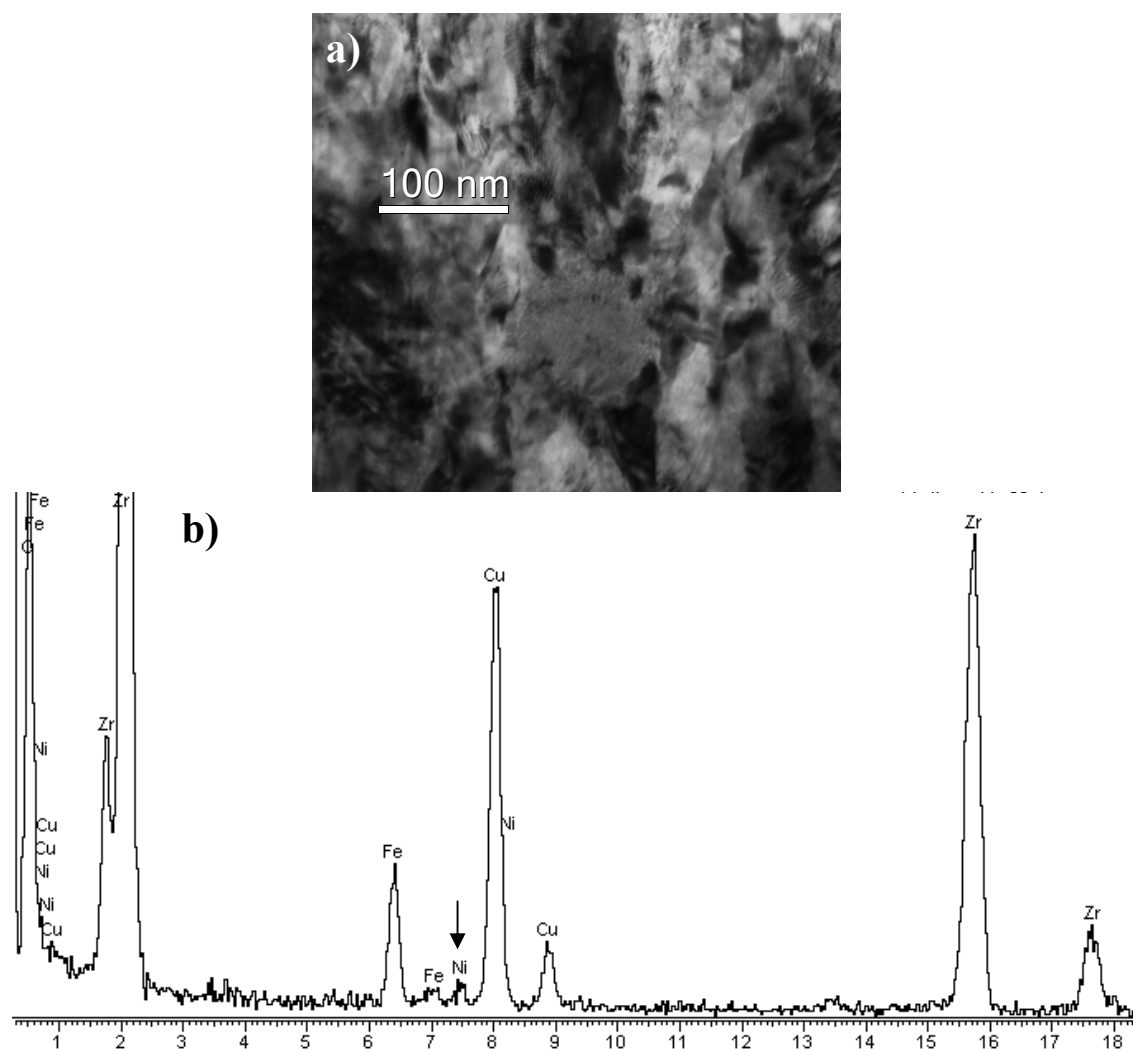


Figure 5.37 a) BF image of an amorphous SPP found in the middle of the 180 days Zircaloy-4 RXA sheet oxide. b) The EDS spectrum shows that it contains Ni in addition to Fe.

Some of the SPPs incorporated in the oxide remain crystalline while some of them become amorphous as would be expected as a result of oxidation. In the oxide within $\sim 1\mu\text{m}$ of the metal-oxide interface, it appears that the amorphous SPPs are bigger than the crystalline ones and contain a high content of Fe. The shortest distance to the metal-oxide interface where a bigger amorphous SPP with high Fe content was observed was only $\sim 270\text{ nm}$. All these observations tend to suggest that the Zr-Nb-Fe type precipitates are oxidized faster than the β -Nb type SPPs when incorporated into the oxide. Yilmazbayhan et al. [138] reported that β -Nb SPPs in Zr-2.5Nb oxides were amorphous more than $\sim 800\text{ nm}$ away from the metal-oxide interface, and Bossis et al. [268] reported amorphous Nb precipitates at $\sim 1\text{ }\mu\text{m}$ for oxide grown on a Zr-1Nb-O alloy. Current work found a similar distance of $\sim 1\mu\text{m}$ above which

amorphous SPPs containing mainly Nb were found. The amorphous SPPs appear to dissolve in the outer oxide further away from the Zr metal as the interface between the amorphous SPP and oxide becomes more diffuse. Again this appears to happen earlier for the Zr-Nb-Fe precipitates, as further away from the interface ($\sim 1.5 \mu\text{m}$ for the sample shown in **Figure 5.33**) only small Nb precipitates were found. The Nb/Fe ratio for the hexagonal $\text{Zr}(\text{Fe,Nb})_2$ type precipitates in the oxide increases compared those in the metal, from ~ 1.3 to $\sim 2.1\text{-}2.5$, similar to the same type of Zr-Nb-Fe precipitates in a $\text{Zr} - 0.7\text{Nb} - 0.1\text{Fe}$ alloy (from 1.86 to 2.83) [269]. Therefore, the oxidation and dissolution is likely to be preceded by out-diffusion of Fe, in agreement with previous studies that suggested that diffusion of Nb from the β -Phase to the surrounding ZrO_2 was difficult [93, 112]. The differences in oxidation behaviour between β -Nb and hexagonal Zr-Nb-Fe precipitates are likely be related to their different alloying elements and crystal structures [270].

$\text{Zr}(\text{Fe,Cr})_2$ type precipitates were observed in Zircaloy-4, as reported in [182]. They show delayed oxidation compared to Zr and remain crystalline in the inner oxide. Further away from the metal-oxide interface they gradually oxidize, characterized by a decrease in the Fe/Cr ratio due to preferential out-diffusion of Fe. A decrease in Fe/Cr ratio to ~ 0.4 was already found for a SPP $\sim 800 \text{ nm}$ away from the interface. All these observations are in good agreement with previous studies [138, 193, 194].

Although not frequently, the presence of SPPs containing Ni and having a BCT $\text{Zr}_2(\text{Fe,Ni})$ structure is observed, which is not expected since Ni is not a normal addition in Zircaloy-4. However, 3D atom probe analysis (D. Hudson, Oxford Materials) has revealed traces of Ni in the same Zircaloy-4 material, confirming the presence of Zr-Fe-Ni precipitates. The only amorphous SPP observed in the oxide below $\sim 2 \mu\text{m}$ from the metal-oxide interface was found to contain Ni, consistent with the observation by Li et al. [197] that $\text{Zr}_2(\text{Fe,Ni})$ oxidized faster than $\text{Zr}(\text{FeCr})_2$.

Due to the delayed oxidation, SPPs will remain metallic while the zirconium metal surface on either side is being consumed. As a result, the volume change around the SPP as new oxide is created will necessarily result in the creation of a void or crack at the top of the particle. Therefore, a crescent shaped crack was always found to be associated with a crystalline SPP when it was incorporated into the oxide, as also observed by other researchers [138, 271]. As a result, the SPPs can serve as a nucleation site for cracks, as will be discussed in more detail in Chapter 7.

Later, oxidation of fully incorporated SPPs can induce extra stresses due to volume expansion, and Fe containing SPPs can dissolve in the zirconia during oxidation. These two effects have been recognized to be helpful in stabilizing the tetragonal phase via stress and dopant effects [215, 222]. The presence of tetragonal ZrO_2 near the oxidized amorphous SPPs was confirmed in this work. The destabilization of tetragonal ZrO_2 and its transformation to the monoclinic phase has been considered to be one of the possible mechanisms correlated to the kinetic transition. Therefore a slower oxidation of SPPs is considered to be beneficial in maintaining a thicker oxide layer where the $t \rightarrow m$ transformation is retarded. This might to some extent explain the slower oxidation rate of Zircaloy-4 compared to that of ZIRLO observed in the current work, since oxidation of Zr-Nb-Fe precipitates in ZIRLO appears to be happening faster than oxidation of the Zr-Fe-Cr precipitates in Zircaloy-4. In addition, the unusual presence of $\text{Zr}_2(\text{Fe,Ni})$ type precipitate found in the studied Zircaloy-4 alloy may also have a harmful effect since this precipitate oxidized even faster.

5.5 Hydride growth

5.5.1 Observations

Acicular hydride precipitates were observed in the metal matrix near the metal-oxide interface of oxidized ZIRLO samples. Examples of these hydrides in several samples are

shown in **Figure 5.38**. The crystal structure of the hydrides was found by micro-diffraction analysis to match face centred tetragonal γ -ZrH ($a = \sim 0.460$ nm, $c = \sim 0.497$ nm) [272] and/or face centred cubic δ -ZrH_{1.5} ($a = \sim 0.479$ nm). The aspect ratio of the hydrides was found to be ~ 10 -15 in the 34 days pre-transition ZIRLO RXA oxide sample. In the grey oxide of the 140 days post-transition sample, some of the hydrides were found to have a more plate-like morphology, with a smaller aspect ratio of ~ 7 -8 (**Figure 5.38c**). Occasionally, micro-diffraction revealed evidence for the presence of face centred tetragonal ϵ -ZrH₂ ($a = \sim 0.352$ nm, $c = \sim 0.445$ nm) [273] in the 100 and 120 days ZIRLO RXA oxide samples, but no well-defined morphology of the hydride was found.

Figure 5.39 shows back-scattered electron images of the metal below the oxide scale for the 34 days RXA ZIRLO oxide sample and the 140 days grey oxide sample, where clusters of hydrides are seen with a darker contrast in the metal. The hydrides appeared to concentrate in the metal within some distance from the metal-oxide interface. The distances were found to be bigger in the 140 days post-transition sample than in the 34 days pre-transition ZIRLO RXA sample, $\sim 5\mu\text{m}$ and $\sim 2\mu\text{m}$ respectively.

Similar hydrides were found in oxidized Zircaloy-4 samples. An example is shown in **Figure 5.40** for the 180 days post-transition oxide on Zircaloy-4 RXA sheet. The aspect ratio of the hydrides was found to be in the range of 8-20, bigger than in the post-transition ZIRLO oxide samples.

5.5.2 Discussion

It has been shown from glow discharge spectroscopy that the hydrogen profile had a peak located at the metal-oxide interface in a post-transition Zircaloy-4 oxide [27]. The authors suspected that it could be due to hydrides in the metal just below the metal-oxide interface, which is the location where the hydrides were observed in this work.

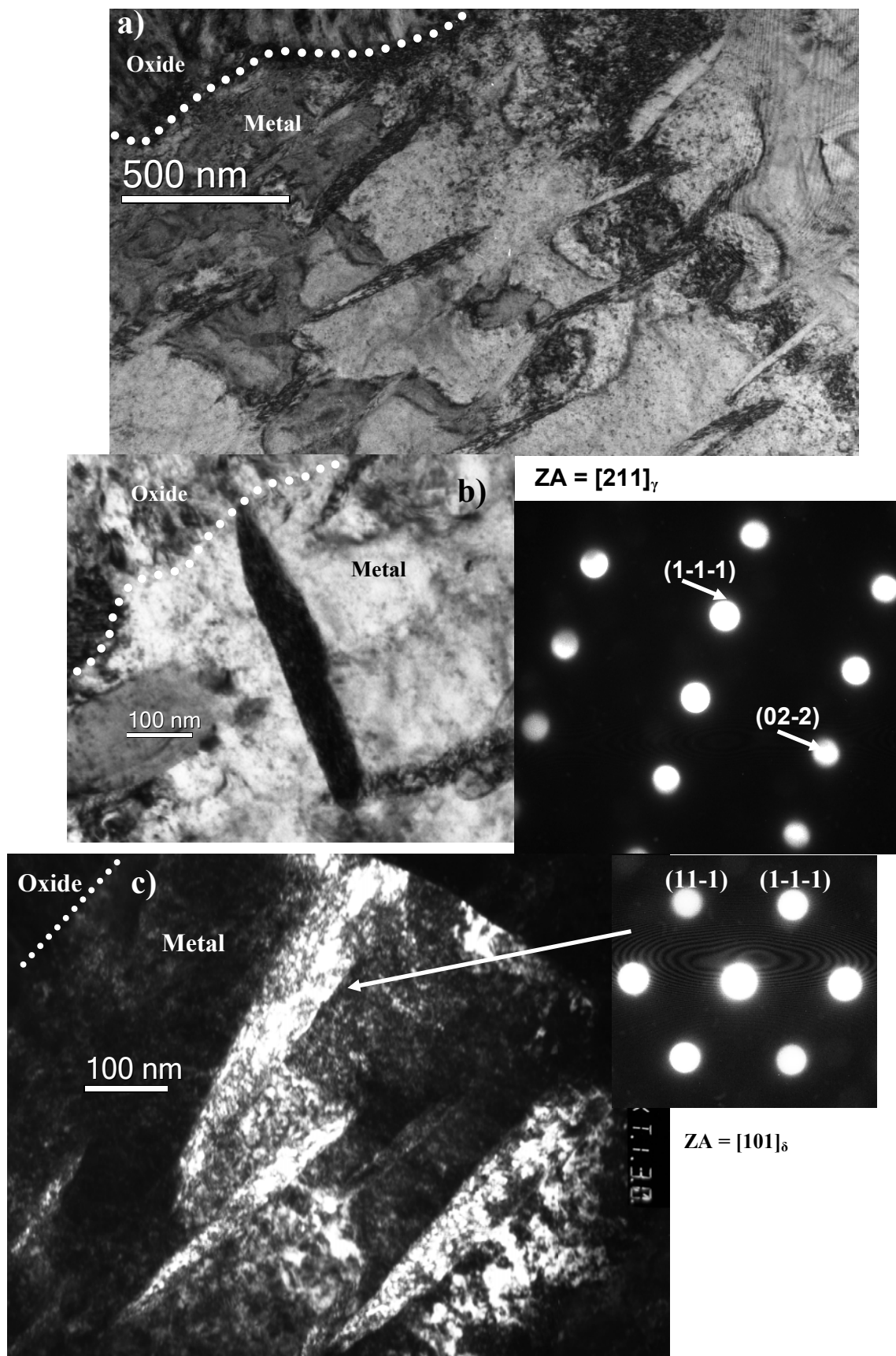


Figure 5.38 a) BF of hydrides observed in the metal of 34 days ZIRLO RXA oxide sample. b) BF of hydrides observed in the metal of 140 days ZIRLO RXA grey oxide sample together with its micro-diffraction pattern showing a γ -ZrH structure. c) DF of hydrides observed in the metal of 140 days ZIRLO RXA grey oxide sample and its micro-diffraction pattern showing a δ -hydride structure.

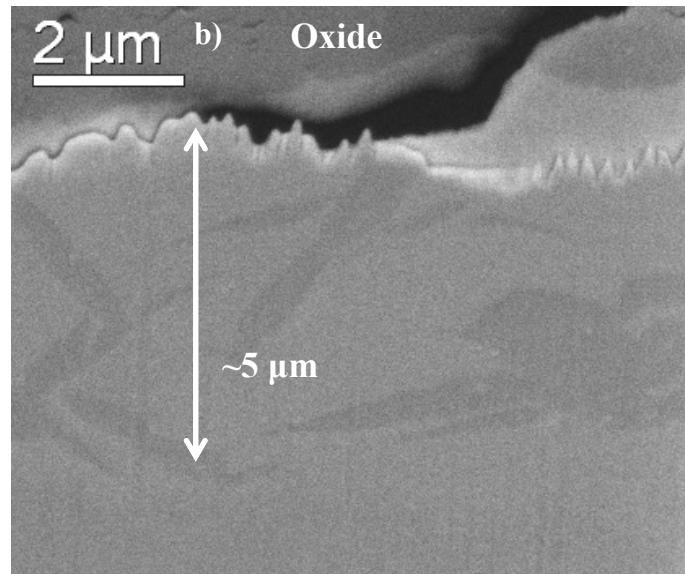
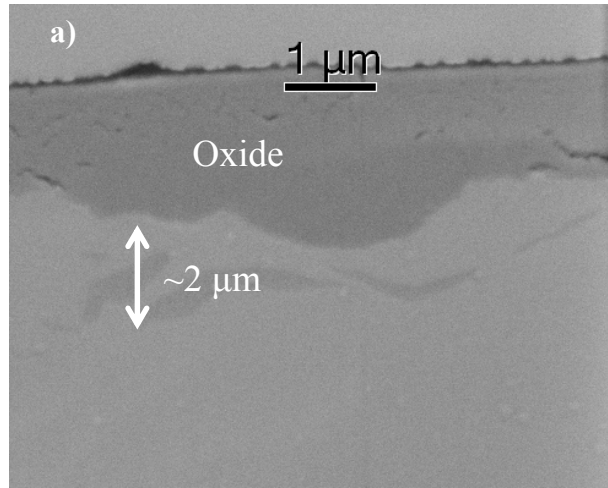


Figure 5.39 Back scattered electron images of the metal below the oxide scale in a) the 34 days RZA ZIRLO corroded sample and b) the grey oxide of the 140 days RZA ZIRLO sample.

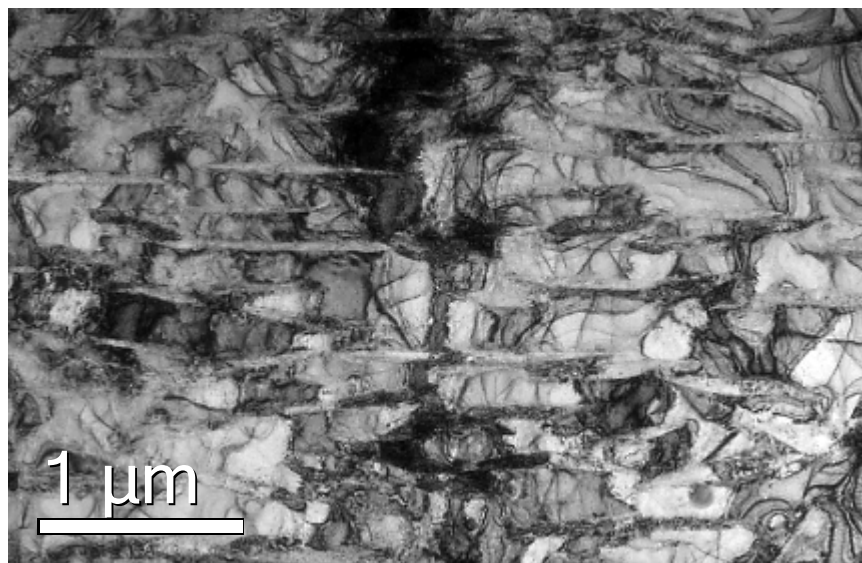


Figure 5.40 BF of hydrides observed in the metal of 180 days Zircaloy-4 RZA oxide sample.

In this work, distinguishing between γ - and δ - hydrides was often impossible due to the similarity in lattice parameters between the two structures. In some cases one structure showed a better match to the experimental pattern than the other, which leads to a conclusion that both types were present. For ZIRLO samples, there was a trend that hydrides with a smaller aspect ratio (more plate-like) matched better to the δ phase, which agrees with previous observations that δ phase was more blocky [274].

The γ -ZrH hydride, which is metastable, has been reported to be favoured in the case of low hydrogen content and faster cooling rate, and was shown to be present in Zr-2.5Nb with 7 wppm hydrogen [274]. Therefore it is likely that some of the hydrides observed in this work, probably γ -ZrH, were formed already in the metal before oxidation since the starting alloys are expected to contain traces of hydrogen (~ 3 -5wppm according to data reported for ZIRLO supplied by Westinghouse Corp.[10]). On the other hand, hydrogen uptake during the oxidation process in high temperature water is expected, and upon cooling to room temperatures, hydrides will form due to a decreased solubility of hydrogen in Zr [2, 5, 274]. Hydride formation may also be induced by the FIB milling process, as has been shown for Ti [275]. However, the FIB process in the vacuum condition is not expected to provide a strong source of hydrogen pick-up. Other processes involved in the sample preparation procedure, for example cleaning of the samples with acid or acetone before and after autoclave oxidation, may have led to some hydrogen absorption in the sample. But the hydrides observed in different samples are still considered to be comparable since all the samples were treated with the same process. In addition, as the hydrides were found only near the metal-oxide interface, it is not likely that they are just artefacts from the sample preparation process. It has been found that both the width of the region below the metal-oxide where hydrides concentrate and the density of hydride, especially the plate-like hydride (probably δ phase), has increased from the 34 days pre-transition oxide to the post-transition oxide. This indicates an increasing

hydrogen pick-up, which can only result from the aqueous oxidation process. This may have led to the growth of pre-existing hydrides and favoured the formation of δ -ZrH_{~1.5} hydrides, resulting in the more plate-like hydrides observed in the metal adjacent to the metal-oxide interface in post-transition ZIRLO oxide. Therefore, a correlation between higher oxidation rate and higher hydrogen pick-up in the post-transition oxide is suggested by these observations, in agreement with previous studies [13, 72]. Whether faster oxidation is a result of hydride formation or vice versa is an open question, but the latter is probably the case in this work since no dramatic morphology change was observed associated with these hydrides.

6 Characterization of the Zr metal-oxide interface

Understanding the processes that occur at the metal-oxide interface is crucial for a full mechanistic model of the oxidation process as this is where new zirconium oxide forms. In this chapter, the characterization of the interface morphology, chemistry and crystallography in samples at different stages of the oxidation weight-gain curve shown in **Figure 4.2** will be described and discussed.

6.1 Interface morphology

2-4 specimens for each oxide sample have been prepared and in each specimen a length at least 2-3 μm of the metal-oxide interface have been investigated.

Figure 6.1 shows typical bright field images of the metal-oxide interface in the pre-transition 90 days Zircaloy-4 RXA tube oxide. A metal-oxide interface well defined by the abrupt termination of columnar oxide grains is apparent in **Figure 6.1a**. A particularly interesting feature is the existence of strongly diffracting grains between these columnar oxide grains and the more 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 6.1b, c and d**, and small equiaxed grains of this type were always found along the metal-oxide interface in this oxide sample.

Figure 6.2 shows typical bright field images of the metal-oxide interface in the oxides grown on ZIRLO RXA sheet after 34, 100 and 140 days (grey oxide). The first two pre-transition oxides (**Figure 6.2a and b**) exhibit similar interface morphology to that described for the pre-transition Zircaloy-4 RXA tube oxide, but sometimes with saw-tooth morphology

of strongly diffracting grains at the interface. The interface in the post-transition grey oxide of ZIRLO RXA (**Figure 6.2c**) shows more often columnar oxide grains directly growing from the large metal grains with occasionally smaller interfacial grains (~20 nm or below) of rectangular shape.

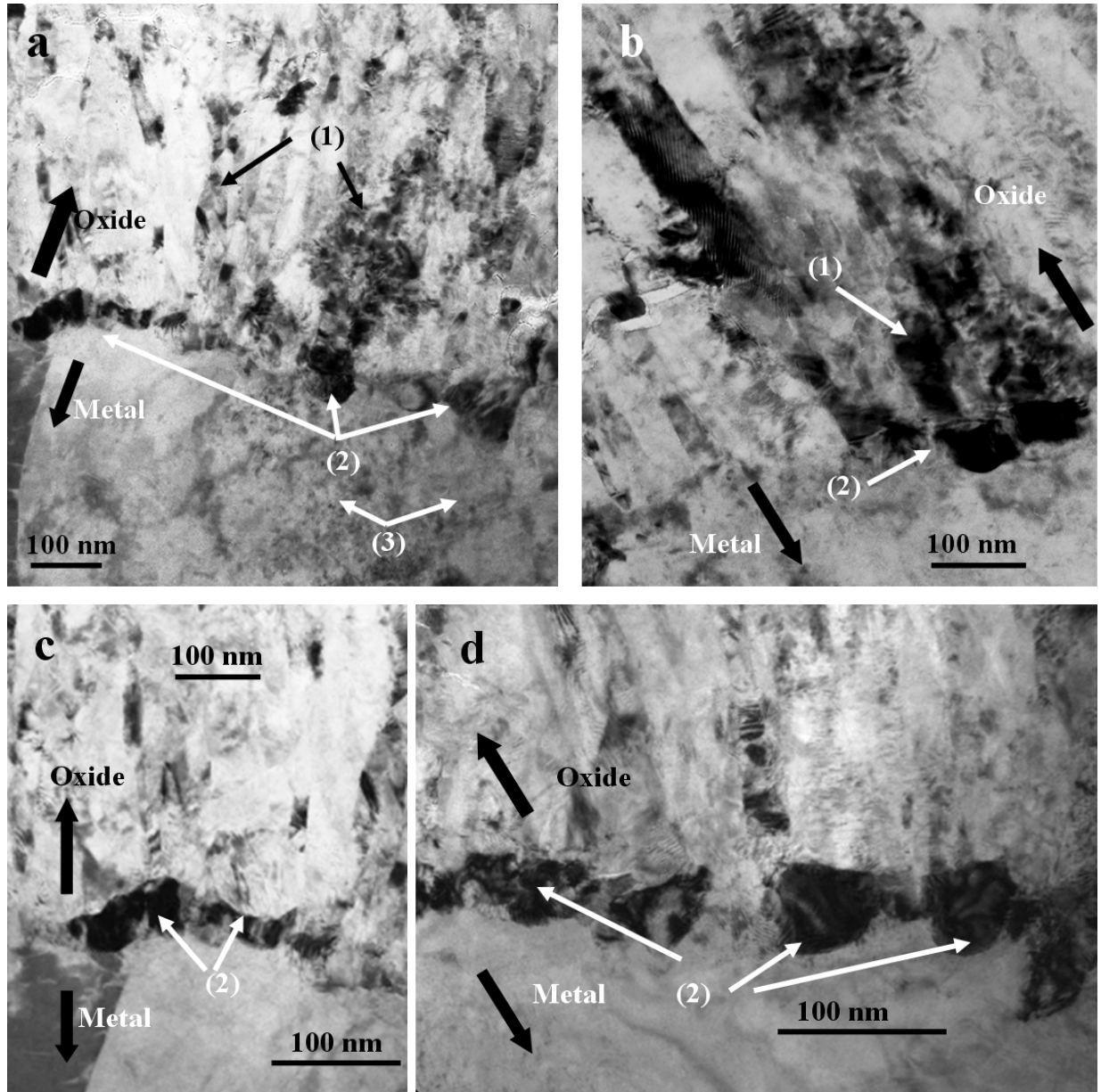


Figure 6.1 a) A typical TEM bright field image of the 90 days Zircaloy-4 RXA oxide where the metal-oxide interface is clearly defined by the termination of the characteristic morphology of the columnar monoclinic grains (1). An intermediate structure (2) may be seen between the columnar oxide and equiaxed metal grains (3). More examples of this intermediate structure in different specimens of the same oxide are given in bright field TEM images b), c) and d).

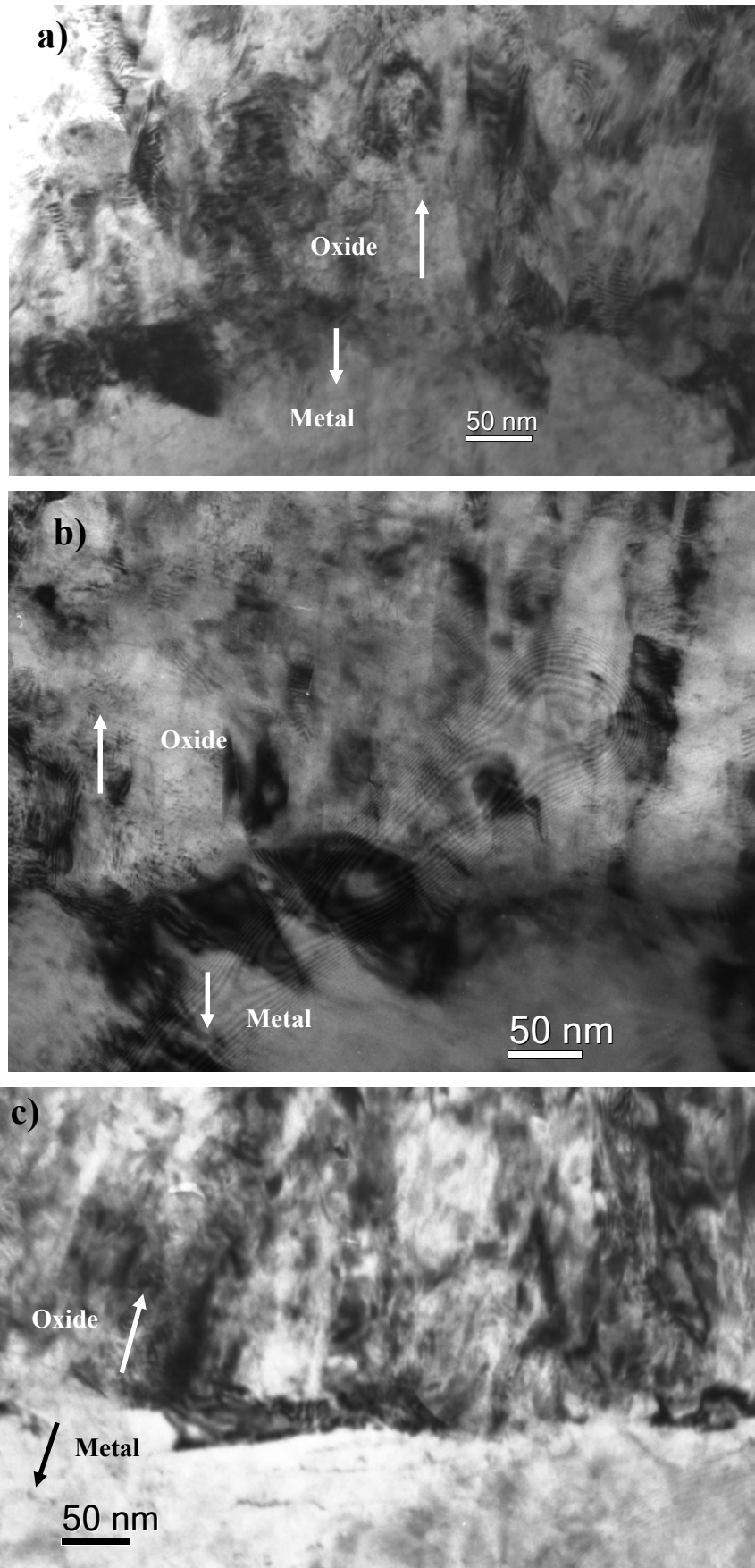


Figure 6.2 BF images of metal-oxide interface morphology for a) 34 days, b) 100 days and c) 140 days (grey oxide) ZIRLO RXA samples.

Bright field and dark field images of the metal-oxide interface in the post-second transition Zr-Nb-Ti oxide are shown in **Figure 6.3**. The interface is less well-defined compared to other samples. Equiaxed oxide grains are seen on the top of large metal grains. In the dark field image, the metal region just beneath the interface was also diffracting strongly, due to the use of a big objective aperture which included mainly the oxide reflections but also some of the metal reflections.

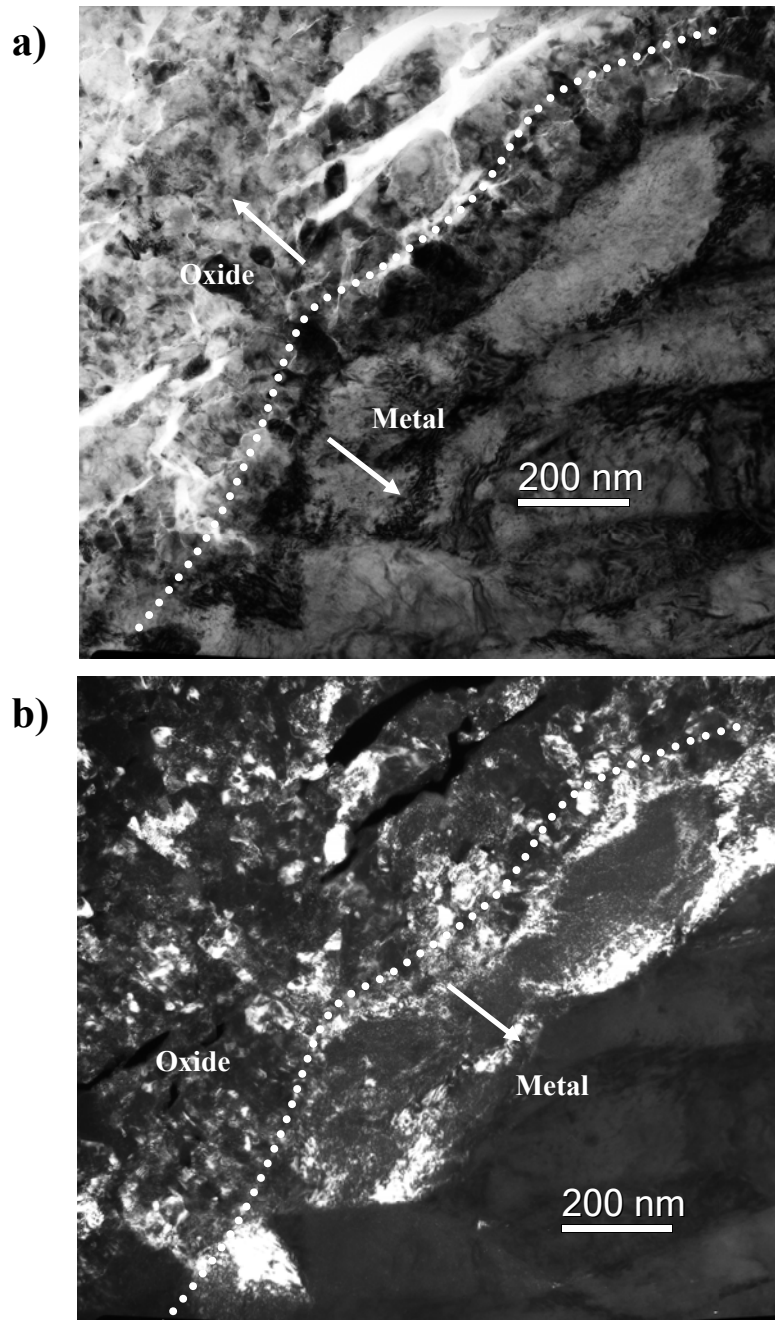


Figure 6.3 a) BF and b) DF of the metal-oxide interface in the post-second transition Zr-Nb-Ti oxide

6.2 Analysis of oxygen content at metal-oxide interface

The images in **section 6.1** suggest that a crystalline material distinct from the Zr metal substrate and the bulk ZrO_2 oxide scale can sometimes be identified at the metal-oxide interface. The oxygen content at the metal-oxide interface has been studied to investigate the possibility of suboxide at the interface.

6.2.1 Quantitative EELS analysis

Reliable quantification of the oxygen content at the metal-oxide interface has been obtained by EELS after care was taken over both the preparation of suitable TEM samples and the methodology for quantification of the EELS data. This includes inelastic partial scattering cross-section calibration against a ZrO_2 powder standard and estimation of the effective inelastic mean free path of high energy electrons in oxidised Zr-alloys. The details are described in Appendix B. An accuracy of $\pm 1\text{-}2$ at.% at best, and smaller than ± 5 at.% in general, can be estimated for the measured oxygen concentration, which allowed the detection of large stoichiometry variations at the metal-oxide interface with confidence. Details of experimental conditions used for TEM and EELS can also be found in Appendix B.

6.2.2 EFTEM characterization

EFTEM analysis has also been carried out at the metal-oxide interface for some of the samples. EFTEM spectrum images were acquired from 100eV to 650eV energy loss in steps of 10 eV so that the Zr- $\text{M}_{4,5}$ and O-K edges were included for quantification of Zr-O composition. As the EFTEM data was obtained in the Jeol 2100 at the University of Warwick, the experimentally obtained k-factor for calibrating the measured oxygen content (described in Appendix B) could not be used. However, from previous EELS measurements, it was found the oxide away from the metal oxide interface was stoichiometric ZrO_2 with ~ 67 at. % oxygen.

Therefore, the EFTEM quantification was internally calibrated using the stoichiometric oxide region.

6.2.3 Pre-transition oxides

Compositional analysis of the metal-oxide interface in the Zircaloy-4 oxides is shown in **Figures 6.4 and 6.5**. **Figure 6.4** shows the characterization of the metal-oxide interface in the 54 days Zircaloy-4 RXA sheet oxide. The HAADF image in a) shows a distinct layer of intermediate contrast ~50 nm thick between the metal and the columnar oxide. The EELS line profile in b) across the same interface (along the line in a)) reveals an intermediate (sub-stoichiometric) suboxide layer of similar thickness with a relatively constant oxygen content of ~ 45 % (as opposed to the ~66% oxygen measured in the bulk oxide). The oxygen content then decreases to 20 at. % within ~50 nm. A similar observation for the 90 days Zircaloy-4 RXA tube oxide is shown in **Figure 6.5**, where a ~60 nm suboxide with ~ 48 at. % oxygen can be seen. It is also clear from **Figure 6.5** that the suboxide has a complex 3D morphology and that in this region the widest region of suboxide is around 100 nm.

The observations in ZIRLO oxide samples are given from **Figures 6.6 to 6.9**. **Figure 6.6** shows the HAADF image and EELS line profile across the metal-oxide interface in the 34 days ZIRLO RXA oxide. A ~30 nm suboxide containing ~40 at.% oxygen was detected. The oxygen content then decreased slowly to ~25 at. % in the metal.

In the 100 days oxide (**Figure 6.7**), the suboxide has a width of ~40 nm. The oxygen content then decreases to ~30 at.% in the metal, which is close to the ~29 at.% solid solution limit of oxygen in zirconium metal for temperatures below 1200°C [276]. **Figure 6.8** shows bright field image of a different location at the metal-oxide interface in the same sample, the EFTEM Zr and O elemental maps, and the oxygen composition map. When a line scan extending to deeper in the metal is performed in the oxygen composition map, it appears that the oxygen

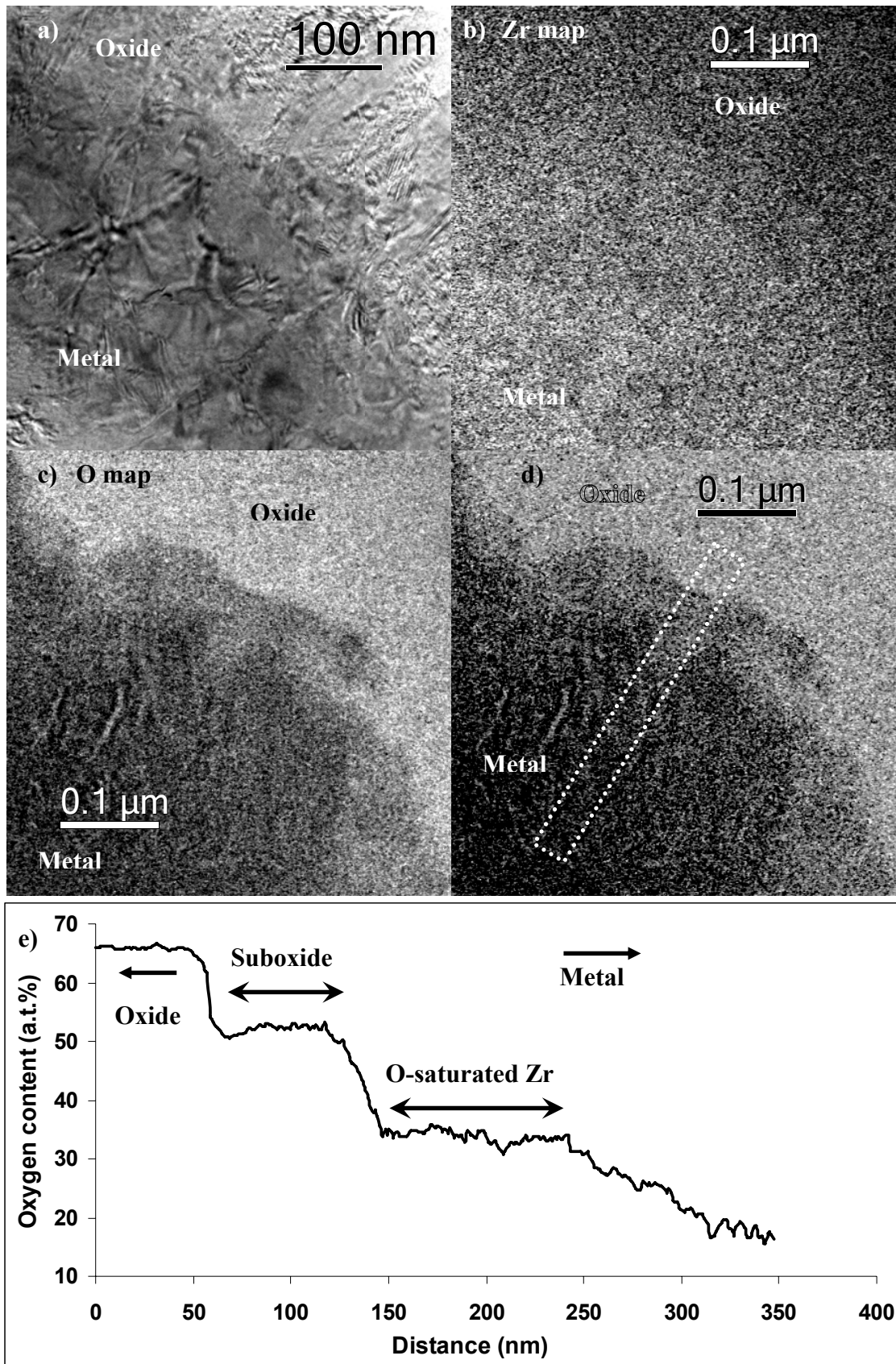


Figure 6.8 a) Bright field image of metal-oxide interface in the grey oxide of 100 days ZIRLO RXA sample. b) and c) are EFTEM elemental mapping of Zr and O respectively. d) is the oxygen composition map and e) shows a line scan across the interface region as indicated in d).

In the black oxide of the 140 days ZIRLO patchy oxide sample, the presence of a suboxide layer was detected in some regions but not in others. **Figure 6.9** gives two examples of EELS line analysis, where a very wide suboxide was detected at one position (**Figure 6.9a and b**) but in another no evidence of a suboxide was found (**Figure 6.9c and d**). In the HAADF image for the first example (**Figure 6.9a**), the complex contrast in the underlying Zr metal towards the bottom of the image makes it difficult to decide if there is a region of intermediate contrast that might suggest a suboxide layer. However, the EELS line profile (**Figure 6.9b**) across the same interface (indicated by the line in **Figure 6.9a**) shows a plateau region ~140 nm wide in the oxygen concentration with a constant value of ~50 at.% beneath the ZrO₂ with ~66 at.% oxygen, revealing the existence of a suboxide layer. Again, an oxygen concentration plateau ~120 nm wide with ~30 at.% oxygen below the suboxide can be seen in the concentration profile before the oxygen content decreases again. A similar oxygen saturated metal layer is seen in **Figure 6.9d** even when there is no clear suboxide.

6.2.4 Post-transition oxides

In most of the observations of post-transition samples, no suboxide or only a very thin suboxide layer was detected. For instance, **Figure 6.10** shows the HAADF image and EELS line analysis across the metal-oxide interface in the grey oxide of the 140 days ZIRLO RXA sample. The width of suboxide is less than 10 nm if it is present at all. It is noted that the contrast in the bright field images, which seems to suggest an intermediate layer between the metal and the oxide, is actually misleading due to the contribution of diffraction contrast in the HAADF image. **Figure 6.11** shows the bright field image and EFTEM characterization of another interface area in the same grey oxide of the 140 days ZIRLO RXA sample. Line profiles across the interface at different locations in the oxygen composition map also suggest that the suboxide is either absent or very thin (< 20nm). Here we have defined “suboxide” as a

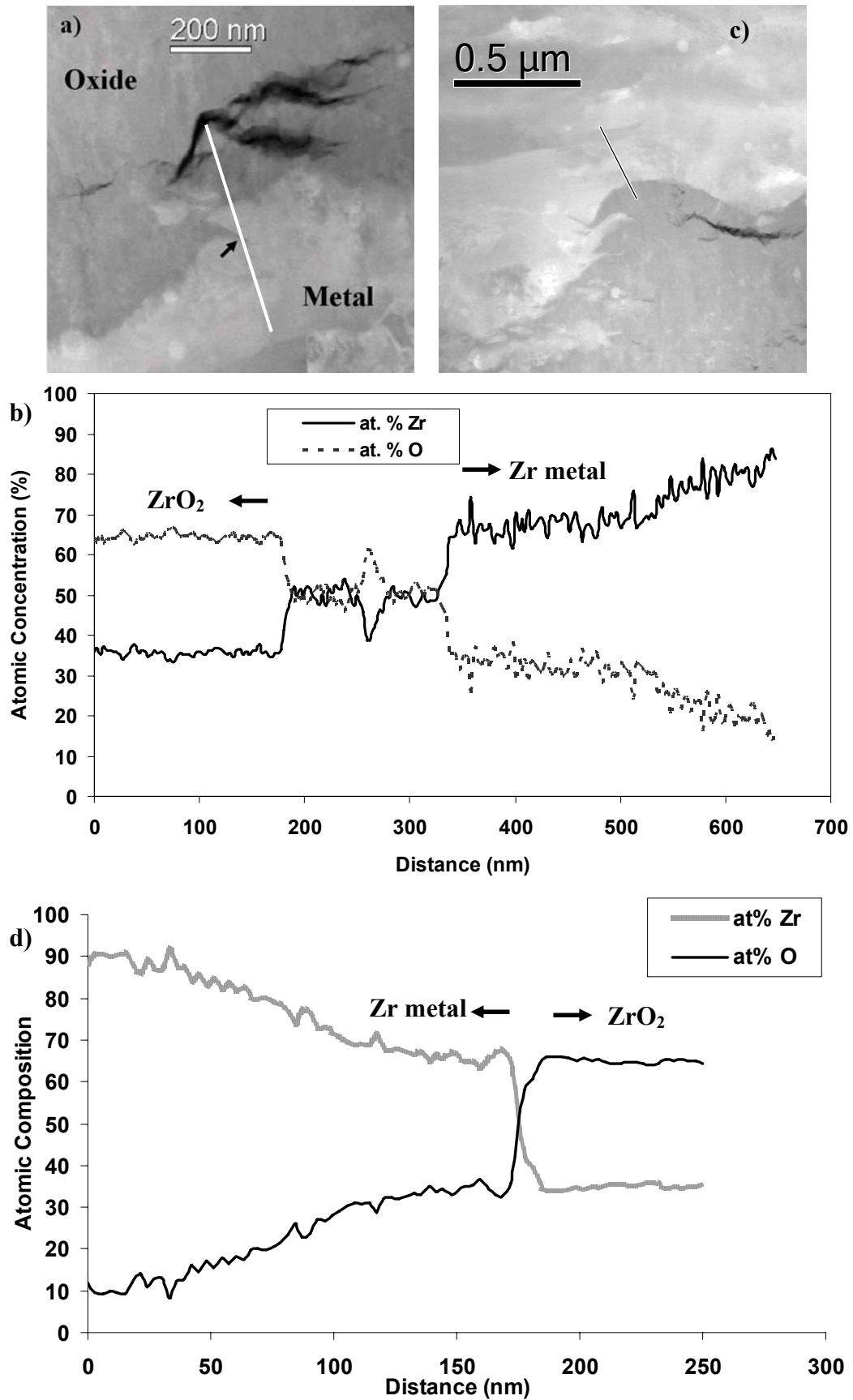


Figure 6.9 a) HAADF image of the metal-oxide interface region and b) EELS oxygen concentration line profile across the metal-oxide interface in the black oxide of 140 days ZIRLO SR tube sample showing the presence of a ~150 nm sub-stoichiometric oxide layer, while at another region in c), no suboxide was detected from the d) oxygen concentration line profile, only a layer of ~ 50 nm O-saturated Zr.

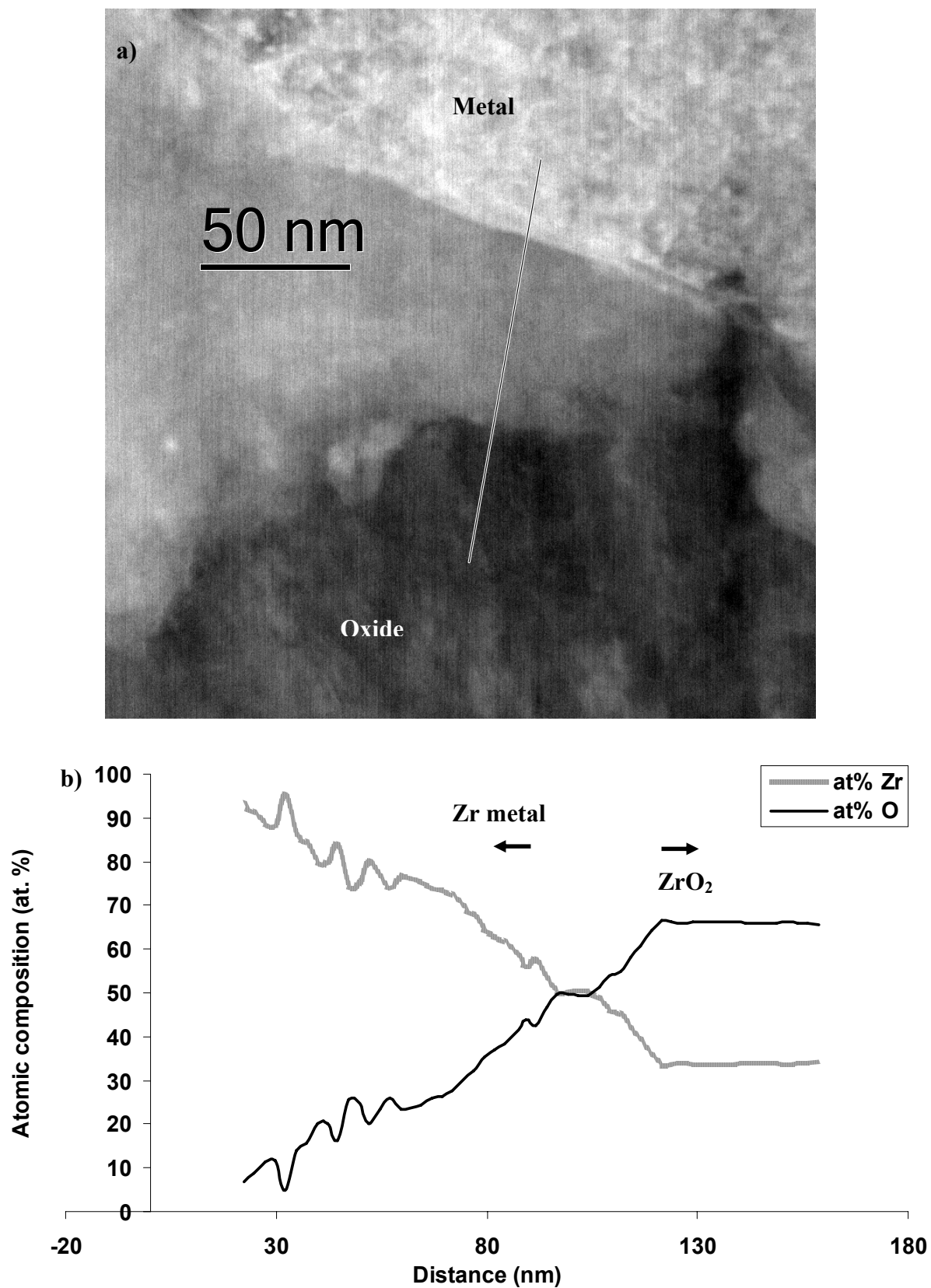


Figure 6.10 a) HAADF image of the metal-oxide interface region and b) oxygen concentration line profile across the metal-oxide interface in the grey oxide of 140 days ZIRLO RXA sample, showing no or very thin suboxide of ~ 10 nm.

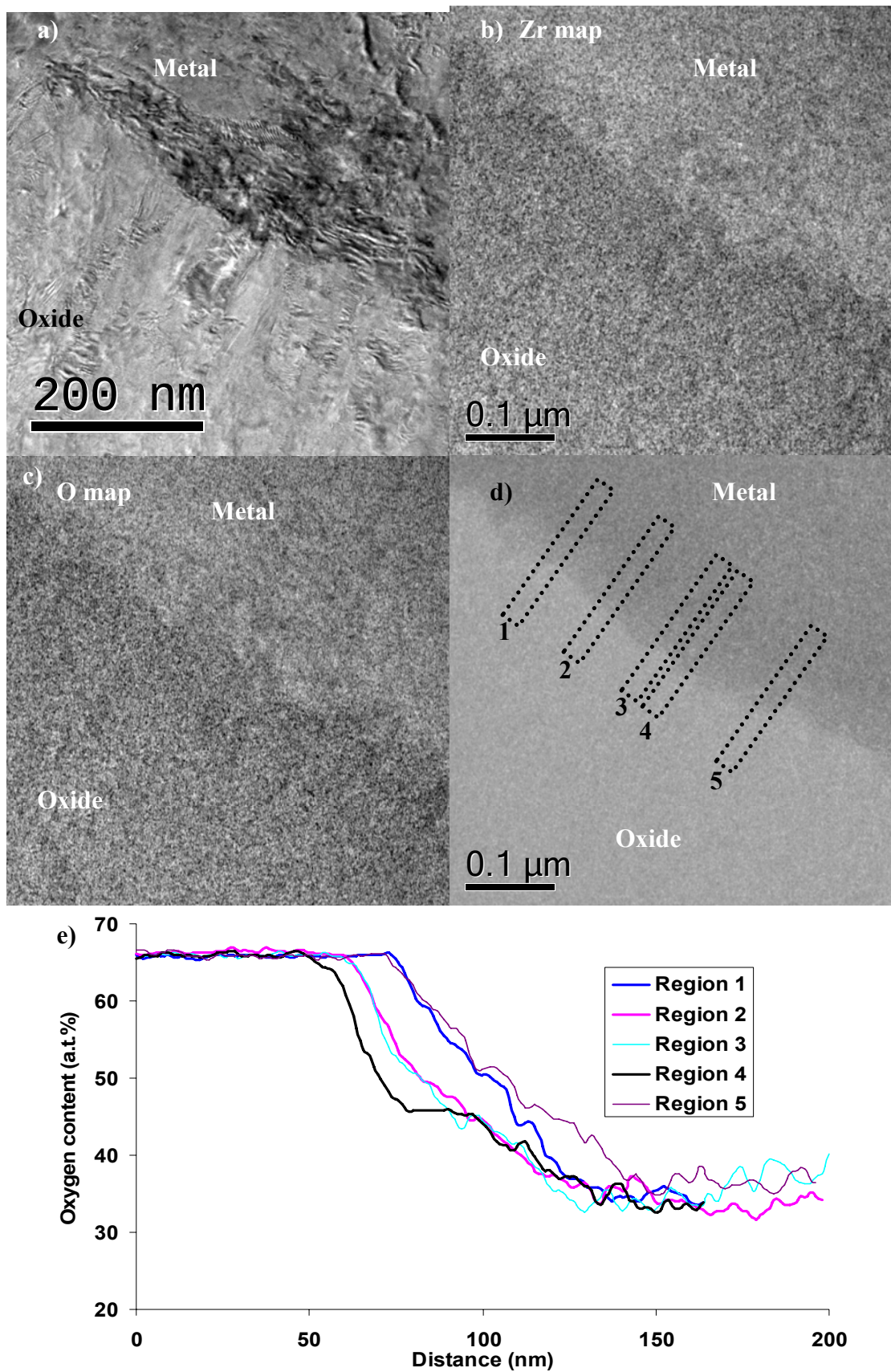


Figure 6.11 a) Bright field image of metal-oxide interface in the grey oxide of 140 days ZIRLO RXA sample. b) and c) are EFTEM elemental mapping of Zr and O respectively. d) is the oxygen composition map and e) shows line scans across 5 interface regions as indicated in d). Four of which (region 1,2,3, and 5) do not exhibit the presence of a suboxide and one (region 4) tentatively suggests a ~20 nm suboxide.

layer with a constant oxygen level, as observed in the pre-transition oxides. Obviously there is a region ~50 nm thick beneath the oxide where the oxygen concentration decays gradually but was still higher than the ~29 at. % theoretical oxygen solid solution limit in Zr. An inclined interface with respect to the beam might have led to a broadening of an atomically abrupt interface (32° for a ~50 nm interface if a ~80 nm sample thickness is assumed), which is not unlikely especially for a complex 3D interface in the samples. In the grey oxide of the 140 days ZIRLO SR sample, local variations in the presence of the suboxide have been detected. Along the interface shown in **Figure 6.12**, no suboxide was found at the more advanced oxidation interface location but a suboxide ~50 nm thick was detected at the location below a large crack where the oxidation interface is retarded. This shows that special care must be paid before making statements about the presence or absence of a suboxide layer in a particular sample without undertaking multiple measurements.

6.2.5 Post-second-transition oxide

Figure 6.13 shows a HAADF image and an EELS line profile across the metal-oxide interface in the Zr-Ti-Nb oxide, which is a post-second transition oxide. No signs of a suboxide layer can be identified. The oxygen content decays rapidly from 67.9 ± 0.4 at. % in the bulk oxide to ~10 at. % in the metal within ~40 nm. **Figure 6.14** shows a bright field image of the metal-oxide interface in the same oxide, the EFTEM Zr and O elemental maps, and the oxygen composition map. The oxygen composition line scans across the interface give no evidence for the presence of a suboxide layer. The regions containing an oxygen level higher than the ~29 at. % seen in all the datasets were quite thin (10-20 nm). In this case, a $7\text{-}15^\circ$ inclination of the metal-oxide interface with respect to the electron beam direction in a sample 80 nm thick would be sufficient to produce the observed apparent interface width. Therefore it is believed with confidence that there is little evidence for any intermediate layer at this interface.

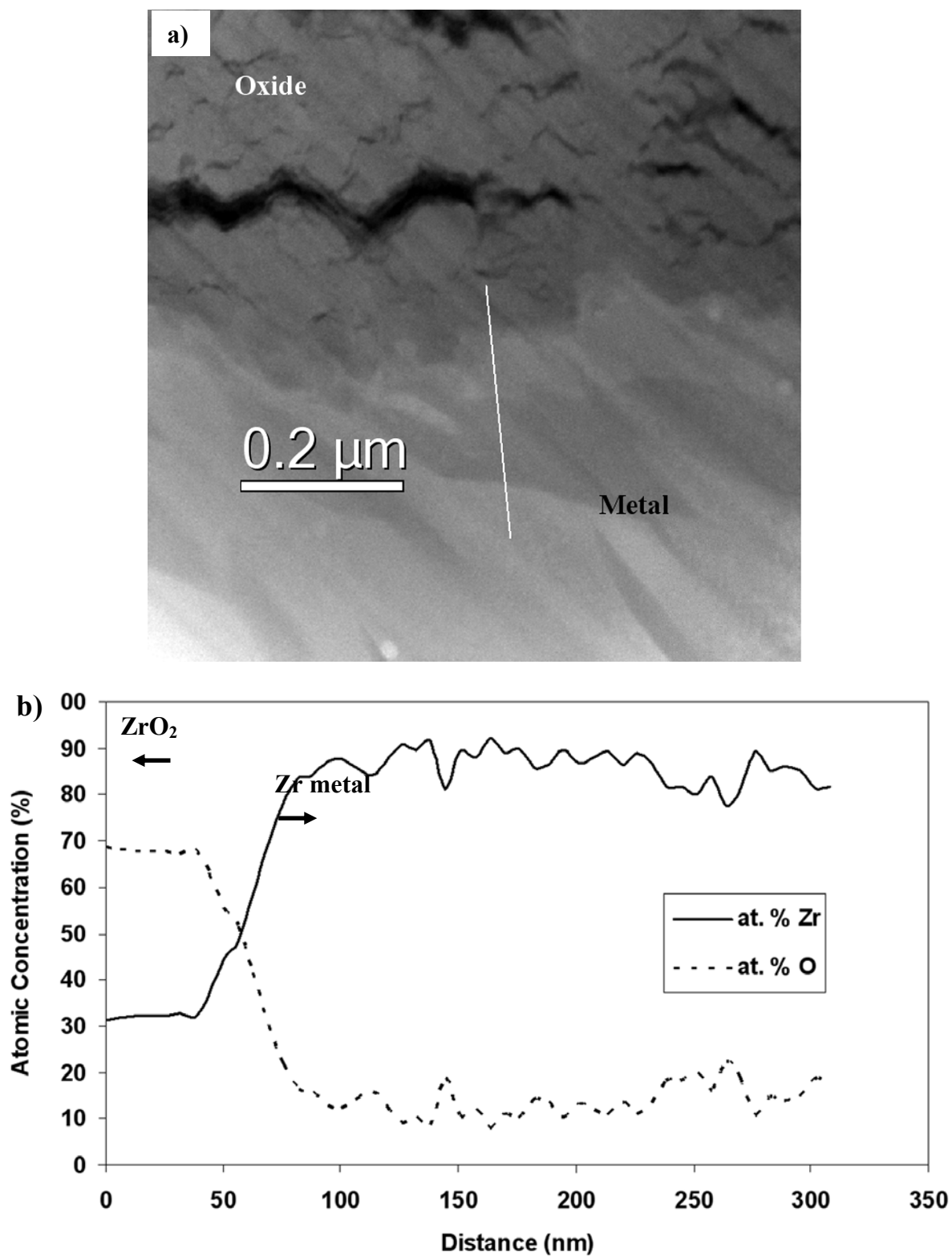


Figure 6.13 a) HAADF image of the metal-oxide interface region and b) oxygen concentration line profile across the metal-oxide interface in the $\sim 78\mu\text{m}$ post-second transition oxide grown on the model Zr-Ti-Nb-Fe alloy, where no suboxide layer can be identified.

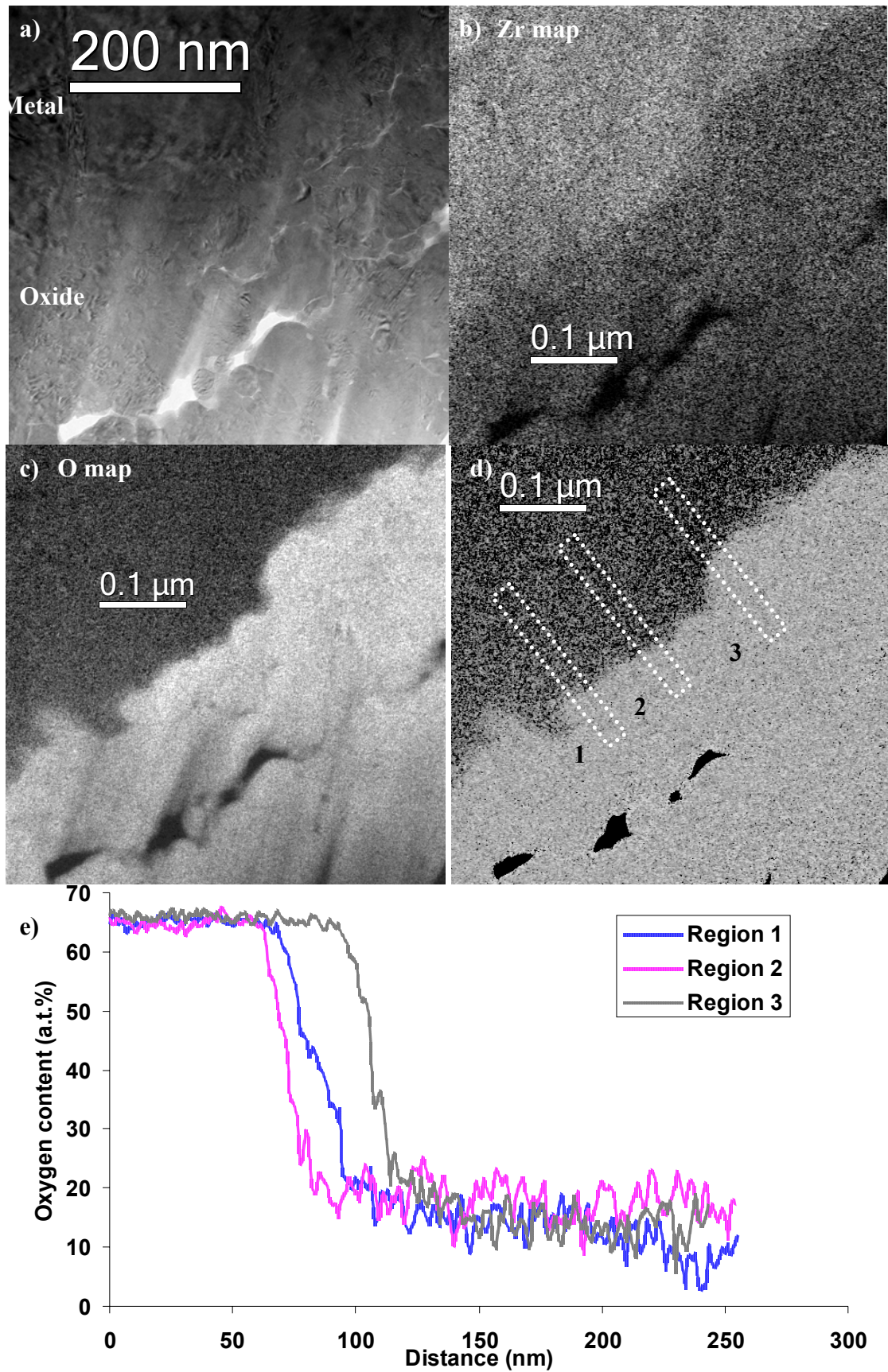


Figure 6.14 a) Bright field image of metal-oxide interface in the $\sim 78\mu\text{m}$ post-second transition Zr-Ti-Nb oxide. b) and c) are EFTEM elemental mapping of Zr and O respectively. d) is the oxygen composition map and e) shows line scans across 3 interface regions as indicated in d). No obvious suboxide layer can be seen from these regions.

6.3 Identification of interface crystal structure

The crystal structure of the interfacial grains, as shown in **Section 6.1**, has been investigated by micro-diffraction from single grains and by HRTEM in the interface regions. The investigated regions were mainly from the interface to several hundred nm into the metal, where suboxide was detected in oxide samples by nanoanalysis in **Section 6.2**.

6.3.1 Pre-transition oxides

Pre-transition oxides investigated include Zircaloy-4 RXA tube 90 days oxide, Zircaloy-4 RXA sheet 34 days oxide, ZIRLO RXA sheet 34, 100, 120 days oxides. Most frequently identified structures in the metal-oxide interface region were identified as monoclinic ZrO_2 and $\alpha\text{-Zr}$. **Figure 6.15** shows examples of strongly diffracting grains at the metal-oxide interface, the first being a monoclinic oxide grain and the second an $\alpha\text{-Zr}$ grain, with their micro-diffraction patterns. Growth of monoclinic oxide directly on $\alpha\text{-Zr}$ grains can be confirmed in some cases (**Figure 6.16**). The $\alpha\text{-Zr}$ grains were found to be orientated with their $\{01\text{-}10\}$ pole perpendicular to the oxide growth direction. Small tetragonal oxide grains were sometimes found at the metal-oxide interface, as shown already in **Figure 5.13**.

Metastable $\omega\text{-Zr}$ grains with a hexagonal structure ($a = \sim 0.503$ nm, $c = \sim 0.311$ nm) [277-279] are also commonly found in the pre-transition samples in this work. **Figure 6.17** shows an example of an $\omega\text{-Zr}$ grain with its micro-diffraction pattern, and in **Figure 6.18** more examples of the characteristic $\omega\text{-Zr}$ grain morphology can be seen. A saw-tooth shape was sometimes obvious. The $\omega\text{-Zr}$ structure grains were present mixed with the $\alpha\text{-Zr}$ grains, growing between the $\alpha\text{-Zr}$ grains and the monoclinic oxide.

Some grains had diffraction patterns that matched both Zr hydrides ($\gamma\text{-ZrH}$ or $\delta\text{-ZrH}_{1.6}$) or the FCC ZrO phase ($a = \sim 0.462$ nm) reported by [175]. An example found in the 34 days Zircaloy-4 RXA sheet oxide is given in **Figure 6.19**, where the bright field image and the

indexing of the micro-diffraction patterns are shown. In addition, the experimental diffraction pattern parameters are compared with the theoretical values calculated for the 3 possible phases. It can be seen that the experimental data matches almost equally well to the FCC ZrO, γ -ZrH and δ -ZrH_{1.6} phases. In this example, a needle-shaped morphology appears to be present where the diffraction pattern was obtained, which might suggest a hydride particle [274, 280]. But in some other cases, the characteristic hydride morphology was not obvious, for example in **Figure 6.21d**.

Diffraction patterns that matched the rhombohedral Zr₃O structure [122] were also found occasionally. But this structure was seen deeper into the metal, up to ~400 nm away from the metal-oxide interface. An example of such grains found in the metal ~400 nm away from the metal-oxide interface of the 100 days ZIRLO RXA oxide is given in **Figure 6.20**. A same micro-diffraction pattern that matches the Zr₃O structure was found repeatedly when the beam was moved around across a wide region in this location.

There were some cases where no good match of the micro-diffraction patterns to any known phase in the Zr-O system could be achieved. Therefore they might be better described as an “unidentified” phase, although they usually show lattice spacing quite close to those of ZrO₂, metallic Zr or Zr₃O. **Figure 6.21** shows BF images of this type of grains found at the interface region of the 34 days, 100 days ZIRLO RXA oxide and the 34 days Zircaloy-4 RXA sheet samples, together with their micro-diffraction patterns. These grains are normally smaller than those with identified structures, but don’t appear to be morphologically very different. HRTEM images of the metal-oxide interface area (**Figures 6.22** and **6.23**) also reveal the presence of regions containing unidentified grains in the 90 days Zircaloy-4 oxide and the 100 days ZIRLO RXA oxide. The individual grains appear to be smaller than ~10 nm in the HRTEM images. In the investigated 100 days ZIRLO RXA oxide, it appears that a layer of ~40 nm containing unidentified grains is present between the monoclinic oxide and the metal.

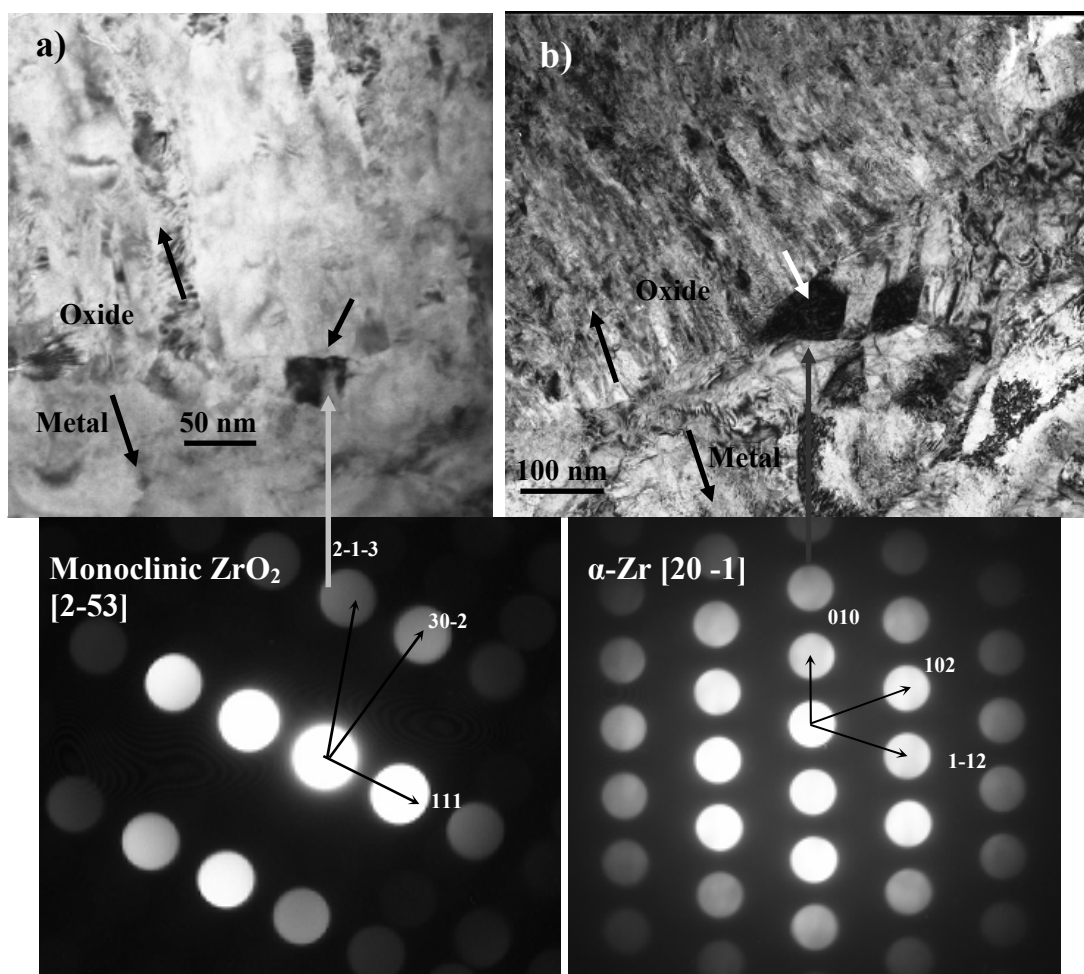


Figure 6.15 Examples of identified interface particles (arrowed) and their convergent beam diffraction patterns in the pre-transition Zircaloy-4 RZA tube oxide: a) a particle showing a monoclinic ZrO_2 structure and b) a particle showing a α -Zr structure.

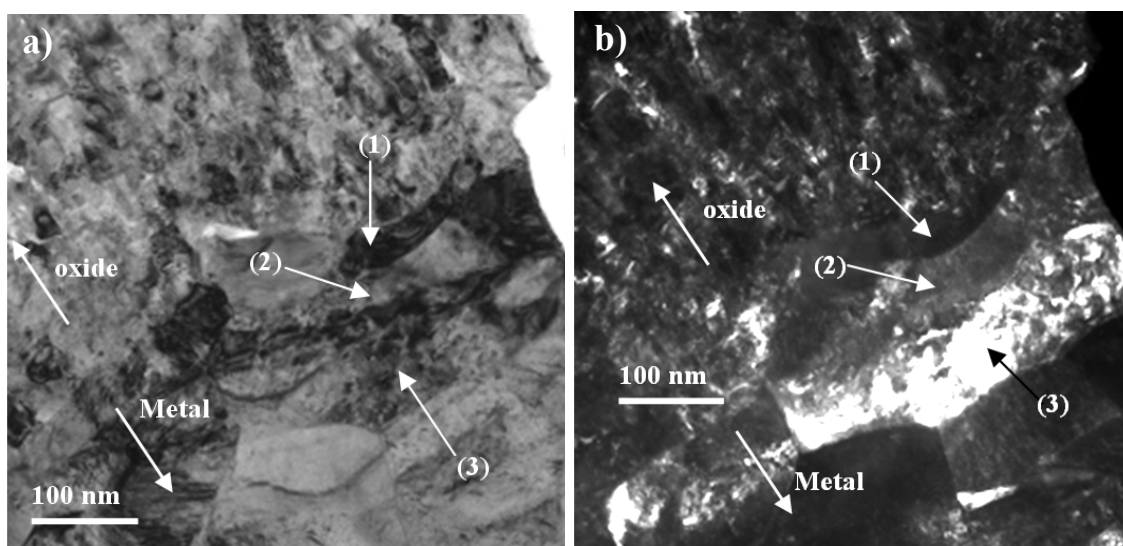


Figure 6.16 TEM images at a particular interface location of the Zircaloy-4 RZA tube oxide, showing a small monoclinic oxide particle (1) directly on the top of α -Zr grains (2) and (3). a) bright field image, b) dark field image using mainly reflections from the metal.

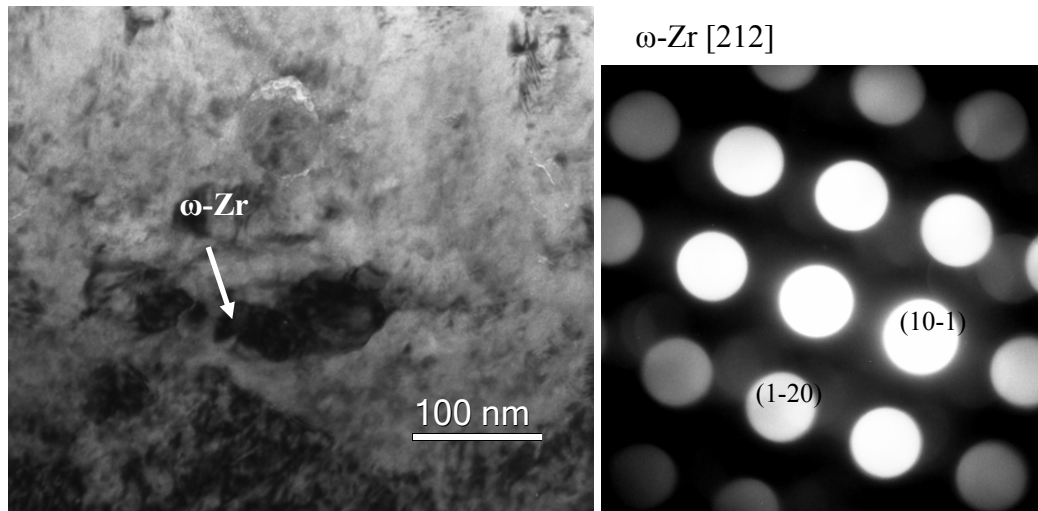


Figure 6.17 Bright field image of an example of ω -Zr grains and the convergent beam diffraction pattern in the pre-transition 34 days ZIRLO RXA oxide.

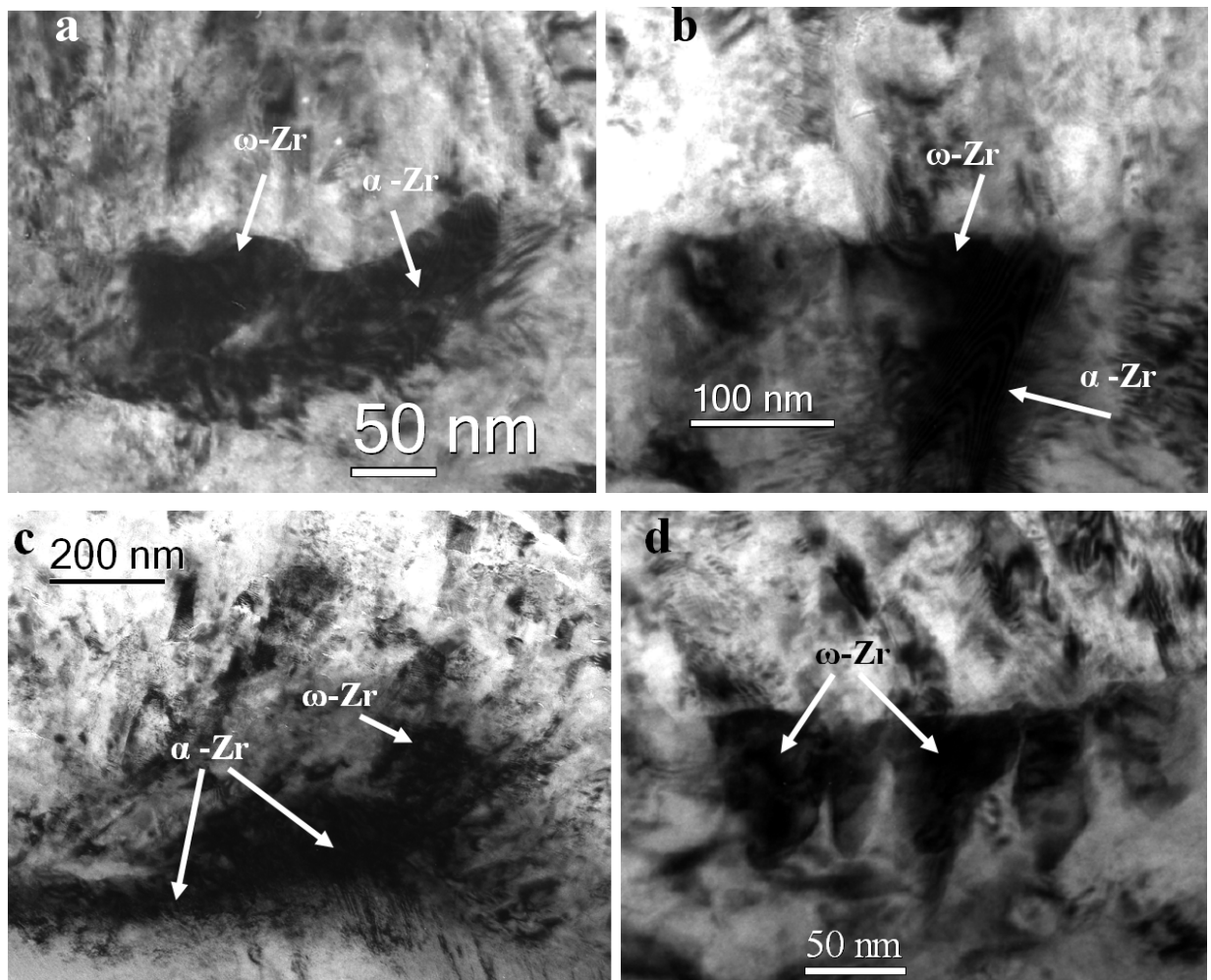
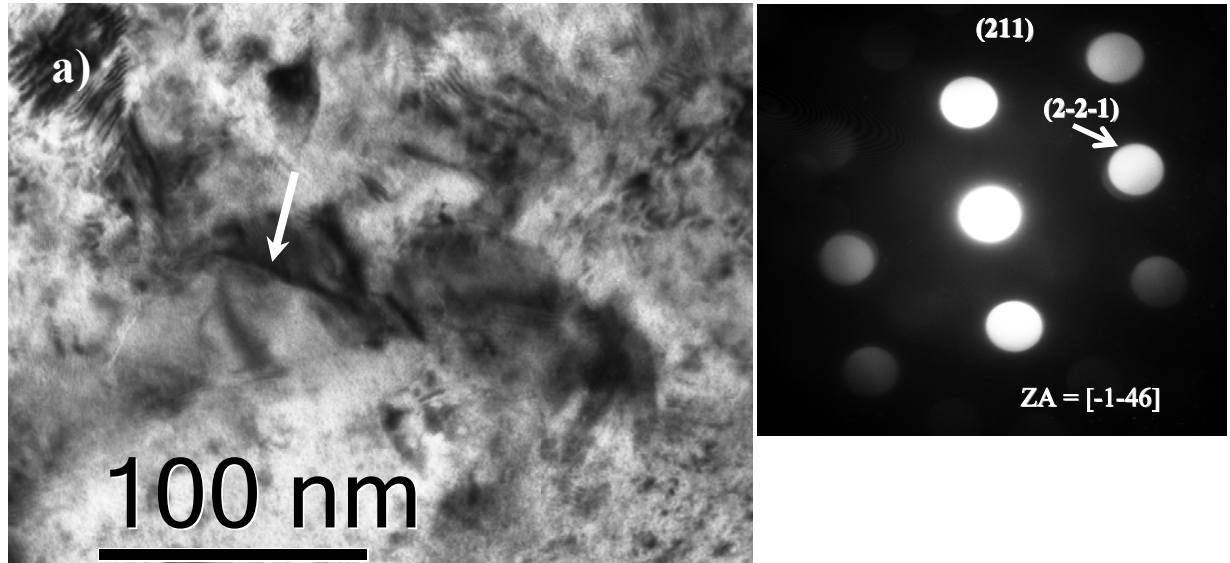


Figure 6.18 Observations of ω -Zr grains at the metal-oxide interface in pre-transition oxides. a) from ZIRLO RXA 34 days oxide, b) and c) from ZIRLO RXA 100 days oxide, d) from Zircaloy-4 RXA sheet 34 days oxide. The metal-oxide interface runs horizontal and the oxides are on top of each image.



b)	Experimental	FCC ZrO	FCC δ -hydride	FCT γ -Hydride
Spacing 1 (2-2-1) ($\text{\AA}$)	1.58 ± 0.04	1.54	1.6	1.54
Spacing 2 (211) ($\text{\AA}$)	1.93 ± 0.03	1.89	1.96	1.90
Angle (degree)	81.7 ± 1	82.2	82.2	80.9

Figure 6.19 A metal-oxide interface grain in the 34 days Zircaloy-4 oxide was found to match at the same time three types of structure: FCC ZrO, FCC δ -hydride and FCT γ -hydride, with the same ZA [-1-46]. a) Bright field image with the micro-diffraction pattern. The location where the micro-diffraction pattern was obtained is arrowed. b) a list of measured diffraction pattern parameters and theoretical values for the three phases.

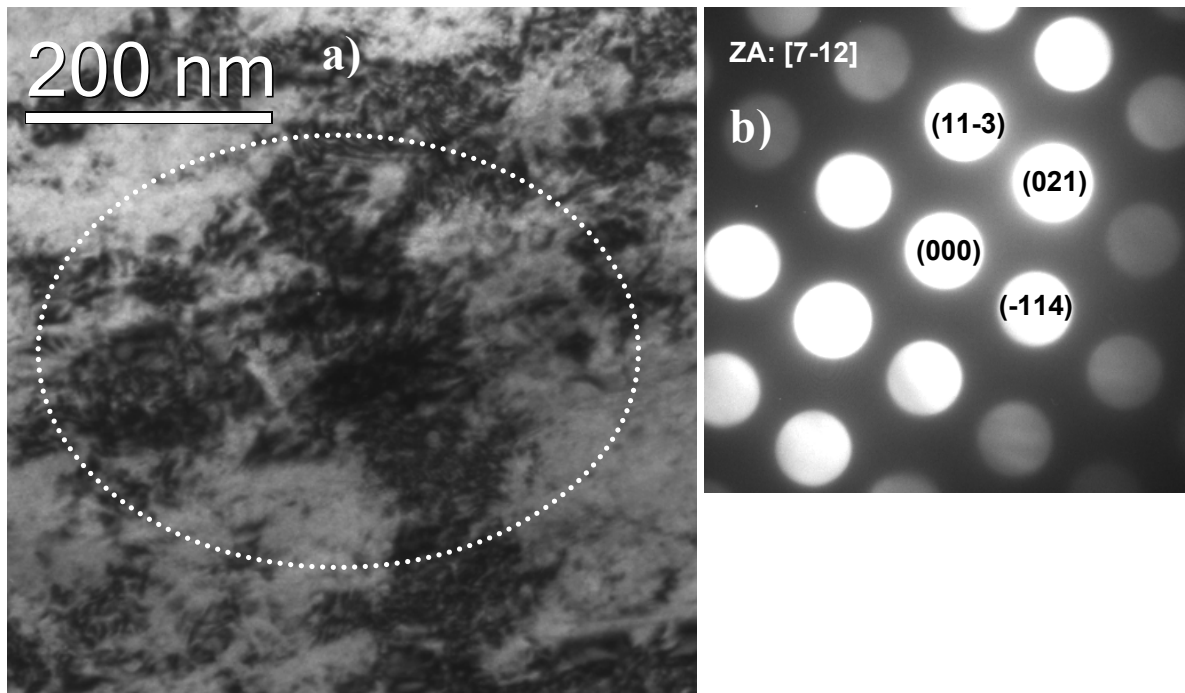


Figure 6.20 a) Bright field image of the metal ~400 nm away from the metal-oxide interface in the 100 days ZIRLO RXA oxide. A same micro-diffraction pattern that matches the Zr_3O structure as shown in b) was found across a wide region shown in a).

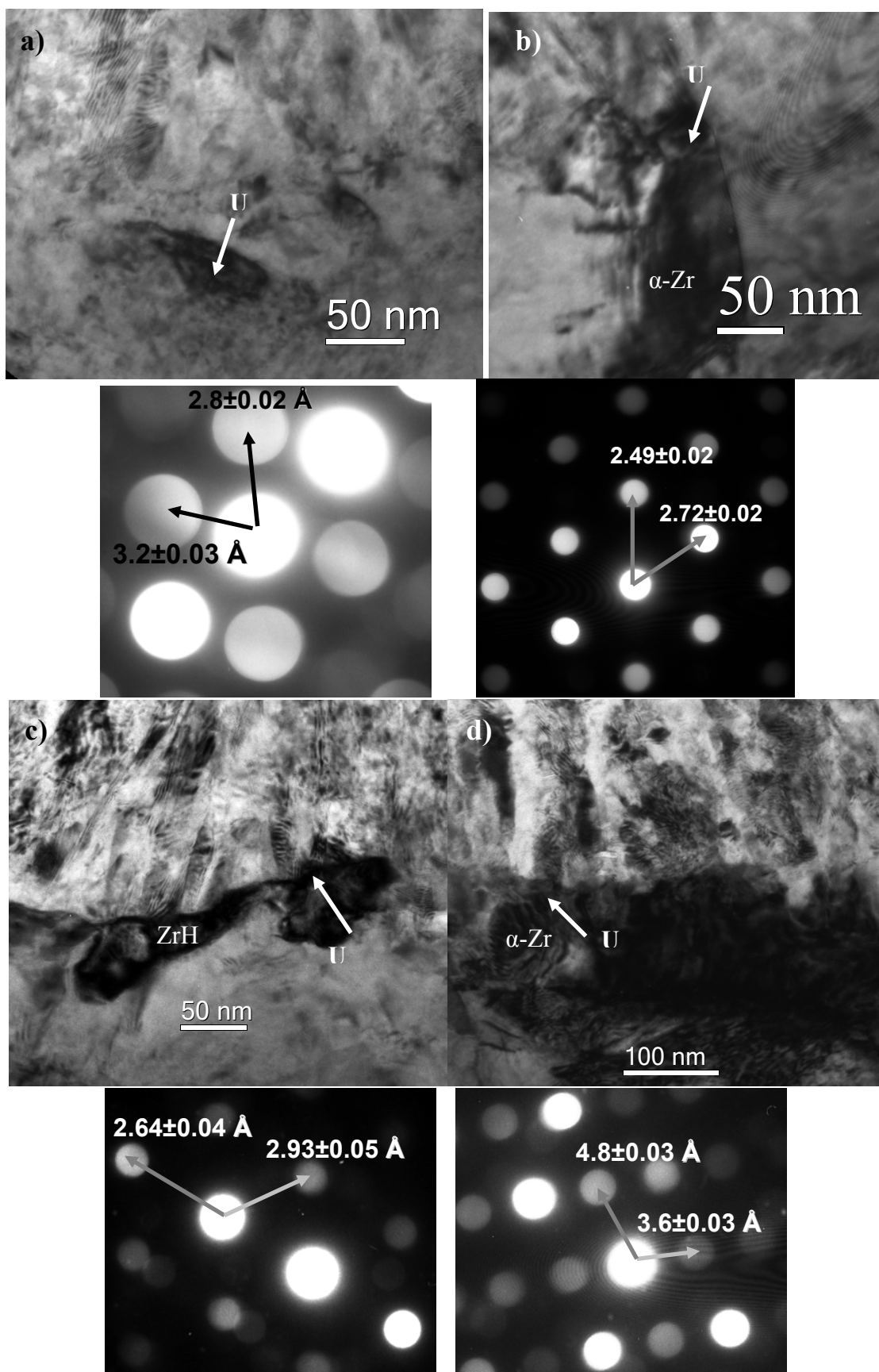


Figure 6.21 Images of unidentified grains observed at the metal-oxide interface in pre-transition oxides. The micro-diffraction patterns from the grains are shown below each bright field images. a) 34 days ZIRLO RXA oxide b) 100 days ZIRLO RXA oxide c) and d) 34 days Zircaloy-4 RXA sheet oxide. The metal-oxide interface runs horizontal and the oxides are on top of each image.

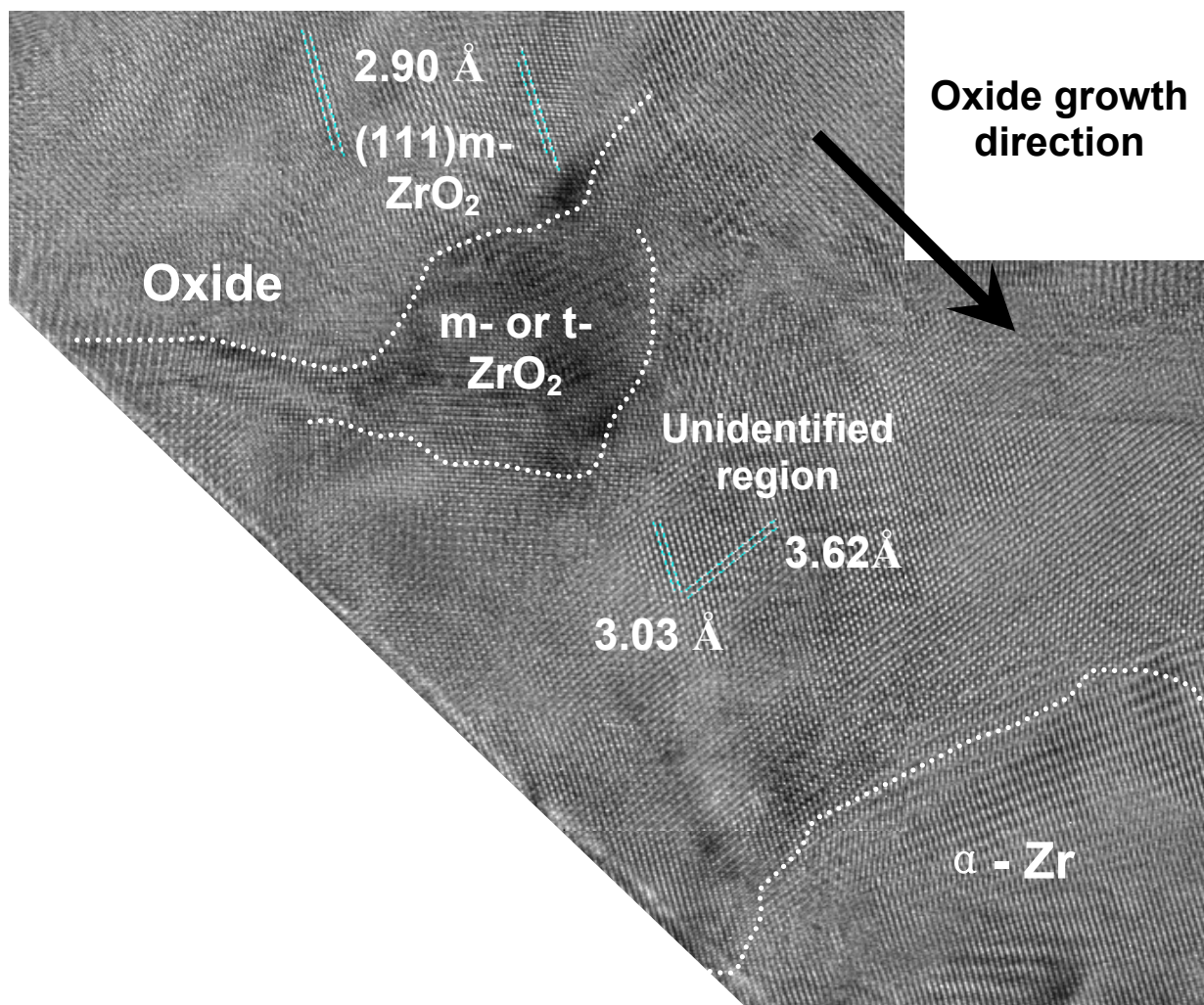


Figure 6.22 HRTEM image of the metal-oxide interface in Zircaloy-4 RXA tube oxide, showing a region containing unidentified grains.

6.3.2 Post-transition oxides

The post-transition oxide investigated in the most detail is the grey oxide of the 140 days ZIRLO RXA sample. Micro-diffraction analysis of grains at the metal-oxide interface shows the presence of monoclinic ZrO_2 or $\alpha\text{-Zr}$. Examples of $\alpha\text{-Zr}$ grains are given in **Figure 6.24**. There is no sign of any suboxide layer between the metal and the columnar monoclinic ZrO_2 grains.

In most cases HRTEM reveals the growth of monoclinic or tetragonal ZrO_2 grains directly on $\alpha\text{-Zr}$ metal (**Figures 6.25** and **6.26**). The growth relationship for monoclinic oxide grains was found to be $(200)\text{m}$ or $(020)\text{m} // \{10\text{-}10\}\alpha\text{-Zr}$ and $(11\text{-}1)\text{m}$ or $(111)\text{m} // \{11\text{-}20\}$ or

$(011)_m \parallel \{10\cdot10\}\alpha\text{-Zr}$. The (110) or (-110) planes of tetragonal oxide were found to be parallel to $\{0001\}$ planes of $\alpha\text{-Zr}$. Grains with unidentified structure were also sometimes revealed (**Figure 6.27**).

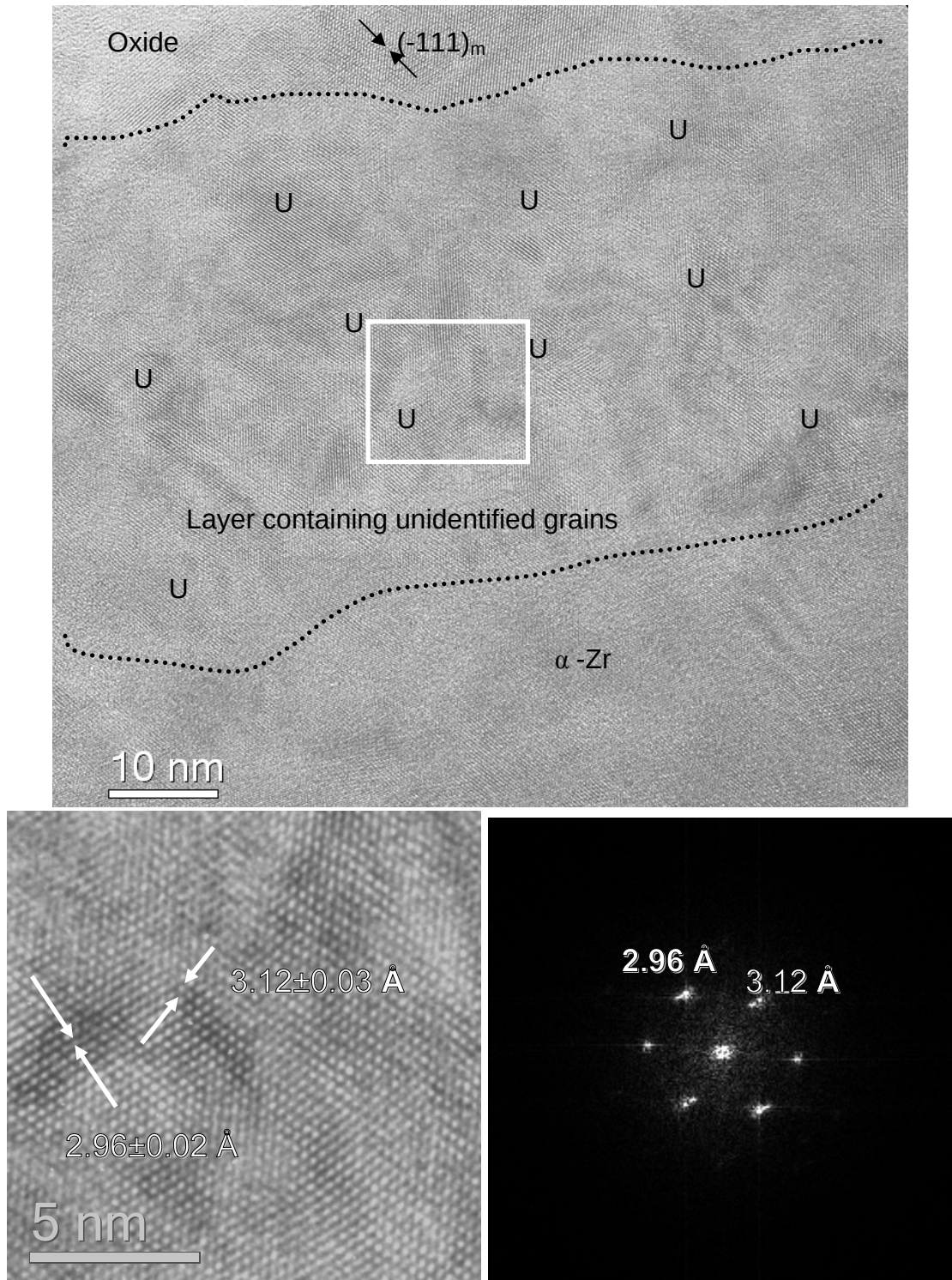


Figure 6.23 HRTEM image of the metal-oxide interface region in the 100 days ZIRLO RXA sample, showing a layer containing unidentified grains. Bottom left shows the zoomed in image of the region indicated with the white box. Bottom right shows the diffractogram of this region, which can not be matched to any known phase.

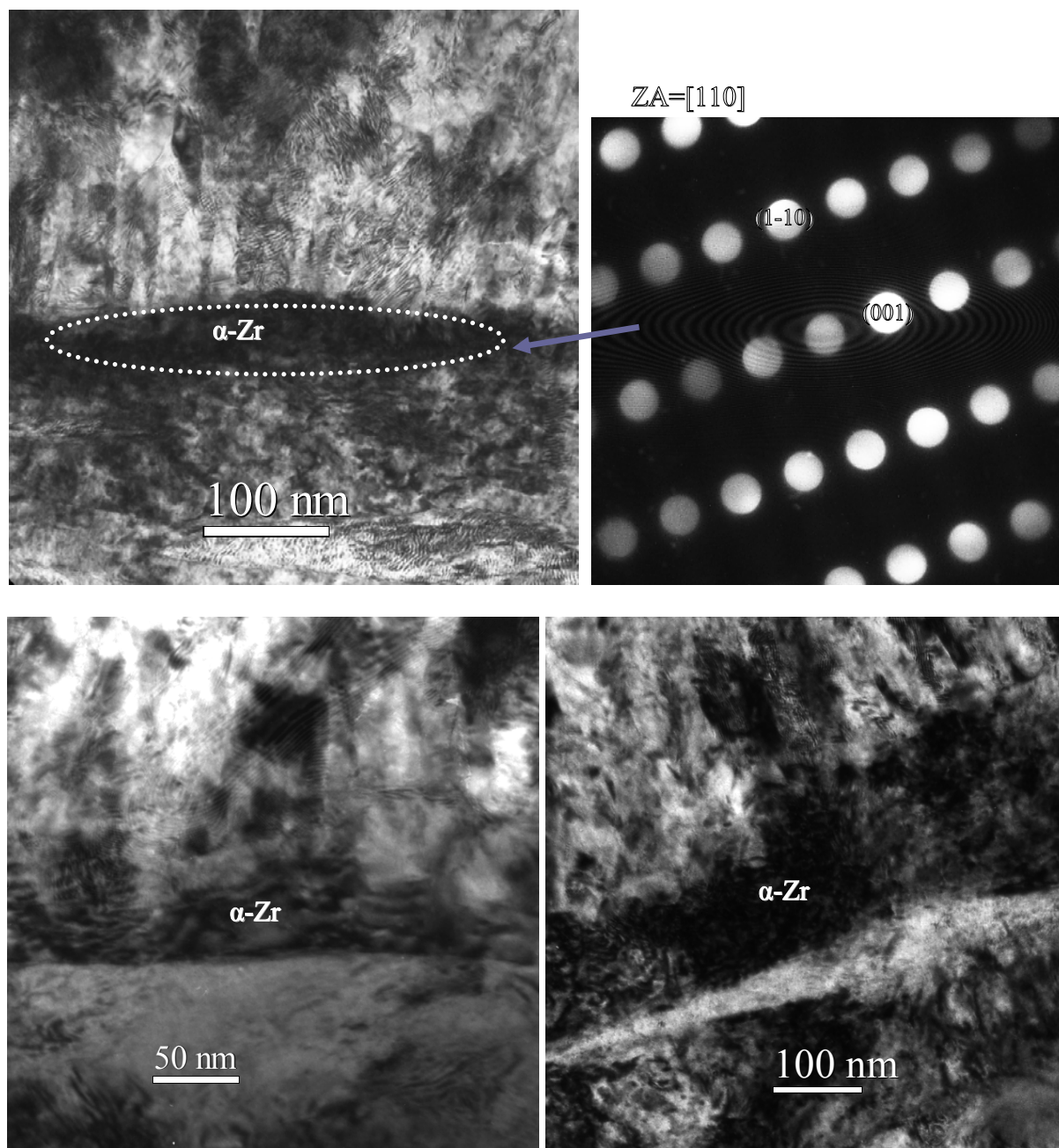


Figure 6.24 Bright field images of metal-oxide interface grains in the grey oxide of the 140 days ZIRLO RXA sample, showing elongated α -Zr grains. A micro-diffraction pattern for the grain in the top image is also shown. The metal-oxide interface runs horizontally and the oxides are on top of each bright field image.

A structure that matches both hydride and FCC ZrO was also identified frequently in this sample by both micro-diffraction analysis and HRTEM.

6.3.3 Post-second-transition oxides

Monoclinic ZrO₂, tetragonal ZrO₂ and α -Zr grains have been identified by micro-diffraction analysis in the metal-oxide interface region for the $\sim 78 \mu\text{m}$ post-second-transition

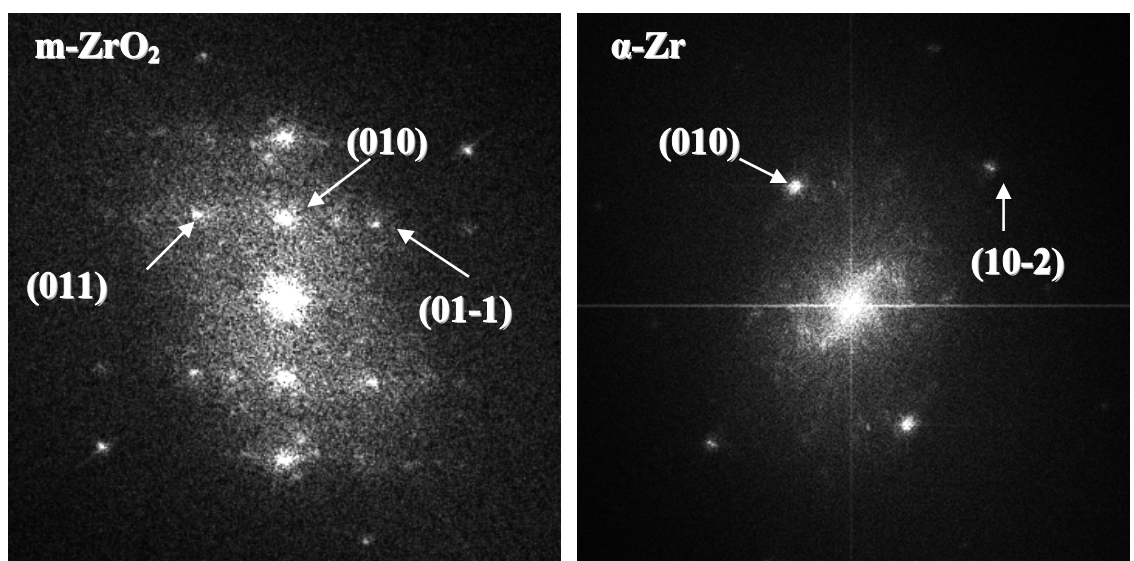
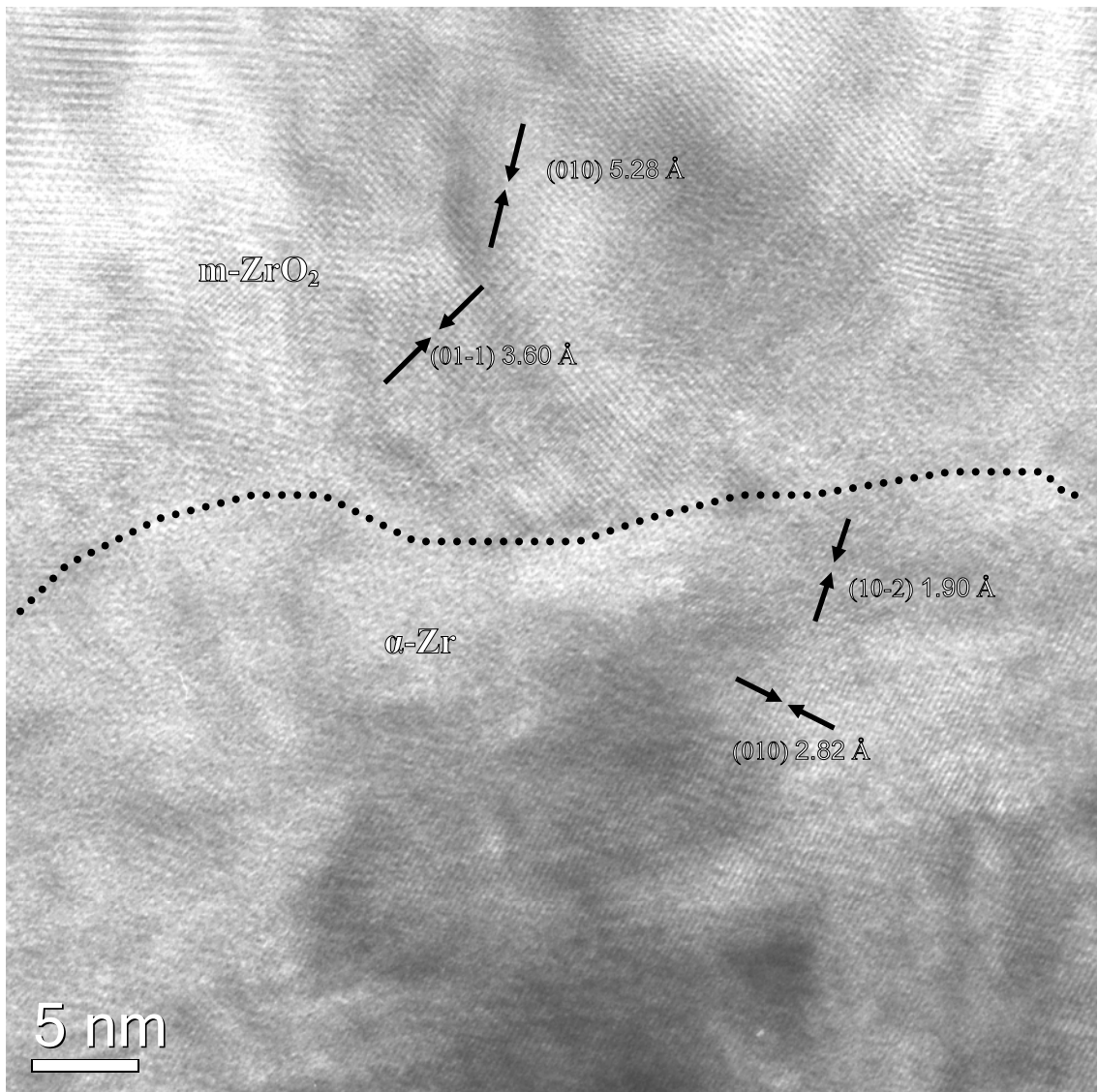


Figure 6.25 HRTEM image of metal-oxide interface grains in the grey oxide of the 140 days ZIRLO RXA sample, showing monoclinic grains growing on $\alpha\text{-Zr}$ metal.

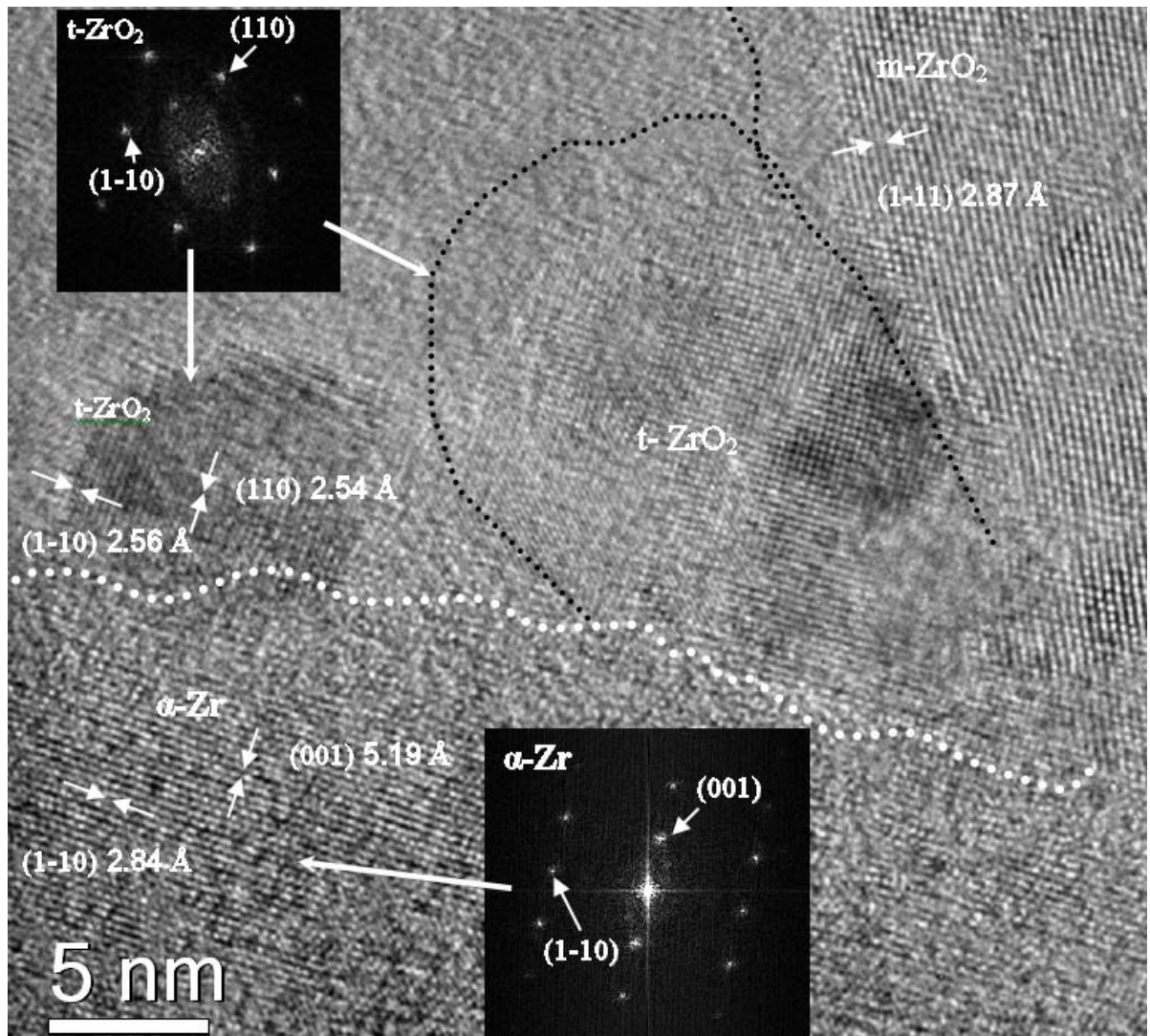


Figure 6.26 HRTEM image of metal-oxide interface grains in the grey oxide of the 140 days ZIRLO RXA sample, showing tetragonal and monoclinic grains growing on α -Zr metal.

Zr-Nb-Ti oxide. A phase that matches both the δ -hydride and the FCC ZrO structure as described for earlier samples was also frequently found. An example of a tetragonal oxide grain has already been shown in **Figure 5.13b**. **Figure 6.28** gives examples of monoclinic ZrO_2 , α -Zr and hydride/ZrO grains.

6.4 Discussion

6.4.1 Interface morphology

A distinct morphology at the metal-oxide interface containing blocky or rectangular grains has been found, especially in the pre-transition oxides. This is very similar to the observation

reported in [138] for a Zr-2.5Nb metal-oxide interface, although the author didn't specify if that oxide was pre- or post-transition. The “sawtooth” morphology at the metal-oxide interface reported previously for pre-transition Zircaloy-2 and Zircaloy-4 oxides [80, 101, 122] was also observed in the pre-transition Zircaloy-4 and ZIRLO oxides investigated in this work. All these characteristic morphologies suggest that there is probably a phase at the interface different from either the bulk oxide or the bulk metal.

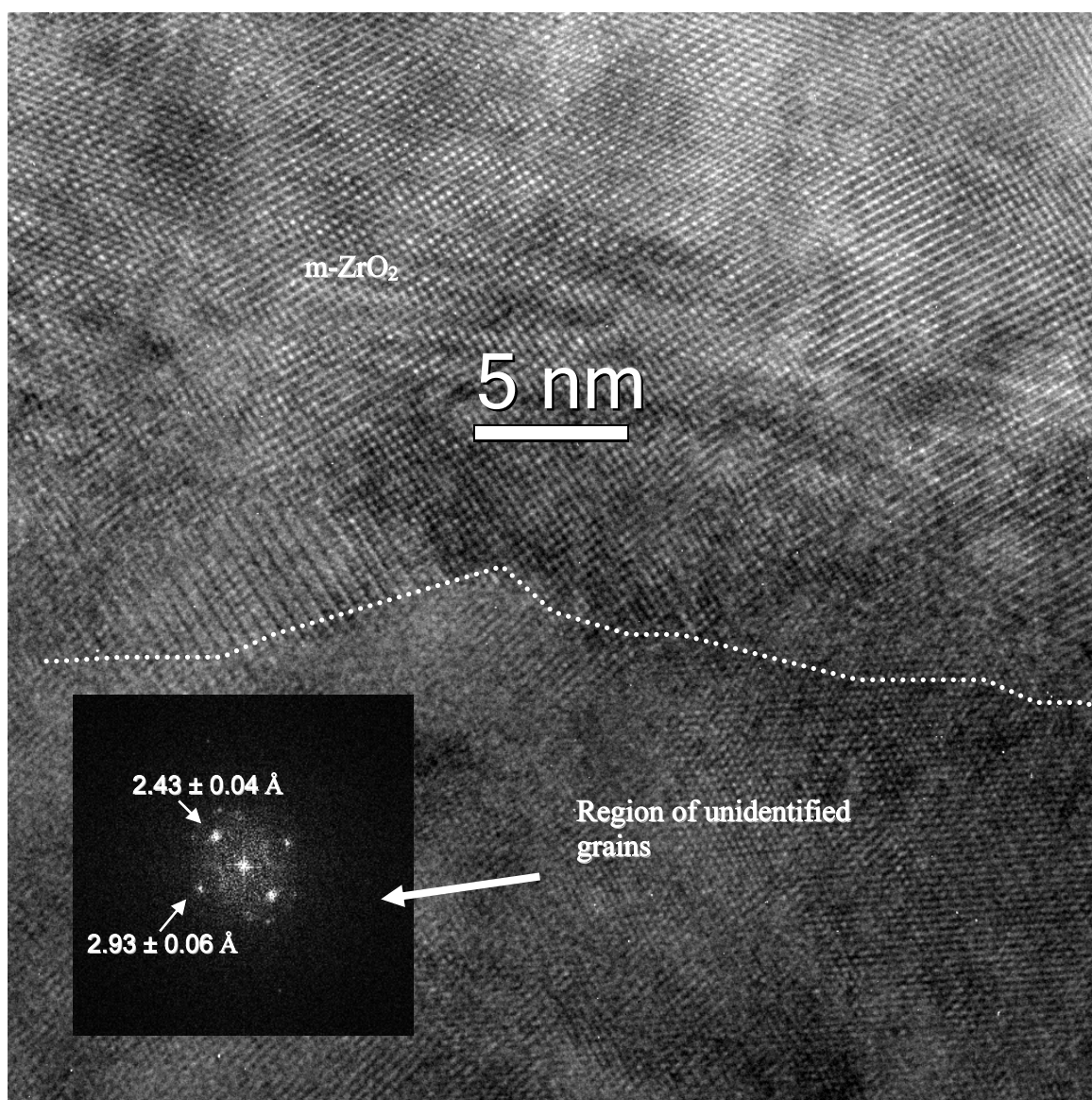


Figure 6.27 HRTEM image of metal-oxide interface grains in the grey oxide of the 140 days ZIRLO RXA sample, showing a region adjacent to the oxide containing grains with an unidentified structure.

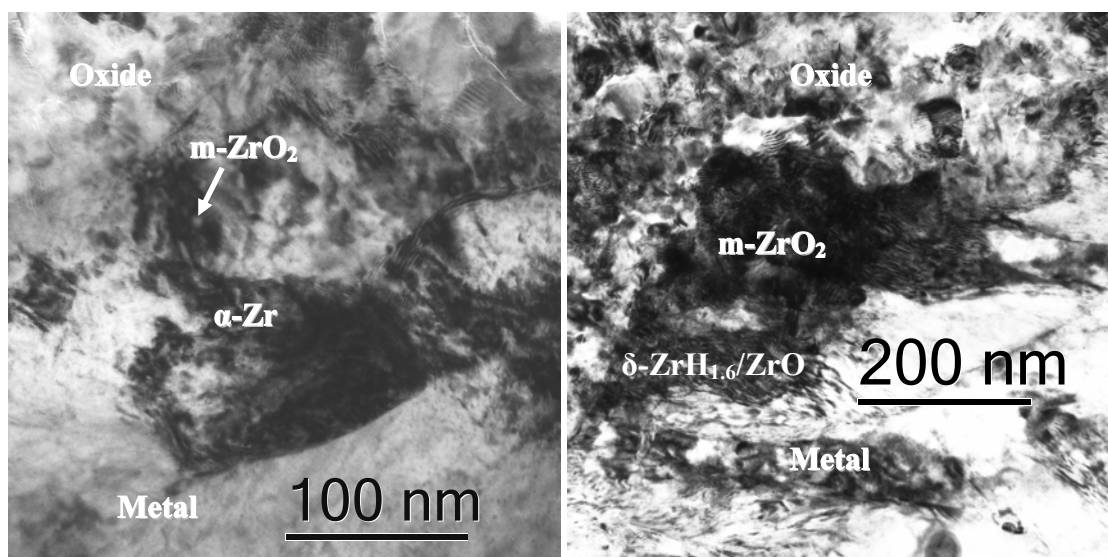


Figure 6.28 Bright field images of the metal-oxide interface in the post-second-transition Zr-Nb-Ti oxide showing monoclinic oxide, α -Zr and hydride/ZrO grains.

6.4.2 Analysis of oxygen content at metal-oxide interfaces

The presence of an oxygen-rich region at the metal-oxide interface has often been reported and described by some authors as a suboxide phase [101, 120, 123, 138, 173]. Sitting at the place where the oxide growth is occurring, this suboxide could play a very important role in the oxidation process, but there is still considerable disagreement on its precise composition, as described in the literature review **section 1.3.3.2**.

The choice of EDX for the identification of oxygen content in all previously reported work is not ideal, since it is not optimized for light element analysis such as oxygen for reasons given in **section 3.6.1**. Therefore, the alternative EELS technique has been explored in this work. A good agreement was achieved between the measured oxygen concentration in the bulk oxide on the zirconium alloys and the expected stoichiometric ZrO_2 concentration (see Appendix B). Using this method, a suboxide was found to be present and have, instead of a graded concentration profile as reported in some previous studies [138], a more or less constant (40-50 at. %) oxygen concentration over at least several tens of nanometers as shown in the Zircaloy-4 90 days oxide (**Figure 6.5**). Parallel 3D atom-probe analysis of the same sample has also shown suboxide with very similar oxygen content [281]. The confidence in

the results from this work is enhanced by the fact that very similar quantitative compositional data were obtained from analysis techniques based on very different physical principles. Both have a high enough spatial resolution to detect composition variations on the nanometer scale.

It is noted here that in many cases the concentration profile across the metal-oxide interface became noisier when entering the metal side. One of the contributing factors to this is the decrease in oxygen content, which leads to decreasing intensity and therefore lower signal to noise ratio. However, the main reason, especially for those shown **Figures 6.5, 6.6 and 6.12b**, is believed to be some degree of beam damage to the specimen caused by the incident electrons. There are several reasons for this speculation. First of all, from the oxide to the suboxide region, it was found that the intensity of the oxygen edge did not decrease very much but the noise level increased significantly, which can not be explained solely in terms of the oxygen concentration changes. The absolute oxygen intensity profile across the interface used for calculating the concentration profile in **Figure 6.6** is shown in **Figure 6.29** for an illustration. Secondly, in the 34 days ZIRLO oxide specimen where **Figure 6.6** data was acquired, the line scan in the STEM mode was found to drill holes in the specimen, preferentially in the metal side. Finally, in the line profiles that were obtained under less aggressive conditions (lower current density or lower voltage), the data from the metal showed less fluctuations. For example the line profiles extracted from EFTEM datasets (**Figure 6.8**), and the data taken at a lower acceleration voltage (100kV), as is the case for **Figure 6.7**. These observations tend to suggest that the zirconia is more radiation resistant at voltages above 100kV than the metallic zirconium. The degree of damage has been seen to be different in different TEM specimens. The specimen thicknesses, although expected to be a possible controlling parameter, is not found to correlate with the damage level. It is suspected that the damage may depend on the crystallographic orientation of the sample. The cleanness of the specimen could also have an effect. Hydrocarbon diffusion from surface/holder/column contamination towards the beam is known to minimize sample damage.

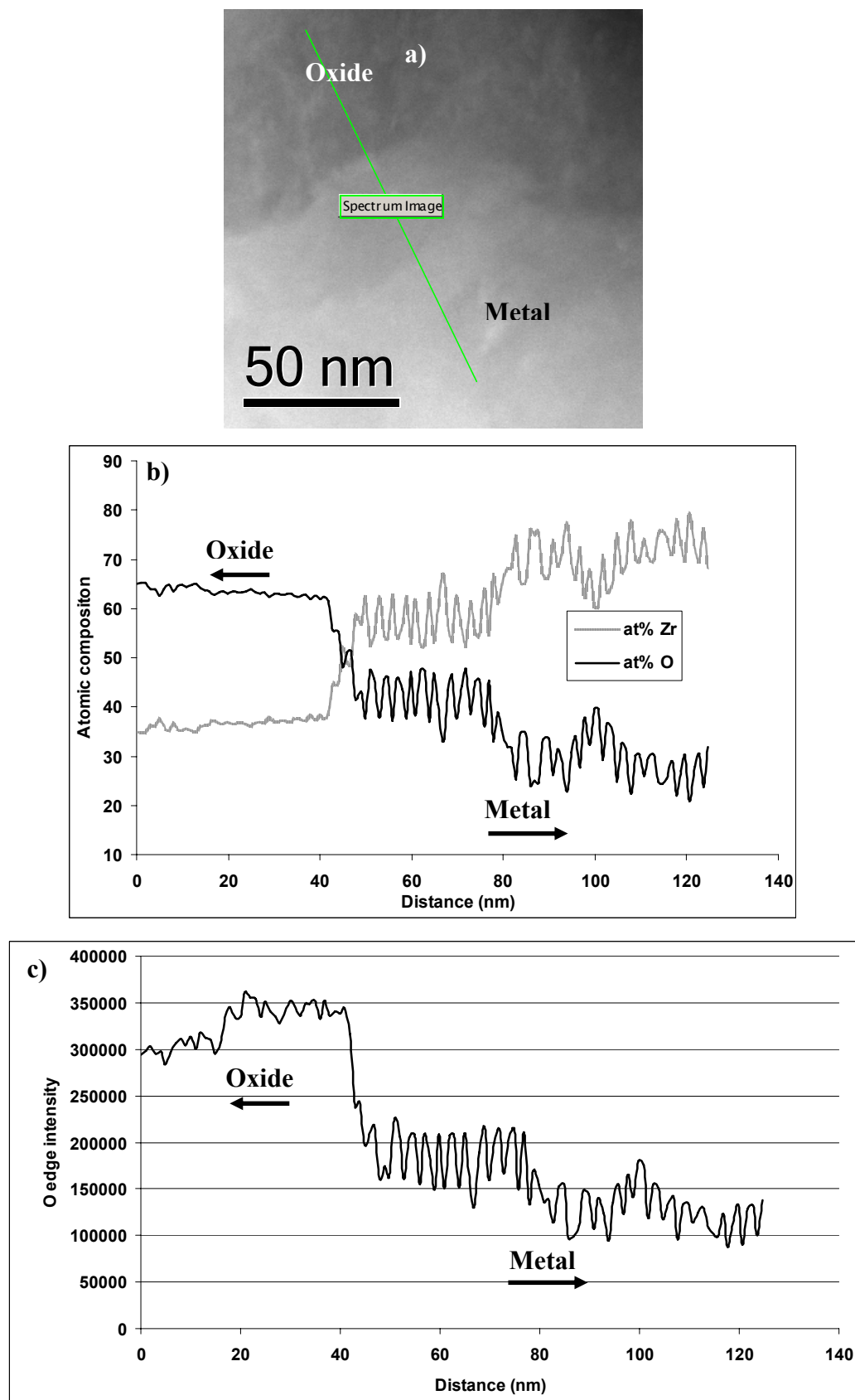


Figure 6.29 a) and b) reproduced from Figure 6.6. a) HAADF image of the metal-oxide interface region and b) EELS oxygen concentration line profile across the interface in the 34 days ZIRLO RXA oxide. c) The absolute intensity line profile of the oxygen edge.

For ease of discussion, a summary of the observations on the interface chemistry of ZIRLO oxide in this work is given in **Table 6.1**. The suboxide layer was found to be present in all investigated Zircaloy-4 and ZIRLO pre-transition oxides. Local variations in the thickness of the suboxide layer were found when evaluated by EELS line profiles at different interface locations. This may partly be a result of the complex 3D morphology exhibited by the suboxide, as shown in images like **Figure 6.5**. The employment of EFTEM characterization has improved the analysis statistics and showed that the suboxide varies in thickness even within small regions along the interface (**Figure 6.11**).

Within the series of ZIRLO samples oxidized for increasing times, a thickening of the suboxide layer from the 34 days oxide to the 100 days sample found in 3D atom probe analysis (D. Hudson, Oxford Materials) couldn't be confirmed by the observations presented in this work, as the suboxide thicknesses in the region of interest were usually around 30-50 nm. However a thickening over the time in the pre-transition stage may occur, as a ~140 nm suboxide was found in the black oxide of the 140 days sample.

In the post-transition grey oxide of the 140 days ZIRLO RXA sample, generally either very thin suboxides (~10-20 nm) or no layer at all was found. Also for the post-second transition Zr-Nb-Ti oxide, no evidence of suboxide can be found. In one EELS line profile performed across the interface in the post-transition grey oxide of the 140 days ZIRLO SR sample (**Figure 6.12c**), a relatively thicker suboxide of ~50 nm was found beneath a delayed portion of oxidation front, which may have caused or been caused by a locally slower oxidation rate.

The situation is more complicated in the black oxide of the 140 days corroded ZIRLO sample. A rather big variation of suboxide characteristics was observed. In some regions, the suboxide layer was the widest found among all investigated pre-transition oxides, while in other regions no suboxide at all was detected. Considering this oxide to be around the onset of the transition point, it is possible that some locations in the sample where the suboxide was

present had already passed the transition resulting in a faster local oxidation rate losing the suboxide characteristic of a slowly oxidizing interface.

Table 6.1 Summary of investigations on the metal-oxide interface chemistry

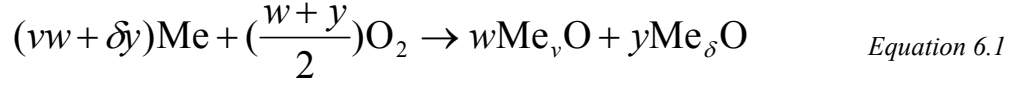
Sample		Oxidation Stage	Suboxide layer	Oxygen level in the metal (at %)
Zircaloy -4	34 days sheet oxide	Early pre-transition	~40-60 nm (~40-45 at. % O)	Decreased from ~40 % to ~20 % over 50 nm
	90 days tube oxide	Not known explicitly	~ 60 nm (~45-50 at. % O)	Not investigated
ZIRLO	34 days RXA sheet oxide	Early pre-transition	~40-50 nm (~39-42 at. % O)	Decreased from ~40% to ~25 % over ~ 40 nm up to the investigated depth
	100 days RXA sheet oxide	Late pre-transition	~40 nm in total consisting of two sublayers of ~15 nm of ~47 at. % O and ~25 nm of ~ 45 at. % O.	~100 nm of ~30 % below the suboxide, then decreased to ~15 % over ~100 nm
	Black oxide of the 140 days SR tube oxide	Around the onset of the kinetic transition	Big variation: as wide as ~140 nm of ~ 50 at.% O or not detected	~120 nm of ~30 % below the suboxide; or ~50 nm of ~30 % below the oxide (when no suboxide), then gradually decreased to ~10 % over ~100 nm
	Grey oxide of the 140 days RXA sample	Early post-transition	Thin (10-20 nm of ~44-50 at. O) or not present; a gradual decrease from ~67 at. % to ~30 at.% over 50-70 nm distance	Gradually decreased from ~67 % to ~10 over ~90 nm
	Grey oxide of the 140 days SR sample	Early post-transition	Generally not detected; ~ 50 nm of ~47 at. % found in one location where exhibited a delayed oxidation below a crack	~30 % across ~130 nm below the oxide up to the investigated depth
Zr-Nb-Ti		Post-second transition	Not detected	Not detected

Therefore the presence of the suboxide is apparently favoured by the slower oxidizing metal-oxide interfaces in the pre-transition oxides. Although previous studies have also suggested a similar correlation, they were based on microstructural rather than compositional observations [120, 122]. The results presented in this work are the first evidence for the importance of the suboxide layer based on systematic quantitative TEM chemical analysis at the metal-oxide interface.

In addition to the suboxide layer, an oxygen saturated (~ 30 at. % O) metal region has been found beneath the suboxide in pre-transition oxides, especially for the 100 days ZIRLO RXA oxide and the black oxide of the 140 days ZIRLO sample. In the post-transition grey oxide of the 140 days ZIRLO sample, the oxygen content decreases more gradually than that in the post-second transition Zr-Nb-Ti oxide, resulting in a wider metal region saturated with oxygen in the metal adjacent to the metal-oxide interface compared to the Zr-Nb-Ti oxide. As a result, the total width of a region beneath the metal-oxide interface with an oxygen content above or near the solid solution limit decreases following the sequence of the (late) pre-transition oxide, the post-transition oxide and the post-second transition oxides, in agreement with the increasing oxidation rate observed in the same samples. The oxygen level in the metal far from the interface was measured by EELS to be 13 ± 4 at.% in the Zr-Nb-Ti sample, in reasonable agreement with the 3D atom probe data from the same oxide which showed an oxygen concentration of ~ 10 at. % [281]. This agreement gives confidence that possible artifacts, from oxide layers on the TEM specimen surfaces for instance, cannot account for the observed difference in measured oxygen content in the metal matrix between samples at different stages of oxidation.

It would be useful at this point to consider a kinetic model that deals with the relative thickness of the oxide layers of different stoichiometry.

A theory of multi-layered scale growth on pure metal has been described by Yurek et al. [282]. For a two-layered scale as schematically shown in **Figure 6.30**, the total oxidation reaction is written as:



The treatment in the paper yields that the rate of thickening of the inner layer Me_vO $d\xi/dt$ is

$$\frac{d\xi}{dt}(\text{Me}_v\text{O}) = \frac{k_p(\text{Me}_v\text{O})}{\xi\left(1 + \frac{\delta y}{vw}\right)}, \quad \text{Equation 6.2}$$

and the rate of thickening of the outer layer Me_δO is

$$\frac{d\eta}{dt} = \frac{k_p(\text{Me}_\delta\text{O})}{\eta\left(1 + \frac{w}{y}\right)}, \quad \text{Equation 6.3}$$

where $k_p(\text{Me}_v\text{O})$ and $k_p(\text{Me}_\delta\text{O})$ are the parabolic rate constant for growth of Me_vO and Me_δO respectively. **Equations 6.3** and **6.4** say that the ratio of the growth rates of the two layers is proportional to the ratio of their parabolic rate constant.

Integration of the two equations from time zero to time t gives the ratio of the two layer thicknesses at any time t of a steady state progress:

$$\left(\frac{\eta}{\xi}\right)^2 = \frac{[1 + \delta y/vw]k_p(\text{Me}_\delta\text{O})}{[1 + w/y]k_p(\text{Me}_v\text{O})}. \quad \text{Equation 6.4}$$

In the case of $\eta \gg \xi$, it has been shown that

$$\frac{\eta}{\xi} \cong \frac{\delta V_{\text{Me}_v\text{O}} k_p(\text{Me}_\delta\text{O})}{v V_{\text{Me}_\delta\text{O}} k_p(\text{Me}_v\text{O})}, \quad \text{Equation 6.5}$$

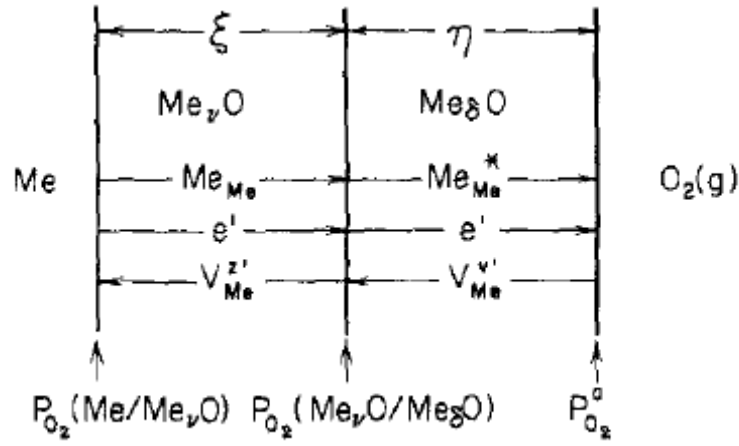


Figure 6.30 Schematic model of the growth of a hypothetical two-layered scale on a pure metal. [282]

where $V(\text{Me}_v\text{O})$ and $V(\text{Me}_\delta\text{O})$ are the average molar volumes of the two oxides respectively.

The theory assumed that the growth of both scales is diffusion controlled, with the outward migration of metal cations much faster relative to the inward migration of oxygen anions. The same relationship as **Equation 6.4** can be achieved if it is assumed for the system studied in this work that the thickness of a ZrO_2 outer layer and a ZrO suboxide layer are both controlled by inward diffusion of oxygen ions. Since the suboxide layer is much thinner than the ZrO_2 oxide scale, the ratio of the ZrO_2 thickness and the ZrO layer thicknesses $t_{\text{ZrO}_2} / t_{\text{ZrO}}$ will be given by:

$$\frac{t_{\text{ZrO}_2}}{t_{\text{ZrO}}} = \frac{V_{\text{ZrO}} K_p(\text{ZrO}_2)}{2V_{\text{ZrO}_2} K_p(\text{ZrO})} \quad \text{Equation 6.6}$$

If this relationship holds, then we can deduce from the relative thickness observed for the ZrO_2 scale and the suboxide layer that $K_p(\text{ZrO})$ must be much smaller than $K_p(\text{ZrO}_2)$.

Considering a steady state established shortly after the kinetic transition, it can be reasoned that due to the reduced effective thickness of ZrO_2 scale (taken as the thickness of the protective ZrO_2 oxide which is free of connected porosity along oxide growth direction, as described in **Section 5.3**) the suboxide must become thinner accordingly. This is in agreement

with the observation in this work that sometimes only a very thin suboxide layer can be detected in the early post-transition oxides. The thickness of a protective ZrO_2 layer is expected to be even smaller in the post-second transition Zr-Nb-Ti oxide, as indicated by the interconnected nano-porosity and cracks in the oxide down to the metal-oxide interface, so that the suboxide would be predicted to be extremely thin so could not be detected in my experiments.

From the kinetic point of view, the instantaneous growth rates of the ZrO_2 -ZrO interface and the ZrO-Zr interface are controlled by the thickness of the ZrO_2 layer and ZrO layer respectively. At transition, a dramatic reduction of effective thickness of the ZrO_2 layer would lead to an increasing rate in the advance of the ZrO_2 -ZrO interface, while the movement of the ZrO-Zr interface remains invariant until the thickness of the ZrO layer changes. As a result, the faster moving ZrO_2 -ZrO interface will consume the ZrO layer rapidly, resulting in a much thinner ZrO layer at dynamic equilibrium.

6.4.3 Identification of interface crystal structure

There is also considerable disagreement in terms of the crystallography of the interfacial region in previous studies, as summarized in the literature review **section 1.3.3.2**.

In the current study, the ω -Zr structure was found at the metal-oxide interface only in the pre-transition oxides, showing either a saw-tooth morphology, as reported by [80], or lath-like structure as in [121]. Similarly, Foord and Newcomb [121] have reported the presence of this phase in a pre-transition oxide film formed on Zircaloy-4, but not in the post-transition oxide formed on a low corrosion resistance Zircaloy-4 in lithiated water, and noted a correlation between a destabilization of the ω -Zr phase with a sharp increase in the rate of oxidation. In contrast, other studies have shown ω -Zr in both pre- and post-transition oxides formed on Zircaloy-2 in air at 450°C [80] and in a post-transition oxide formed on Zircaloy-4 in an

autoclave at 415°C [101]. ω -Zr is a metastable phase that is only stable for pure Zr under high compressive stress [283], while here tensile stress is present for the metal adjacent to the metal-oxide interface [158] since the oxide is under compression due to the volume expansion when metal is converted into oxide. Therefore it has been speculated that the stabilization of ω -Zr in the metal near the metal-oxide interface is caused by a possible compressive elastic stress arising from the expansion of Zr lattice when it dissolves oxygen [80]. As a result, the higher oxygen concentration in the suboxide adjacent to the metal-oxide interface seen here in the case of pre-transition oxides could favor the presence of ω -Zr. Furthermore, local plastic deformation concentrated in the metal beneath the delayed portion of the oxidation front [285] could help the α -Zr to ω -Zr transformation [284]. Based on this consideration, ω -Zr would be more likely to form in the pre-transition metal-oxide interface containing a suboxide layer.

A phase that matches both Zr hydrides and an FCC ZrO structure has often been identified in both pre- and post-transition oxides. It is often difficult to distinguish these phases in TEM because they have essentially very similar lattice parameters. However, it can be concluded that the phase observed is much more likely to be a hydride instead of a ZrO phase based on the following reasons: 1) a structure that matches only hydrides was also often found at the metal-oxide interface, while in no cases was a structure that only matches the ZrO phase found; 2) this structure has been found frequently in all samples and at different locations up to 2-3 μm away from the metal-oxide interface, where a ZrO stoichiometry is not measured but hydrides are frequently observed; 3) The ZrO phase has been doubted by some earlier workers [286, 287]. The main studies that reported the FCC ZrO phase are by Furuta and Motohashi [175] and Moseley and Hudson [176]. The oxides investigated in their work were formed either in water or steam, therefore the possibility of hydride formation can not be excluded. The first work didn't examine this possibility. In the second work the distinction between the hydrides and the ZrO phase based on electron diffraction data of (200) plane

spacing was briefly mentioned, but no detailed evidence was presented. There is only ~ 0.0005 nm difference in the (200) plane spacing between the ZrO phase and the δ -hydride (~ 0.2 %), while the precision normally claimed for structure determinations by TEM varies from 10 % down to 1 % [288].

Unidentified grains were found in all the pre-transition oxides. Their diffraction patterns/HRTEM images showed individual plane spacings close to those of either t-ZrO₂, m-ZrO₂ or α -Zr but could not give a complete match to any reported phase in the Zr-O system. They were less evident in the post-transition oxides and not observed in the post-second transition oxide. This is in agreement with previous HRTEM studies that also reported an unidentified structure for pre-transition Zr-0.4 Nb oxides [125] and a Zircaloy-4 oxide only in its pre-transition stage [120]. In this work, the location where the unidentified grains were found was in the suboxide region with ~ 40 -50 at. % oxygen, suggesting that the suboxide contains a distinct phase which has an unknown structure. However, it has to be noted that the confidence in defining a structure as “unidentified” has been limited by the following facts: 1) in micro-diffraction analysis, the patterns that have been considered as unidentified were usually from smaller grains and as a result had worse quality than those from other identified phases such as α - and ω -Zr; 2) In HRTEM characterization, grain overlap could be present considering the small size of these nano-grains, which can induce the error in pattern indexing. In addition, small deviation (several degrees) from the zone axis in HRTEM imaging has been shown to significantly change the spacings of HRTEM lattice fringes [289].

In the post-transition and post-second transition oxides where no suboxide was found at the metal-oxide interface, growth of m-ZrO₂ or t-ZrO₂ grains directly on the α -Zr has been generally found. On the other hand, for pre-transition oxide with the suboxide present, multiple crystal structures including m-ZrO₂, t-ZrO₂, α -Zr, ω -Zr and unidentified structures have been found simultaneously in almost every sample. Therefore it is not completely

resolved what exact phase of the suboxide is when it contains an oxygen level higher than the maximum solubility of ~30. at. % in the metal.

The Zr_3O structure was found further away from the metal-oxide interface in the pre-transition ZIRLO oxides with a suboxide layer. Therefore this structure appears to correspond with the observed oxygen saturated metal layer (with ~30 at. % oxygen) below the metal-oxide interface in the post-transition oxide and beneath the suboxide region in the pre-transition oxides. This is reasonable, as the Zr_3O structure has been described as an ordered oxygen solid solution in $\alpha\text{-Zr}$ to achieve the maximum oxygen solubility in Zr [176].

Tetragonal oxide grains were found at the metal-oxide interface in both pre-transition and post-transition oxides, and thus its presence only in pre-transition oxides (as found in [120]) could not be confirmed in this work.

The presence of possible amorphous region at the interface, such as shown by Warr et al. [64] and Ploc [174] could not be confirmed in this work. Although sometimes very small amorphous looking regions were found, it was more likely to be caused by an off-zone axis alignment of that particular region. The very small size of the possible amorphous regions and the complex interface morphology has made the examination of the same area at different tilting angles very difficult, which is necessary to be sure of identifying a region as amorphous.

7 Microstructure investigations by 3D FIB slicing

3-D microstructural characterization using high resolution FIB sectioning has been performed to provide a quantitative description of the oxide microstructure, from which parameters such as crack density, crack distribution and interface roughness can be extracted with good statistics. The details of the methodology and experimental procedure were described in **section 3.7**.

The stress-relieved ZIRLO alloy tube oxidized in simulated PWR primary water in an autoclave at 360 °C for 140 days was initially selected for this work. As mentioned in section 4.1, while the weight gain vs. corrosion time curve (**Figure 4.2**) indicates that this sample is post-transition, it exhibits a patchy oxide containing both black and grey areas (**Figure 4.3**). Therefore, both regions from the same sample, one with the black oxide (Sample 1 - black) and the other with the grey oxide (Sample 1 - grey), were studied to investigate similarities and differences in the oxide microstructure. Another three materials (samples 2, 3 and 4) were also included for comparison. They are the oxides grown on recrystallized ZIRLO sheet alloy in the same autoclave conditions at 360°C for 34, 60 and 180 days. **Figure 4.2** has shown that the oxidation behaviour of stress-relieved ZIRLO alloy tube and the recrystallized ZIRLO sheet are very similar in terms of the weight gain kinetics despite a different macroscopic geometry and heat treatment history, so I believe that it is possible to make a direct comparison of the microstructures of all 5 samples. A list of the samples studied in this chapter is given in **Table 7.1**.

7.1 Reconstructed 3D data

The dimensions of the reconstructed volumes and the associated voxel sizes are listed in **Table 7.2**. X, y and z directions are as defined in **Figure 3.13**. The x and y dimensions of the voxels were determined from the resolution of the SE images, and the z dimension from the

experimental separation between two sequential 2D SE images. The reconstructed volumes are large enough to allow statistically significant analysis of the key microstructural features.

Table 7.1 List of samples investigated

	Base Zr alloy	Corrosion time at 360°C	Position at the weight gain vs corrosion time curve
Sample 2	ZIRLO recrystallized sheet	34 days	<i>before</i> transition
Sample 3	ZIRLO recrystallized sheet	60 days	<i>before</i> transition
Sample 1 Black oxide	ZIRLO stress- relieved tube	140 days	<u>Shortly after</u> transition (based on the average weight gain from both black and grey oxides)
Sample 1 Grey oxide	ZIRLO stress- relieved tube	140 days	
Sample 4	ZIRLO recrystallized sheet	180 days	<i>after</i> transition

Figure 7.1 shows images of each of the reconstructed 3-D volumes in order of increasing oxide thickness. X, y and z directions are defined as above. For sample 1, the oxide is thinner in the black regions than where the surface is grey, and all the oxide layers contain, as widely reported in the literature [44, 101, 138], micron-scale cracks and a rough metal-oxide interface. By inspection we can see that in the inner and middle part of each oxide the cracks run approximately parallel to the metal-oxide interface, while towards the oxide surface they are replaced by a lower density of more equiaxed micro-pores. The density of cracks also appears to increase with increasing oxide thickness. By looking at the 3-D images we find that the micro-cracks near the metal-oxide interface frequently lie above less deeply oxidized regions of the interface, especially for cracks closest to the metal-oxide interface. From the

reconstructed images it also appears that the roughness of the metal-oxide interface varies from sample to sample, for example the interface is rougher in the black oxide sample than the grey oxide as will become more obvious from the statistical analysis in the next section.

Table 7.2 Dimensions of the analysed 3D volumes and the three dimensional pixel (voxel) sizes for the 5 samples.

	Analyzed 3D volume				Voxel size (nm)		
	X (μm)	Y (μm)	Z (μm)	Total (μm ³)	X	Y	Z
Sample 1 Black oxide	~17	~4	~14	~950	16	16	54
Sample 1 Grey oxide	~17	~6	~21	~2140	16	16	56
Sample 2	~19	~4	~19	~1571	14	14	81
Sample 3	~19	~5	~11	~1035	11	11	62
Sample 4	~18	~6	~19	~2225	17	17	54

7.2 Statistical analysis of 3D reconstructed data

7.2.1 Oxide thickness

Statistical measurement of the oxide thickness was carried out based on analysis of the whole of each reconstructed 3D volume. The thicknesses of the oxides on sample 2, sample 3, sample 1 - black oxide, sample 1 - grey oxide and sample 4 are respectively 1.3 ± 0.2 μm, 1.7 ± 0.2 μm, 2.2 ± 0.3 μm, 3.1 ± 0.2 μm and 4.4 ± 0.4 μm. The significant variation in oxide thickness measured in a single sample is a result of the undulated metal-oxide interface. Sample 1 – black oxide and sample 4 have bigger variations in the oxide thickness than other samples, arising from a rougher interface.

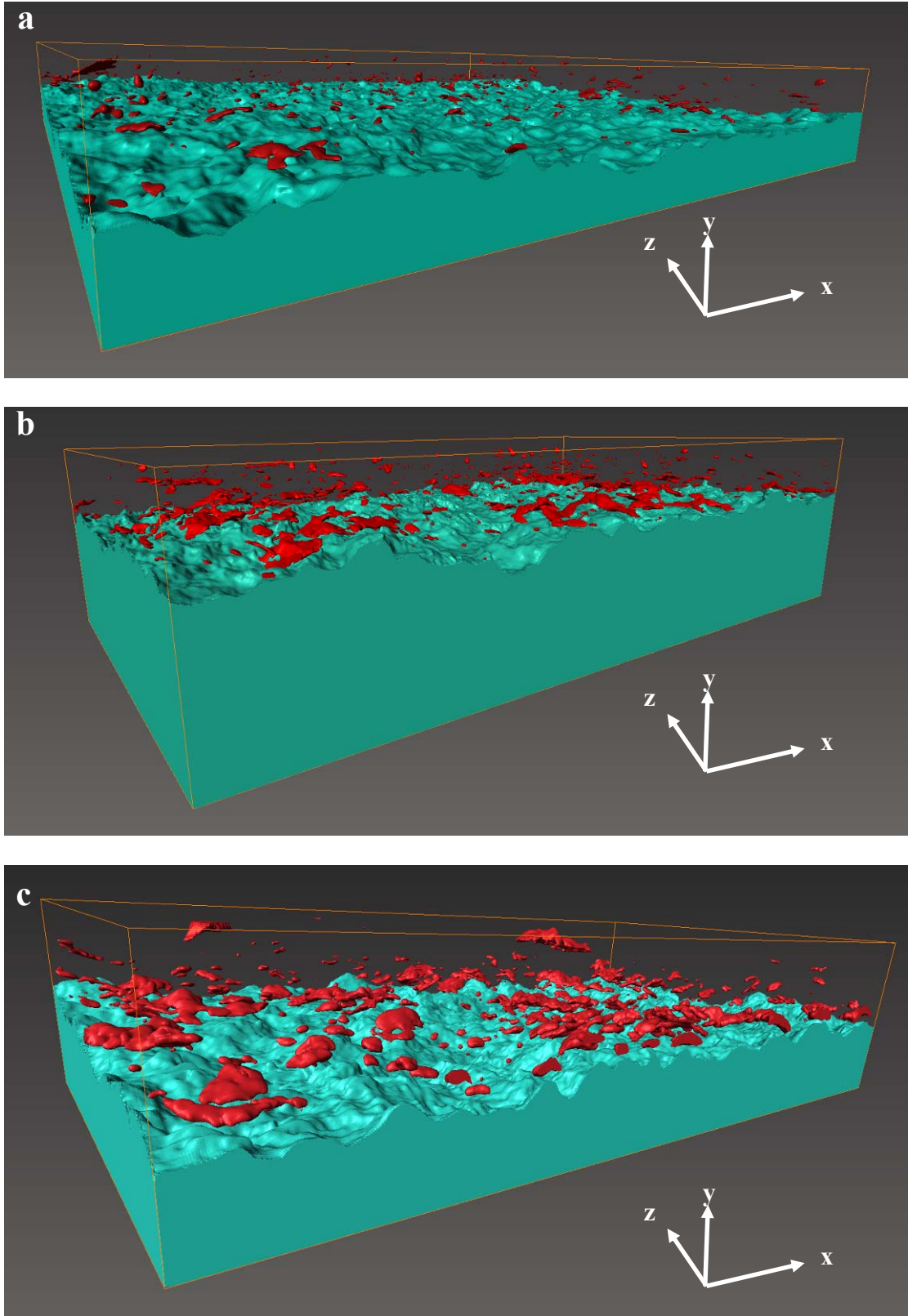


Figure 7.1 Reconstructed 3D images for oxides in order of increasing thickness. (a) sample 2, 34 days; (b) sample 3, 60 days; (c) the black oxide of sample 1, 140 days; (d) the grey oxide of sample 1 140 days, and (e), sample 4 180 days. The dimensions of the reconstructed volumes for each sample are listed in table 7.2. Figures to be continued in the next page.

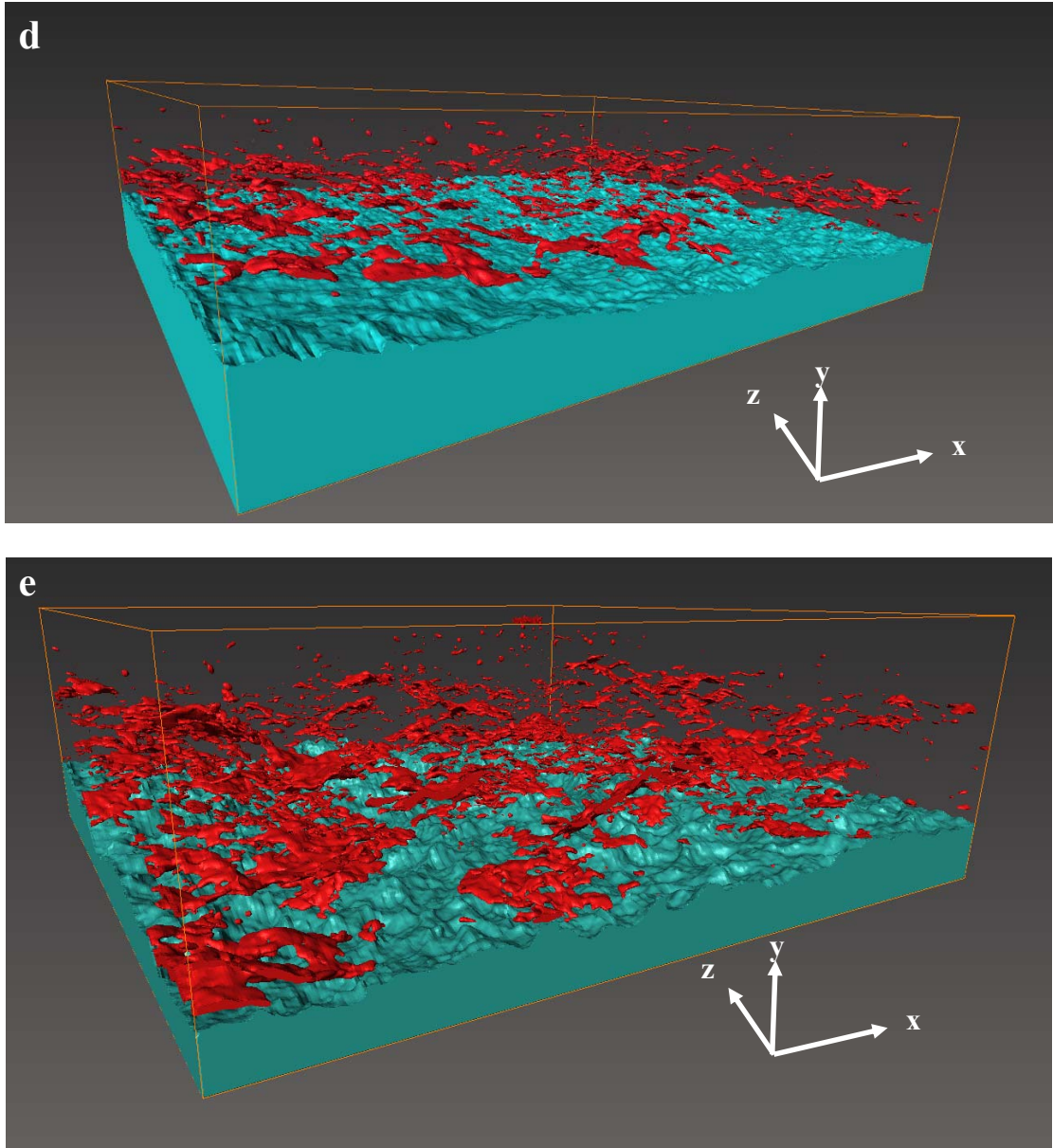


Figure 7.1 Continued. Reconstructed 3D images for oxides in order of increasing thickness. (d) the grey oxide of sample 1 140 days, and (e), sample 4 180 days. The dimensions of the reconstructed volumes for each sample are listed in table 7.2.

Figure 7.2 is a plot of the measured thickness vs. corrosion time. Although the black oxide and the grey oxide are both taken from sample oxidized for 140 days, we have seen that the black oxide is much thinner than the grey oxide. The data points for the pre-transition oxides (including samples 2 and 3) and an oxide thickness of zero at the start of oxidation can be fitted by an approximately cubic rate law $t = 0.38 \cdot d^{0.35}$, where t is the oxide thickness in microns and d the corrosion time in days. This exponent fitted from the thickness data (~ 0.35)

is very close to that obtained from the weight gain data of ZIRLO SR oxidation (~ 0.30 , c.f. **Table 4.2**), and the near cubic rate law is in agreement with the previous studies [2, 3, 256]. Fitting of the data points for the post-transition oxides is not unique because only two data points (sample 1 - grey oxide and sample 4) are available. The same equation to fit the data points after the transition has been used, assuming that in the early stages of oxidation a protective oxide is formed first and grows to a critical thickness of $\sim 2 \mu\text{m}$ before suffering an abrupt breakdown such that the metal surface becomes exposed again to the corroding agent, and a similar protective oxide forms with the same rate law. It can be seen that from this fitting that the black oxide is sitting somewhere around the kinetic transition. This is also expected from the fact the black oxide is taken from a patchy oxide that has passed the transition if judged by the average weight-gain data.

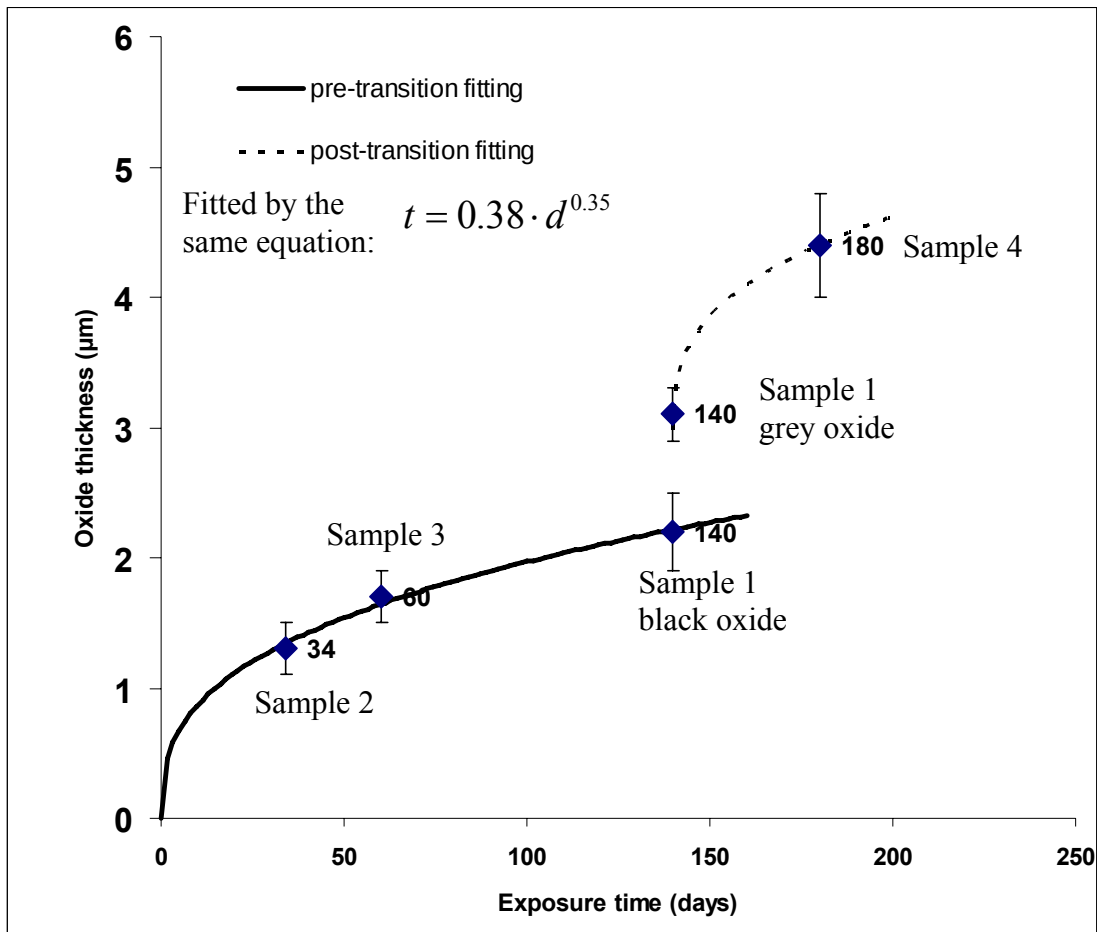


Figure 7.2. Plot of the measured oxide thickness versus corrosion time. The black oxide has a smaller thickness compared to the grey oxide.

7.2.2 Characterization of cracks in the oxide

The volume fraction of cracks in the oxide was determined by counting voxels lying inside cracks, and shows that the crack volume increases monotonically with the oxide thickness (**Table 7.3**). A plot of the total crack volume versus oxide thickness (**Figure 7.3**) indicates an initial period (below $\sim 0.8 \mu\text{m}$ oxide thickness) where few cracks appear, followed by steady development of cracks as the oxide grows. Both black and grey oxides (sample 1) fit this linear region. It is only in the last sample (180 days) that there appears to be faster cracking. There is no indication in any of the data to show a sudden burst of cracking at the kinetic transition.

Table 7.3 Analysis of the crack size distribution in the 5 samples.

Samples (in order of increasing thickness)	Crack volume fraction (vol. %)	Number of Cracks Analyzed	Mean Crack Size (μm^3)	Mean Crack Length (nm)
Sample 2	0.85	390	0.0019 ± 0.0043	311 ± 198
Sample 3	1.1	656	0.0027 ± 0.0091	289 ± 291
Sample 1 Black oxide	1.5	339	0.012 ± 0.047	506 ± 642
Sample 1 Grey oxide	1.7	1338	0.007 ± 0.029	415 ± 517
Sample 4	2.7	2803	0.0081 ± 0.066	347 ± 490

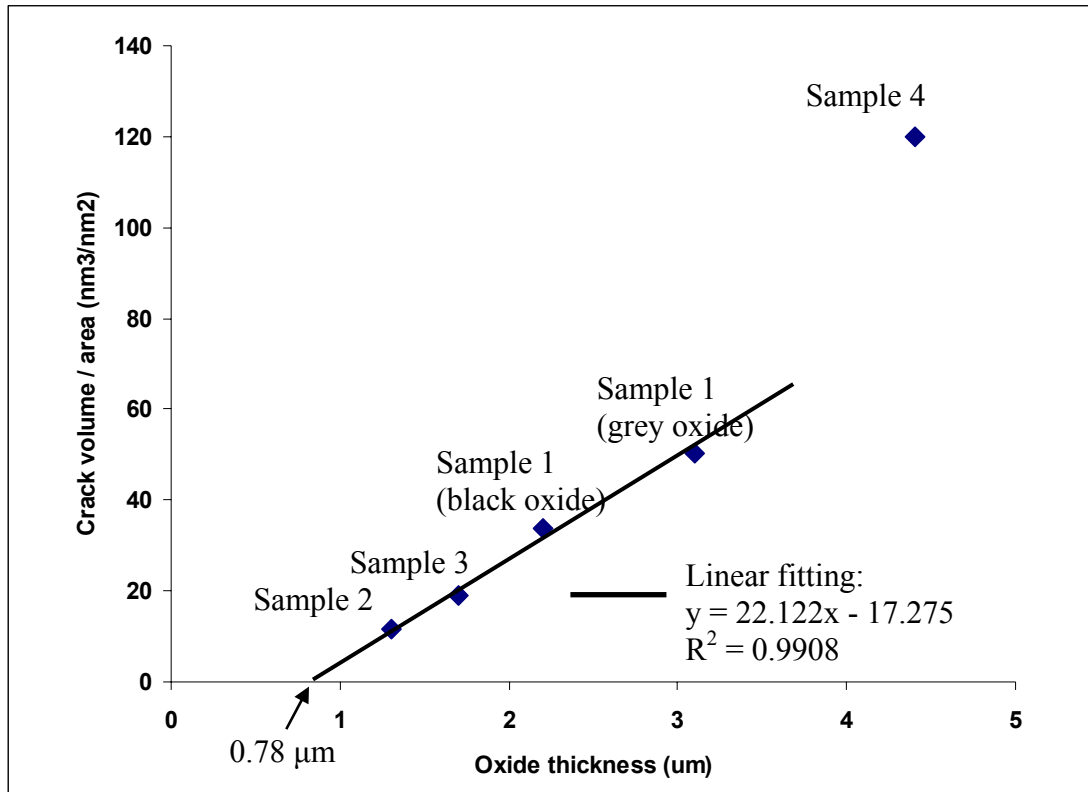


Figure 7.3 The total crack volume plotted against the oxide thickness to show the rate of crack volume increase.

Analysis of the individual crack volumes and lengths was carried out using the Avizo software and the results are shown in **Table 7.3** and **Figure 7.4**. The crack length is taken as the longest dimension of any 3D crack, which almost always lies parallel to the macroscopic plane of the metal-oxide interface. Once more, it was found that both mean crack volume and length increase with increasing oxide thickness until transition. Both parameters then have a lower value in the data from the grey oxide of sample 1, and the crack volume increases again in the 180 day sample.

Projection of the 3-D reconstruction along the z direction gives the distribution of cracks along the oxide growth direction (y direction), as shown in **Figure 7.5a** for the black oxide on sample 1. It can be seen that the cracks appear to form a layer roughly parallel to the metal-oxide interface, and this becomes more clearly defined in **Figure 7.5b** where the effect of the wavy interface has been removed by normalising distances to the local position of the metal surface. The same data can be represented in the form of a histogram of the number of

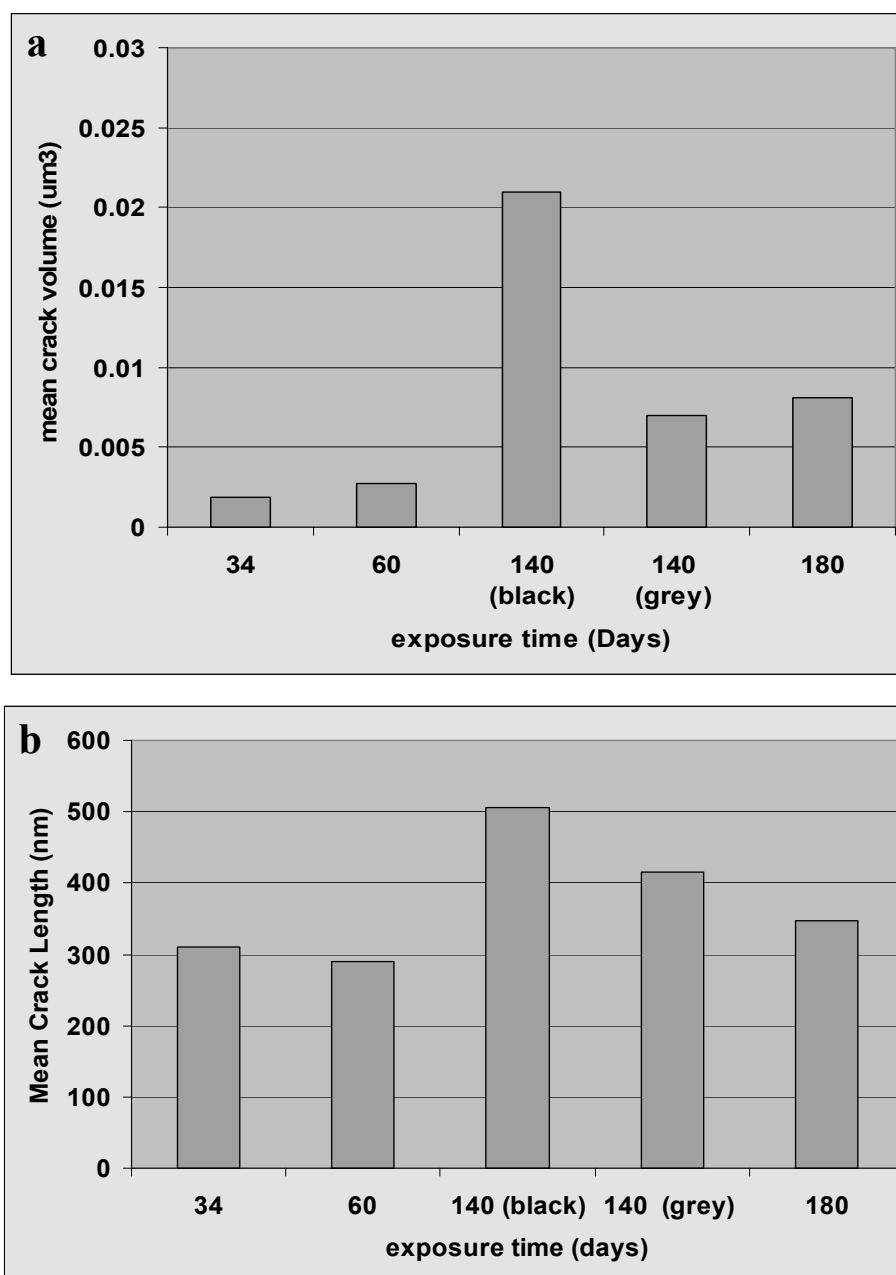


Figure 7.4 Crack analysis of all the samples. a) mean crack volume. b) mean crack length

voxels lying within a crack as a function of distance from this surface (**Figure 7.5c**), with the majority of crack volume being within 200 nm of the oxide/metal interface. **Figure 7.6** shows the same plot of the distribution of crack volume along the oxide growth direction for all 5 samples, taking into account that the number of slices and the depth in the z direction used for obtaining the original 2D projection images were not exactly the same. It can be seen that a first layer of cracks has started to form ~130 nm away from the metal-oxide interface in the earliest oxide sample we studied (sample 2, peak A). A more well-defined first layer of cracks

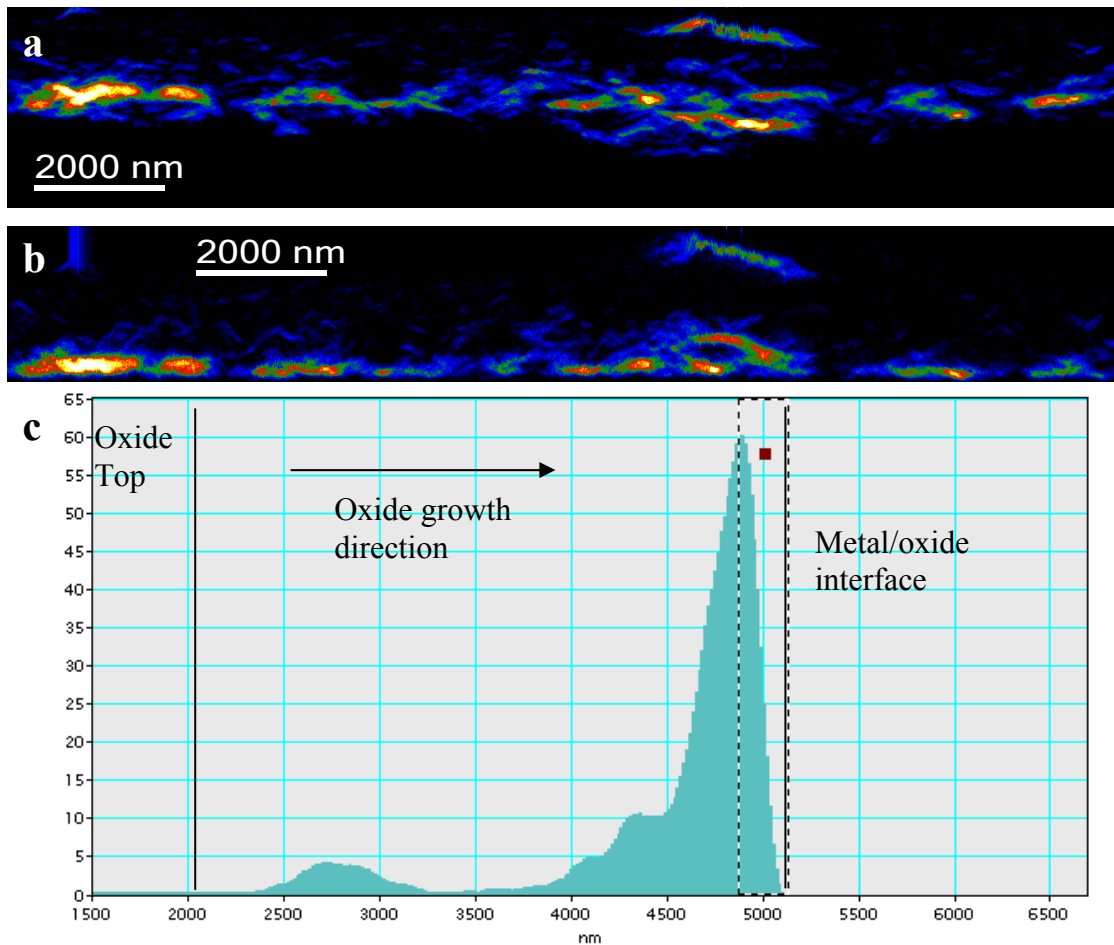


Figure 7.5 Characterization of the cracks in the black oxide. (a) Projected 2D image of the 3D reconstruction image along the z direction, showing the distribution of cracks in the oxide. (b) The same data as (a), but with the metal-oxide interface normalized to a straight line at the bottom of the image. (c) Histogram of the crack distribution along the growth direction extracted from the data in (b).

is seen in sample 3, peak B, but at a distance from the interface that has increased to ~ 220 nm.

We can understand this as a result of the further formation of new oxide under the first layer of cracks in the time interval between 34 and 60 days. With increasing oxidation time, this layer develops a larger volume of cracks and is pushed further away from the interface by the growth of new oxide (~ 260 nm for the black oxide on sample 1, ~ 1 μm for the grey oxide on sample 1 and 2.1 μm for sample 4). But post-transition the depth distribution of the first layer of cracks broadens (peaks D and E), and a second layer of cracks start to nucleate near the metal surface (peaks F and G). In the grey oxide of sample 1 (140 days), the new second layer of cracks is within 100 nm of the metal surface, while in sample 4 (180 days) the new second layer is ~ 390 nm away from the interface. The distance between the first and the

second layers of cracks in sample 4 is $\sim 1.7 \mu\text{m}$, similar to the distance between the first layer of cracks and the oxide top surface in all the samples, (1.4 - 2.1 μm).

In the black oxide on sample 1, a single large crack is present near the top surface of the oxide. The location of this large crack coincides with the area with the lowest interface height in the $950 \mu\text{m}^2$ of analysed volume, i.e. the most deeply oxidized part.

7.2.3 Morphology of the metal-oxide interface

Topography maps of the metal-oxide interface can be derived from distances from the (smooth) oxide surface and represented as contour maps. **Figure 7.7** shows a typical example for the grey oxide on sample 1. From these maps the roughness of the interface can be characterized by two parameters; the difference in height between the highest point and the lowest point of the interface, and the standard deviation from the mean value of the interface height (RMS roughness) over the whole analysed volume. To explore whether the calculated interface

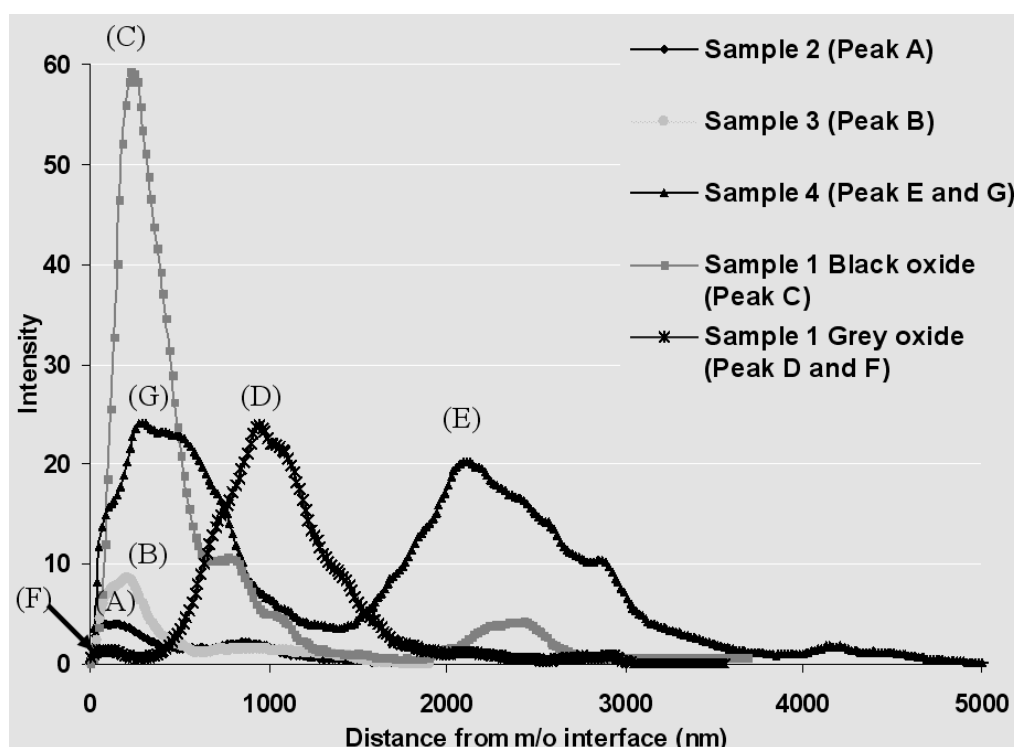


Figure 7.6. Plot of the number of pixels lying inside cracks as a function of distance from the metal-oxide interface. The layered nature of the crack distribution in the different samples is clearly seen. Peaks A-E are the first-formed layers of cracks in the 5 samples gradually moving further from the metal-oxide interface as the oxide thickens, peak F is the second layer of cracks just starting to form in the grey oxide on sample 1 and peak G is the second layer of cracks in sample 4.

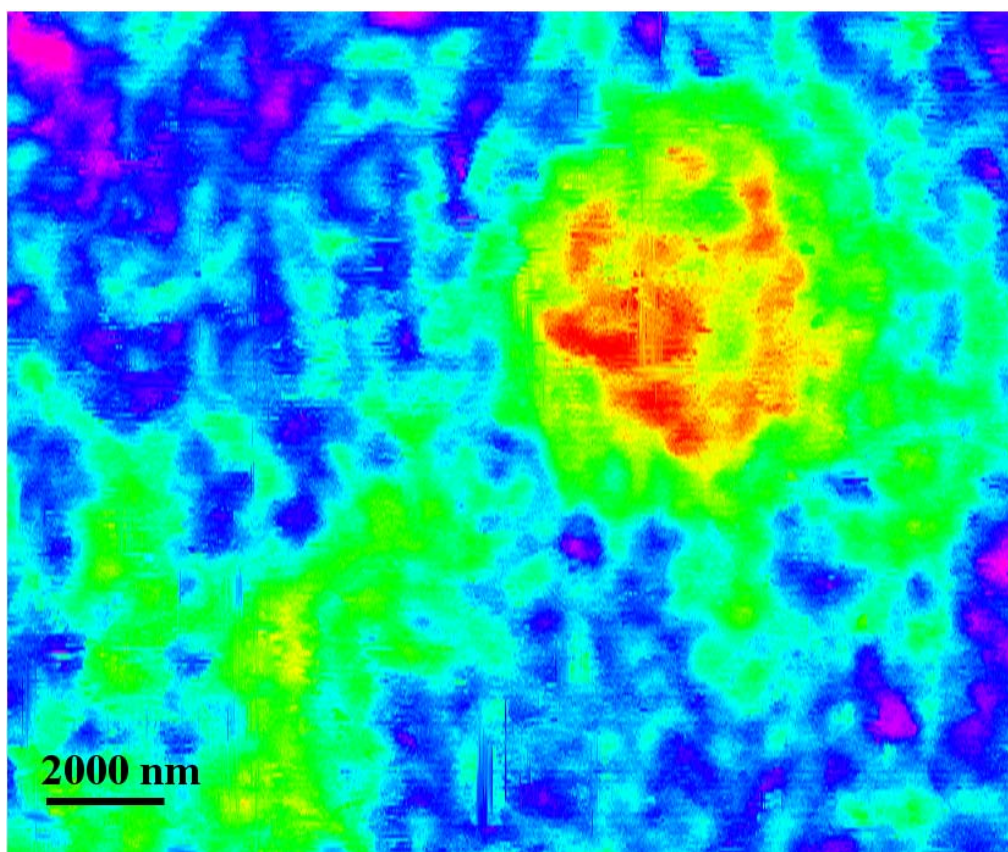


Figure 7.7 Metal-oxide interface topography maps of the black oxide. Red shows regions of thin oxide and blue the thickest oxide.

roughness was the same everywhere in the analysed volume, the roughness was also measured over ~ 150 smaller areas of $1\ \mu\text{m} \times 1\ \mu\text{m}$. The results of this analysis are shown in **Table 7.4** and **Figure 7.8**. There is a clear trend in *all* these roughness parameters (for both the whole analysed volumes and local areas) with oxidation time; a gradual increase from 34 to 140 days, an abrupt decrease in all measures of roughness for the 140 day grey (post-transition) oxide, and then an increase again at 180 days.

As the metal-oxide interface is undulating, its periodicity, defined as the distance between successive maxima or minima, can be measured. Many line profiles (40 to 50 for each 3D data block) have been taken along horizontal, vertical and diagonal directions across the topography maps to yield height scans of the kind shown in **Figure 7.9**. We find that periodicity cannot usually be defined across the whole of the areas analysed, but that it can be detected over a few microns. Over these shorter length scales a minimum of three cycles for

the identification of a characteristic periodicity has been specified, and the results are shown in **Table 7.5**. It can be seen that several different periodicities are present in all the samples, with the longer periodicities being rough multiples of the smallest ones. The most frequent periodicities were found to be 1028 ± 105 nm for the black oxide of sample 1 and 300 ± 26 nm and 506 ± 50 nm for the grey oxide of sample 1 for instance. It is interesting to compare these values with the grain size in the underlying Zr metal. After the mechanical processing used to fabricate the tube or sheet material, both have highly deformed α -Zr grains some 3-5 μ m long in the plane of the oxide/metal interface, and there are also many low angle grain boundaries inside each grain. There is no clear correlation between metal grain size and interface roughness. Another interesting point is to compare with the separation between SPPs. A measurement on the distances between SPPs in the ZIRLO RXA metal matrix was carried out in a number of SEM images. **Figure 7.10** shows a histogram of a 100 measured distances with a binning width of 300nm. The broad distribution of the histogram indicates that the SPPs are not evenly distributed but the average distance is $\sim 2.1 \pm 1.3$ μ m. Therefore, there is also no clear correlation between the SPP separations and the interface periodicities.

Table 7.4 Analysis of the metal-oxide interface roughness for the 5 samples.

Samples (in order of increasing thickness)	Interface Roughness (nm)			
	Difference between Max and Min height		Standard deviation from mean value of the height	
	Overall	local	overall	local
Sample 2	~1200	403	166	81
Sample 3	~1300	444	179	90
Sample 1 Black oxide	~1500	~572	~255	~110
Sample 1 Grey oxide	~1000	~260	~150	~45
Sample 4	~1900	589	307	118

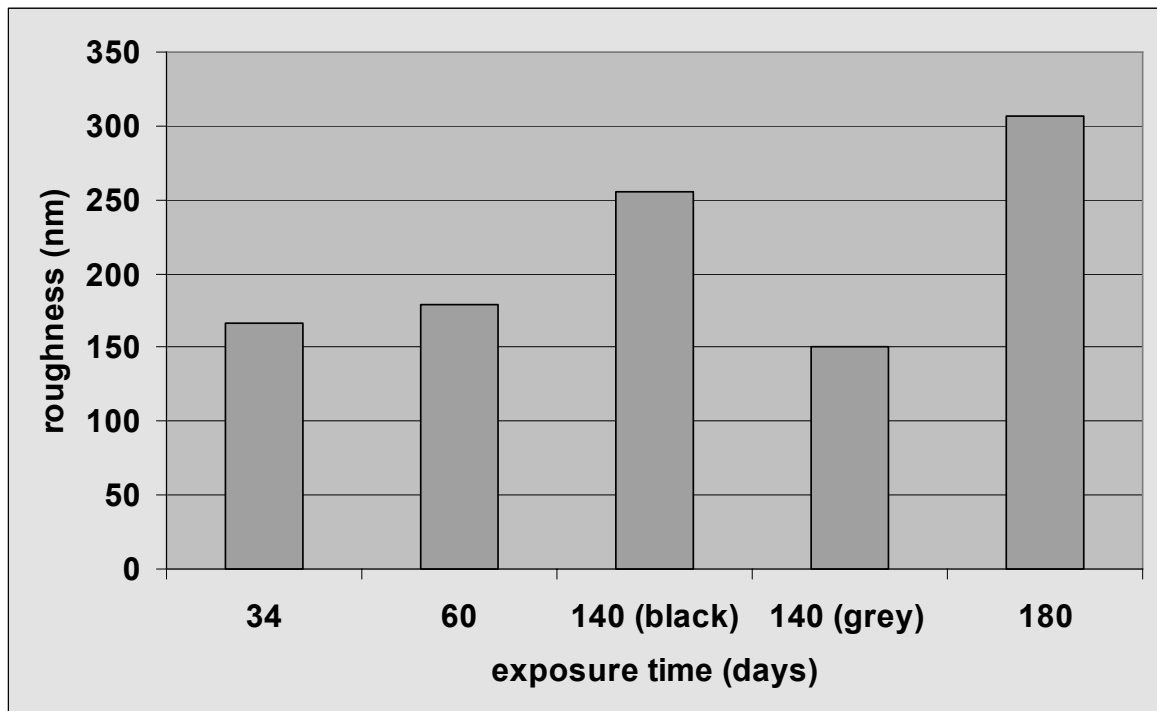


Figure 7.8 Overall RMS roughness of the metal-oxide interface for all the samples. The roughness increases with the increasing oxide thickness but shows a sudden decrease for the oxide just after the transition (grey oxide of sample 1). After that, the roughness increases again.

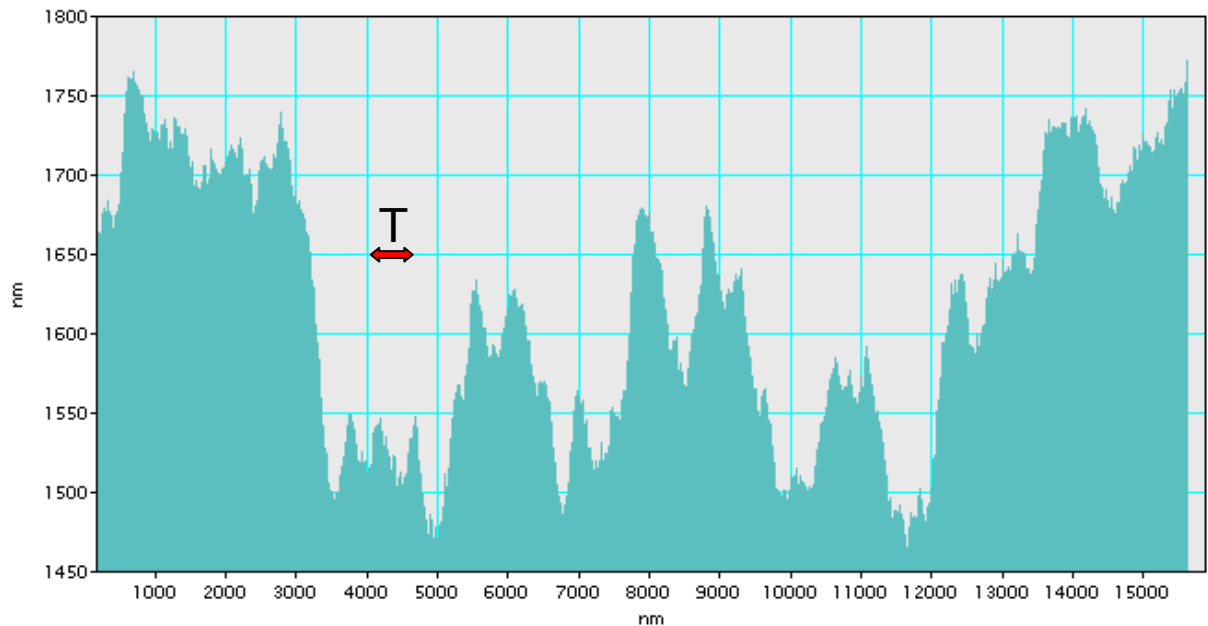


Figure 7.9 Illustration of the method of characterizing the metal-oxide interface periodicity from a lines can across a typical data set of the kind shown in Figure 7.7.

Table 7.5 The metal-oxide interface periodicity of the black and the grey oxide.

Samples (in order of increasing thickness)	Periodicity Detected (nm)	Most prominent periodicity (nm)
Sample 2	683 ± 94 ; 938 ± 88 ; 1299 ± 69 ; 1676 ± 120	683 ± 94 ; 938 ± 88 ;
Sample 3	612 ± 81 ; 916 ± 89 ; 1180 ± 75 ; 1538 ± 98 ; 2877 ± 155	612 ± 81 ; 916 ± 89
Sample 1 Black oxide	306 ± 32 ; 589 ± 52 ; 903 ± 84 ; 1028 ± 105 ; 1592 ± 71	1028 ± 105
Sample 1 Grey oxide	300 ± 26 ; 506 ± 50 ; 943 ± 89	300 ± 26 ; 506 ± 50
Sample 4	340 ± 48 ; 679 ± 45 ; 930 ± 85 ; 1360 ± 144	679 ± 45 ; 930 ± 85

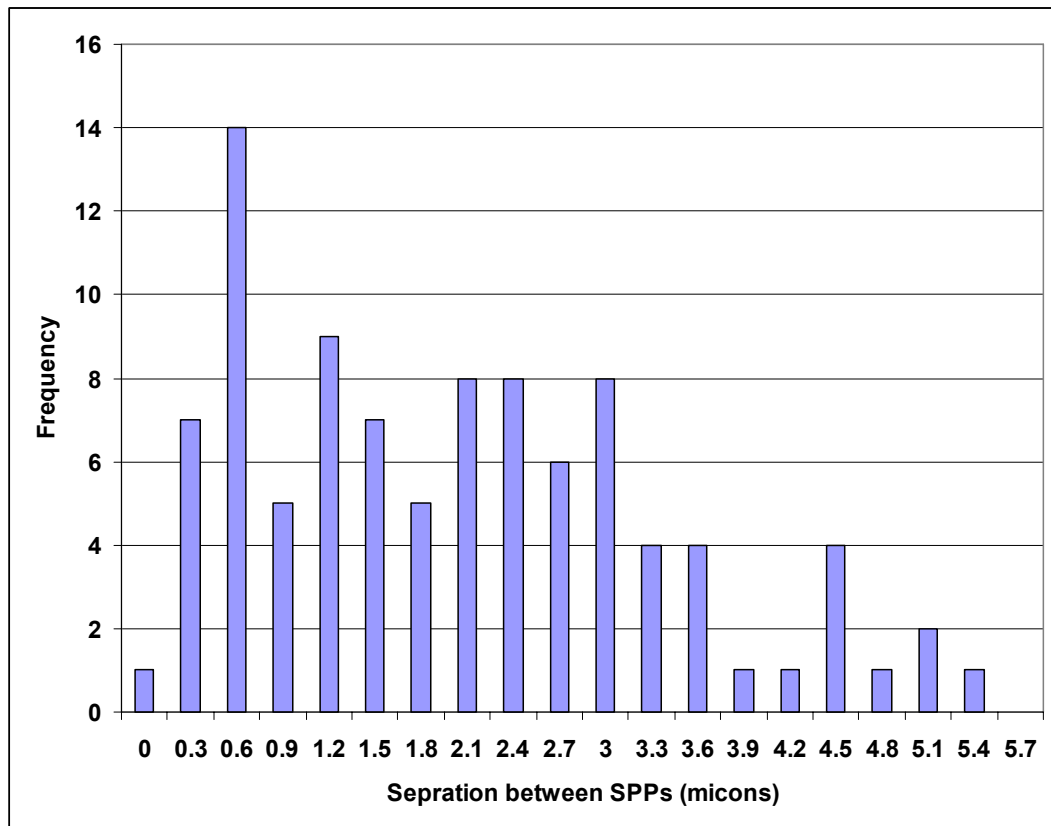


Figure 7.10 Histogram of measured distances between SPPs.

An important observation is that cracks do appear frequently above protrusions (more slowly oxidising regions) on the metal-oxide interface, especially when they are close to that interface. A statistical analysis was carried out for the two layers of cracks observed in the black and the grey oxide of sample 1. It was found that for the layer of cracks in the black oxide which are ~260 nm away from the interface, 209 out of 252 investigated cracks (~83%) are located above less oxidised regions of the metal surface (above a bump in the interface). So in this sample slower local oxidation seems clearly to be associated with the crack positions – or alternatively, cracking to be associated with projections at the interface. On the other hand, for the layer of cracks in the thicker grey oxide where the interface is already ~1µm ahead of the cracks, only 163 out of 349 investigated cracks (~47%) are above protrusions and the rest (186 cracks) are above more deeply oxidized regions, which means that for this sample no obvious link exists between the position of the cracks and the underlying rate of oxidation.

7.3 Discussion

By examining a bigger 3-dimensional volume for oxidized zirconium alloys than can be explored in a typical TEM or SEM study, this work has for the first time provided a quantitative analysis of the density and the location of cracks relative to the metal-oxide interface. As a result of the high resolution achieved in the acquired images (with pixel size <10nm), the 3D reconstruction can represent accurately the volume and microstructure of cracks and pores as small as 100 nm. Smaller cracks and pores, although often visible, were not included in these reconstructions, because they cannot be reliably detected in the images.

The analysis of the characteristic periodicities of the metal-oxide interface have not suggested a close relationship with the grain size of the underlying metal, so that a dependence of local oxidation rate on the crystallography of the Zr metal cannot be predicated.

The examination of average distance between SPPs also shows no clear correlation with the periodicities of the interface undulations.

The metal-oxide interface roughness increases with increasing oxidation time up to the black oxide of sample 1 and shows a decrease for the grey oxide of sample 1 before increasing again in the thicker oxide (sample 4). Therefore the black oxide has the roughest metal-oxide interface. As an oxidising sample approaches transition, we must consider the effect of a significant increase in compressive stress [156, 260]. If the transition happens inhomogeneously across the sample surface, different areas can be expected to have big differences in the stress level, which can influence the local rate of oxidation leading to increased interface roughness since hydrostatic stresses can affect the oxygen diffusion coefficient [290]. In addition, a very clearly defined layer of cracks ~ 300 nm away from the interface was found in this sample. It has been shown in this sample that these cracks are much more frequently localized in the oxide above the peaks of the undulating interface, as previously reported by [101]. The cracks may be introduced by the interface roughness on one hand, as will be discussed later, but on the other hand, when the first cracks are formed, they can increase the interface roughness by slowing down oxidation locally by acting as obstacles for the transport of both oxidizing species and charge carriers (electrons or holes). However, it is interesting to note that in our data for the black oxide on sample 1 a region containing a very big crack near the oxide surface (which should be formed in the very early stage of the oxidation) has developed the thickest oxide, which suggests that the presence of a crack eventually can accelerate oxidation once it is separated from the oxide/metal interface by a significant distance, perhaps when they become connected to the oxidizing media via connected nano-porosities [291].

The flattest metal-oxide interface was observed in the grey oxide on sample 1. This might be a consequence of a relaxation of stress after transition, as reported in [260], or a reducing local

influence of the cracks as they move further away from the interface. The data also shows that the grey oxide has a higher volume fraction of cracks than the black oxide. This also means a big total volume of cracks in the grey oxide since the oxide is thicker. As the 3-D characterization was not performed in-situ on the same area of a single sample at different stages of oxidation it is difficult to know exactly whether the increase in crack volume is a result of the formation of new cracks or the growth of old ones. The analysis of the mean volume and length of individual cracks has shown a decrease in these parameters from the black oxide to the grey oxide. Therefore the observation that the black oxide has a smaller total volume of cracks but a larger mean individual crack volume indicates that the grey oxide contains many smaller (newer) cracks. This strongly suggests a nucleation of new cracks in the second parabolic growth stage after the initial transition, not the growth of existing cracks further from the metal-oxide interface. The black oxide and the grey oxide have an average thickness of 2.2 μm and 3.1 μm respectively. If we assume that the difference of $\sim 0.9 \mu\text{m}$ approximately represents the newly developed oxide after transition, the crack volume fraction in this the $\sim 0.9 \mu\text{m}$ layer can be calculated to be $\sim 1.4\%$. This number is higher than the crack volume fraction found in sample 2 ($\sim 0.8\%$) which has a similar oxide thicknesses ($\sim 1.3 \mu\text{m}$) to that of the newly formed oxide. This may indicate that although fresh oxide forms again after transition, the protectiveness of this newly layer might be reduced compared to the dense oxide formed in the early stages of oxidation before transition, as postulated by previous EIS measurements [101].

A gradual production of cracks throughout the parabolic oxide growth before the first transition in kinetics has been observed (**Figure 7.3**), instead of a sudden burst of crack nucleation at transition as has frequently been assumed from observation of the characteristic layered crack morphology in thicker oxides [19, 43, 44, 137, 138]. In other words, the cracks are not generated as a result of the abrupt increase in oxidation rate at transition, but may

instead play a role in encouraging the transition. **Figure 7.3** also indicates that the cracks in the oxide appear to form after an oxide thickness $\sim 0.8 \mu\text{m}$, corresponding to a weight gain $\sim 12 \text{ mg/dm}^2$. This is in good agreement with the TEM observations on the 7 days Zircaloy-4 oxide, which has a thickness of $\sim 700\text{-}800 \text{ nm}$ and does not show big cracks (**section 5.1**). Dawson [35] have carried out a careful study on the kinetics of the oxidation of Zircaloy-2 at 350 to 500 °C in oxygen and water vapour, which revealed in the pre-transition stage a change from a parabolic rate to a cubic rate of oxidation at $\sim 10 \text{ mg/dm}^2$. The change was attributed to the formation of randomly distributed horizontal cracks at or near the metal-oxide interface. In **Figure 7.2**, the measured oxide thicknesses used for fitting the pre-transition kinetics starts from $\sim 1.3 \mu\text{m}$, so the fitting is expected to reflect kinetics after the change at $\sim 10 \text{ mg/dm}^2$. My fitting gives a near cubic rate ($n=0.35$). Therefore the observation in this work seems to provide further support for the development of a cubic rate law.

It is the nucleation of these cracks that we will now consider. The 3D data sets described above contain some suggestive indications of at least one mechanism for crack initiation. **Figure 7.11** shows selected 2D images from samples at different oxidation times, and there seems to be a clear propensity for cracks to nucleate at peaks (or the slowest oxidizing regions of the interface) and over the top of SPPs near the metal-oxide interface. This second site of crack nucleation has also been seen repeatedly in TEM analysis of the same samples, such as shown already in **Figures 5.29, 5.31** and here again in **Figure 7.12**, and has been reported by other authors [138, 271]. Since under corrosion conditions without neutron irradiation these SPPs do not begin to amorphise and dissolve until much further into the oxide [138], and will not oxidize while the zirconium metal surface on either side is being converted into less-dense oxide, the volume change around the SPP as new oxide is created will necessarily result in the creation of a void or crack at the top of the particle due to generation of tensile stresses. These cracks will initially be of the same size as the SPPs, 50-200 nm in our samples.

Meanwhile, the delayed oxidation of SPPs can also enhance the interface undulations. Parise et al. [205] have used 2D finite element modelling of the stresses around a metal-oxide interface with characteristic undulating shape to predict that significant radial tensile stresses will be generated immediately above bumps. These local radial stresses will act to encourage the propagation along the interface of small cracks formed above SPPs.

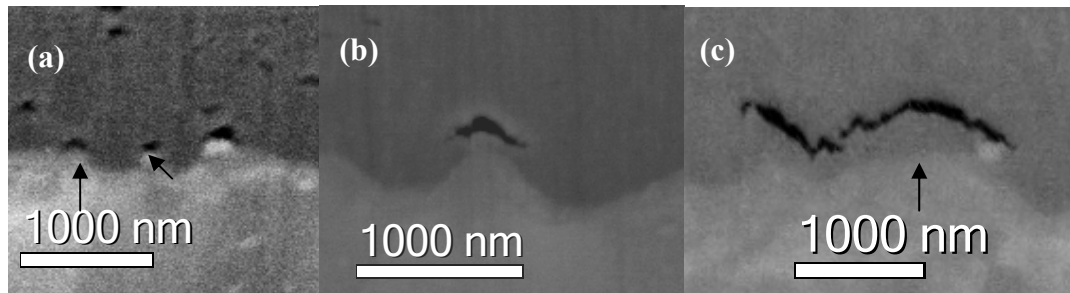


Figure 7.11. Selected images from the 3D dataset illustrating the association of cracks with bumps in the metal-oxide interface and second phase particles (arrowed). a) Sample; 2 b) Sample 3 c) Sample 1 Black

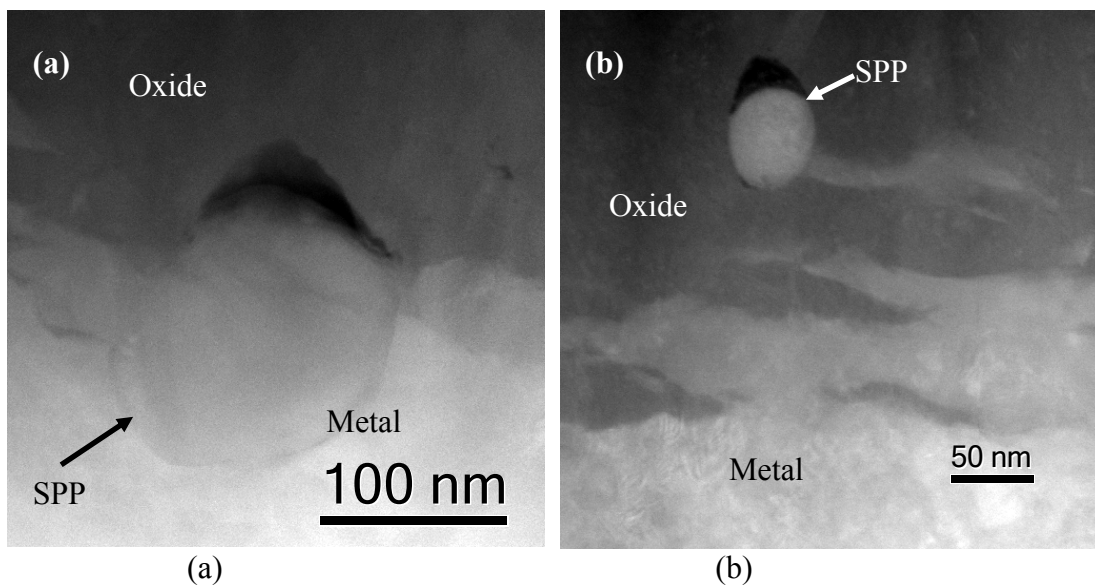


Figure 7.12. Two examples of cracks formed immediately above SPPs, (a) at and (b) just above the metal oxide interface.

It is also interesting to consider another mechanism about the initiation of these horizontal cracks. Confined heterogeneous polycrystalline brittle solids loaded under uniaxial compression have been frequently observed to crack along the loading axis, as schematically

shown in **Figure 7.13** (ref [206] and therein). Compressive stresses can induce tension in the direction perpendicular to the compression and causes cracking along the loading direction. Under uniaxial loading and assuming an isotropic material, a model based on the energy balance between the unsplit system and the split system has estimated the critical compressive stress for splitting σ^* in the absence of confinement stress σ_c [206]. In the case of oxide films grown on Zr metal substrates, the oxide can be regarded to be under a biaxial compression in the plane parallel to the metal-oxide interface without a confinement stress along the oxide grow direction. Although zirconium oxide is highly anisotropic, as an approximation, it can be shown by simple calculation that σ^* under biaxial stresses using the same energy based model is:

$$\sigma^*|_{\sigma_c=0} = \sqrt{\frac{-2\gamma}{d} \frac{E_u E_s}{E_s(1-\nu_u) - E_u(1-\nu_s)}} \quad \text{Equation 7.1}$$

where γ is the surface energy density of the material, d the typical grain size and $\Delta = \frac{1}{E_u} - \frac{1}{E_s}$ the difference related with the Young's modulus of the unsplit system E_u and the split system E_s , ν_u and ν_s the Poisson's ratio for the unsplit system and the split system respectively. As the Poisson's ratio are found to be similar for both systems [206], **Equation 7.1** can be simplified to:

$$\sigma^*|_{\sigma_c=0} = \sqrt{\frac{2\gamma/d}{-\Delta} \frac{1}{1-\nu}} \quad \text{Equation 7.2}$$

Compared with the result for uniaxial loading in [206], it can be found that in the conditions of biaxial loading, the critical stress required for splitting in the oxide is further reduced by $\frac{1}{2} \sqrt{\frac{1}{(1-\nu)}}$, in other words, it is easier to crack the oxide under biaxial loading conditions.

As has often been described by previous authors [101, 137], cracks in the ZrO₂ scale always run more or less parallel with the metal-oxide interface. The stress state in the oxide is

initially biaxial in the plane of the scale, and this compressive stress has been measured on this same set of samples to be well over 1 GPa [260]. A simple consideration of the likelihood of brittle fracture in ZrO_2 ($E \sim 170 \text{ GPa}$ [264]) stressed to 1 GPa (for the worst case - tension) assuming a fracture toughness for zirconia between 6 and $120 \text{ MPa}\sqrt{\text{m}}$ (Table 27.1 in [264]) a critical flaw size of $\sim 30 \mu\text{m}$ is obtained.

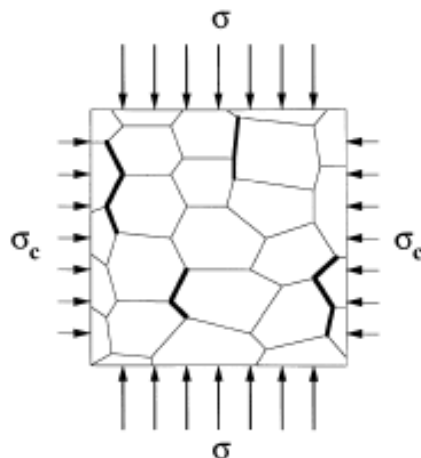


Figure 7.13 Cracking along the loading axis in ceramics confined by σ_c under compressive stresses σ [206].

However, in the 3D data, and the many 2D observations in the literature such as [101, 137], it is observed that the individual cracks never extend in the plane of the interface beyond 1-3 microns in length except at the outer surface of much thicker oxides formed after high burn-up corrosion [292]. So it would be interesting to explain why cracks once nucleated will not propagate at or close to the metal-oxide interface. A simple answer might be that cracks parallel to this interface in a uniformly compressively stressed oxide film will experience no stress concentration at the crack tip, and so no driving force to propagate. Once the ongoing oxidation process moves the crack 200 nm away from the metal-oxide interface, the analysis described above predicts that radial stresses created by interface undulations have almost completely disappeared [205]. However, Evans and Hutchison [204] showed that if a film buckles away from its substrate, large tensile stresses can be generated at the crack tip. This situation is worth considering given the observations above that the small cracks nucleated by interface roughness or SPPs are rarely perfectly parallel to the oxide surface. The equation for

the critical compressive stress, σ_c , to propagate a crack of length $2a$ at the bottom of a film of thickness t is:

$$\sigma_c = \frac{E}{(1-\nu^2)} \left(\frac{t}{a} \right)^2 \quad \text{Equation 7.3}$$

where E and ν are the Young's modulus and Poisson's ratio of the film (oxide) material. If we again take σ_c to be 1 GPa for cracking in our samples, the critical crack length $2a_{\text{crit}}$ from **Equation 7.3** will be at least $25t$ or $\sim 50\mu\text{m}$ taking the oxide thickness to be $\sim 2\mu\text{m}$ at the first transition in kinetics. This is much larger than the cracks that have been seen even in quite thick oxides. An analysis in the same paper including the idea of a maximum stress intensity factor (equation 37 in [204]) predicts even larger critical crack lengths if appropriate values for K_{IC} for typical ZrO_2 materials are used. A very similar conclusion that the critical crack length in the plane of the oxide must be much larger than the film thickness has been reinforced by a later, more sophisticated, analysis by the same authors [293].

This later paper also considers the nucleation of cracks under stressed films, emphasizing the importance of delamination at ‘imperfections’ like surface bumps (Fig.4 in [293]), a geometry extremely similar to that considered in Parise et al [205] and in **Figure 7.11** and **Figure 7.12**. They note that small imperfections can result in surprisingly rapid rates of energy release, and so are likely to form preferentially. However, they also note that once these small delaminations lying out of the macroscopic interface plane are formed, the likelihood of continued growth to a spontaneously propagating crack is very low when the ratio of imperfection height to film thickness < 0.1 (Figures 10b and 15 in [293]) as it normally is in my samples (**Figure 7.1**). Similarly, the critical wavelength of the interface ‘imperfections’ are calculated using appropriate parameters for Al_2O_3 films on Ni alloy substrates to be $> 20\mu\text{m}$ [293], much larger than the wavelength of the interface undulations in **Figure 7.1** and **Table 7.5**.

Another mechanism that will reduce the chance of crack propagation in this system can also be suggested; the well-known mechanism of transformation toughening in zirconium oxides. The martensitic transformation of metastable tetragonal to monoclinic zirconia in the stress field of a propagating brittle crack improves the mechanical properties as a result of a volume increase of $\sim 4\%$ [262, 294]. Retaining tetragonal ZrO_2 down to low temperatures requires either chemical stabilisation or a very fine grain size [295], and the characteristic microstructure in oxide scales grown on Zr alloys in simulated PWR primary water at 360°C satisfies this latter requirement, with columnar grains of monoclinic ZrO_2 of width $\sim 200\text{ nm}$ and a small volume fraction (3-8 vol. %) of retained equiaxed tetragonal grains usually only $30 - 50\text{ nm}$ in diameter [138, 281]. A crack propagating in this material may thus encounter tetragonal grains which could transform to monoclinic grains, as already observed in deliberately toughened ceramics [262].

Another important consideration is how, if as shown in **Figure 7.3** cracks develop at a more-or-less constant rate as the oxide thickens, does the banded distribution of cracks seen in **Figure 7.6** arise? It is suggested that occasional cracks must develop by the mechanisms above until a group of cracks are formed at or near the interface at about the same time. If the rate of oxide growth is slow (i.e. between 50 and 120 days as seen in **Figure 4.2**), all new cracks will lie in a narrow band of depths, as shown in **Figure 7.6**. After that, continuing oxide growth encourages formation of new cracks between or besides pre-existing cracks within the band, rather than at other sites closer to the interface, through interactions between the stress fields of closely spaced cracks. This kind of crack growth should lead to a gradual broadening of the crack band, which seems to be at least true for the crack development from the black oxide to the grey oxide and to the 180 days oxide (Peaks C to D to E) in **Figure 7.6**. Another consideration is, if the splitting model (**Figure 7.13**) is one of the main mechanisms introducing cracking in the oxide, that cracking along the end of columnar grains is expected,

which would lead to bands of cracks determined by the more-or-less layered columnar grain structure. However, it is noticed from the TEM observations, the cracks (especially bigger ones) do not always run along the grain boundaries.

8 Summary and further discussion

8.1 Main observations and findings

8.1.1 Oxide microstructure

- The pre-transition oxides have an inner part which is mainly composed of columnar grains with some micro-cracks and an outer part of several hundred nanometers which contains predominantly equiaxed grains and micro-pores. No obvious difference was observed between oxides grown on Zircaloy-4 and ZIRLO.

The post transition oxide just after the first kinetic transition ($\sim 4\text{ }\mu\text{m}$ thick oxide) is not very different from the pre-transition oxide, in terms of comprising an inner columnar layer and an outer equiaxed layer. But the columnar structure in the middle of the oxide is less well-developed. Equiaxed grains are also predominant between two layers of columnar grains. For the thick post-transition oxide ($\sim 32\text{ }\mu\text{m}$ Zircaloy-2 oxide), the oxide near the metal-oxide interface exhibits a higher fraction of equiaxed grains.

The $\sim 78\text{ }\mu\text{m}$ thick post-second transition Zr-Nb-Ti oxide exhibits generally only equiaxed grains throughout the whole oxide scale.

All these observations suggest that columnar structures have a better corrosion resistance than equiaxed grains.

- The oxides examined (pre-, post-, and post-second transition oxides) were found by TEM electron diffraction to contain predominantly monoclinic oxide and a small amount of tetragonal oxide. The monoclinic grains are mostly columnar structures (except in the post-second transition Zr-Nb-Ti oxide) and strongly textured. The texture decreases from the inner oxide to the outer part. For the particular (101)

tetragonal reflection examined, no obvious correlation of its appearance with the oxide location in the oxide was found. Due to the stress relaxation in TEM specimens, a correlation between the stress and the tetragonal phase could not be confirmed.

- Cracks are present in not only the post-transition but also the pre-transition oxides. This shows a gradual introduction of cracks throughout the parabolic oxide growth before the first transition in kinetics, not a sudden burst of crack nucleation at transition.

The volume fraction of cracks in the developing oxide was found to increase monotonically with oxidation time, but the mean crack volume and length both decrease immediately after the transition. This indicates that the increase in volume fraction after the transition is primarily as a result of the nucleation of new cracks in the second parabolic growth stage after the initial transition, not the growth of existing cracks further from the metal-oxide interface.

Two types of cracks can be distinguished according to size. Cracks below ~ 100 nm long are often associated with equiaxed grains, while bigger cracks can cross the columnar grains.

- Besides cracks, the oxide also contains different forms of nano-porosity. At the metal-oxide interface region, isolated pores of 1-3 nm or interconnected ones along the direction vertical to the oxide growth direction are present. Further away from the interface, they get connected with each other at grain boundaries along the oxide growth direction. The density of interconnected porosity increases towards the oxide surface, evolving over time. In the post-transition oxide, this interconnected porosity develops to significant level closer to the metal-oxide interface than in the pre-transition oxide. In the post-second transition oxide, both connected nano-porosity and

cracks parallel to the oxide growth direction have been seen up to the metal-oxide interface. These observations suggest that porosity develops within the oxide with time.

8.1.2 Metal-oxide interface

- The metal-oxide interface has a wavy morphology both at the micrometer and nanometer scale. The roughness measured by 3D SEM images has been found to increase with the oxidation time until the first kinetic transition, and decreases just after the transition before increasing again with longer oxidation time, i.e. the oxide just before the transition has the roughest interface. This may be related to a sudden increase in the oxide stresses just before the kinetic transition [156, 260] if the transition occurs inhomogeneously across the sample.
- It was also found that the location of the cracks near the metal-oxide interface is closely linked to the interface geometry, i.e. the cracks are predominantly above the delayed (convex) portion of the interface, which may be due to the characteristic stress distribution along an undulated interface, and perhaps to crack nucleation above second phase particles.
- An intermediate suboxide layer between the bulk oxide and the metal substrate was found most obviously in the pre-transition oxides. The composition of this layer has been shown by EELS to be 40-50 at. % oxygen. When two pre-transition ZIRLO RXA oxides formed after different times were compared, it showed that a layer of oxygen-saturated metal was present beneath the suboxide layer for the pre-transition oxide from the stage having lower oxidation rate. The width of the suboxide appears to increase with increasing oxidation time for the pre-transition oxides. The 120 days ZIRLO oxide that was close to the kinetic transition showed a large variation in the suboxide width. Both the widest suboxide layer among all the samples examined and

complete absence of suboxide layer were found at different interface locations, indicating rather inhomogeneous oxidation process for this sample.

- The suboxide was generally thinner or absent for the post-transition ZIRLO oxide, but locally a ~50 nm suboxide layer was detected in an interface location below a crack exhibiting delayed oxidation. The oxygen saturated metal layer was still detected. In the post-second transition oxide (Zr-Nb-Ti oxide), no evidence of either suboxide or oxygen saturated metal layer was found.
- In the pre-transition oxides where the suboxide was detected, α -Zr, ω -Zr, tetragonal oxide and a phase with an unidentified structure were found, suggesting different structures can coexist in the suboxide layer, which may explain the diverse observations in the crystallography of the intermediate layer reported by previous studies. α -Zr, tetragonal oxide and few unidentified grains were found for the post-transition oxide. Only α -Zr grains were identified in the post-second transition Zr-Nb-Ti metal-oxide interface. Evidence from diffraction patterns suggests that the Zr_3O phase is confined within the oxygen saturated metal layer.

8.1.3 Other observations

- In agreement with previous studies, the predominant types of intermetallic precipitates (second phase particles, SPPs) found in ZIRLO samples were of β -Nb and hexagonal $Zr(Fe,Nb)_2$ structures, with the the first type being generally smaller in size.
- The predominant type of intermetallic precipitates found in Zircaloy-4 samples was of FCC $Zr(Fe,Cr)_2$ structure, as expected from previous work.
- Similar oxidation behaviour of the intermetallic precipitates that has previously reported was also observed in this work, i.e the SPPs showed delayed oxidation compared to surrounding Zr. Cracks were usually seen above the delayed SPPs. In

ZIRLO, SPPs containing high Fe contents were found to be oxidized and transform into an amorphous state much earlier than β -Nb when they were incorporated into the oxide. The Zr-Fe-Cr precipitates appeared to be oxidized faster than Nb precipitates but slower than Zr-Fe-Nb ones.

- Hydrides of different types (γ , δ and ϵ) were observed in the metal and metal-oxide region for both Zircaloy-4 and ZIRLO samples. A higher density of hydride was seen in post-transition oxides when ZIRLO samples corroded for different time were compared.

8.2 Oxidation process and breakaway mechanisms

8.2.1 Pre-transition oxidation

The oxidation of zirconium takes place through inward growth of oxide toward the metal. It starts with the formation of equiaxed grains, which form later the observed equiaxed outer layer when the oxide scale thickens. The development of equiaxed structure can be very limited as it was seen to be very thin (less than 100 nm) in the 7 days RXA Zircaloy-4 oxide. During the oxidation, compressive stresses are developed in the oxide layer because the new oxide forms at the metal-oxide interface and the volume of oxide is greater than that of the metal it is formed from (Pilling-Bedworth ratio ~ 1.56). As a result, columnar grains grow on the equiaxed grains almost perpendicular to the metal-oxide interface to minimize the compressive stress. Due to the present stress, the first formed equiaxed and columnar grains can be tetragonal oxide. The compressive stress in the oxide which could help stabilize the tetragonal oxide is highest near the metal-oxide interface and decreases towards the outer oxide surface [260]. As the oxide thickens, the tetragonal oxide initially stabilized transforms to monoclinic oxide. As a result of an increase in volume ($\sim 3\%$), the transformation may

contribute to form the micro-cracks and micro-pores observed in the outer oxide scale (**Figure 5.3**), and may be responsible for the increase in the thickness of the initial formed equiaxed grain layer observed in this work. The columnar grains, with length of 100-300 nm, dominate the 1-2 μm scale in the pre-transition oxides. Equiaxed grains are seen between columnar grains along the growth direction, which suggests that a re-nucleation of this structure at the metal-oxide interface after some development of the columnar structure. These grains might be tetragonal when formed, but transform to monoclinic later aiding the formation of small cracks (first group of cracks as described in **section 5.1.1**) and pores observed in between the columnar grains (**Figure 5.5b**).

Bigger cracks (longer than 300-500 nm, i.e. the second group of cracks as described in **section 5.1.1**), which have been seen and characterized with 3D FIB sectioning and reconstruction, are clearly shown to have formed continuously in the early pre-transition oxides, instead of a sudden burst of crack nucleation at transition as has frequently been assumed from observation of the characteristic layered crack morphology in thicker oxides [19, 43, 44, 137, 138]. Therefore, it is believed that these cracks are not directly related to the kinetic transition.

All the cracks observed in the pre-transition oxide, whether belonging to the first group or the second, are generally parallel to the metal-oxide interface. Observation of cracking in the pre-transition oxide was also reported long ago for Zircaloy-2 oxidized in 350-500°C oxygen or water [32]. The current work has clearly shown that an oxide region containing higher density of lateral cracks showed a smaller thickness (**Figure 5.1d**). Also, the presence of a suboxide in the post-transition oxide, characteristic of a lower oxygen partial pressure at the interface, was only detected across the interface right below a crack (**Figure 6.12**). Therefore, these horizontal cracks are believed to block both the flow of electrons or holes needed for

anodic oxidation at the metal-oxide interface and the inward transport of oxidising species along grain boundaries in the ZrO₂, as has been suggested by Bossis et al.[101].

On a smaller scale, the oxide has been found to contain nano-pores of only 1-5 nm in diameter. In the pre-transition oxides, they remain generally isolated or connected along the direction parallel to the interface, i.e. density of connected pores along the oxide growth direction is very low apart from the top ~300-600 nm oxide.

Considering all these characteristic features, the pre-transition oxide therefore acts as a protective or barrier layer containing cracks or pores as obstacles for oxidation species, which leads to a low and decreasing oxidation rate. A schematic of this situation is shown in **Figure 8.1a**. The thickness of the barrier layer may be as big as ~0.9-1.3 µm estimated using TEM for the samples investigated in this work. Dawson et al. [32] has estimated the activation energy for transporting oxygen species across such a barrier layer due to presence of cracks parallel to the metal-oxide interface in a Zircaloy-2 oxide, and found that the value was about 10-15 kcal/mol for both oxygen and water vapour, consistent with a process of surface diffusion down pores.

A kinetic model of the barrier layer can be described as ([27] and references therein) :

$$\frac{dX}{dt} = \frac{k_1}{X} \exp(-k_2 X)$$

where X is the oxide thickness, t is the oxidation time, k_1 is a constant depending on the diffusion properties of the oxidizing species in the barrier layer and the concentration differences of the species across the barrier, while k_2 is a coefficient representing the number of barriers (in this case cracks) per unit length. This model has been shown to successfully account for the deviation from the exact parabolic law found for the pre-transition oxidation stage, which is also observed in this work (c.f. **Table 4.2 in Section 4.1**).

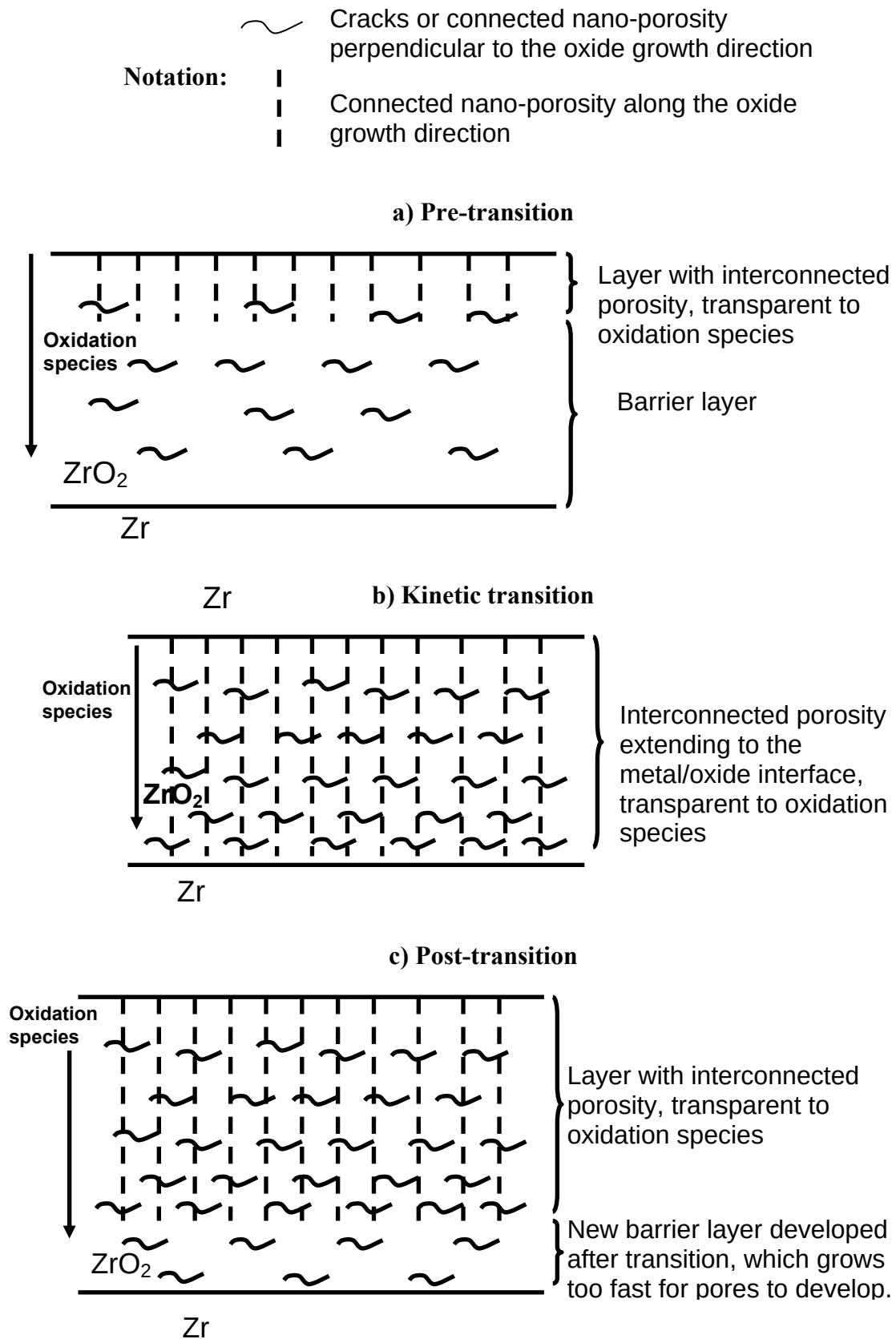


Figure 8.1 Schematic description of the oxidation mechanisms in a) pre-transition b) kinetic transition and c) post-transition stages.

The presence of a prominent suboxide layer and beneath which the oxygen saturated metal layer at the metal-oxide interface in the pre-transition oxides is most evident in the late pre-transition oxides, and is probably a result of the lower oxidation rate rather than a cause. However, a higher oxygen content in the metal near the interface could contribute to a better corrosion resistance by three mechanisms: firstly oxygen in solid solution will increase the lattice parameter of the Zr metal [296], effectively forming a graded interface between the metal and suboxide that might help to accommodate stresses created by the formation of oxide more effectively and reduce cracking or the formation of porosity [291]. Secondly, oxygen also acts as a solid solution strengthener in zirconium [297]. Oxygen has also been found to promote niobium precipitation in ZIRLO, and so produces precipitation strengthening [298]. As a result, the additional oxygen in solution near the interface could enhance the strength and the creep resistance. Finally, it has been found by 3D atom probe analysis that the oxygen increases the solubility of Fe in the metal, leading to a higher concentration of Fe in the matrix in the suboxide region [298]. This would be expected to be beneficial for the corrosion resistance [2, 299]. The crystallography of the suboxide layer remains inconclusive but very likely to correspond with a ω -Zr structure or a structure having similar plane spacings to that of the oxide phases or α -Zr.

8.2.2 Kinetic transition

A previous model has related the transition to the nucleation of a new layer of tetragonal grains and lateral cracking in the oxide [135]. However, it has been shown from this work that there is no sudden formation of cracks at the transition. Furthermore, the problem of this model is that those cracks are parallel to the metal oxide interface and, as have been emphasized several times in this work, not expected to increase the oxidation rate. In fact, Dawson et al. [32] found that for the oxidation of Zircaloy-2 in 450°C oxygen, a small

reduction in the oxidation rate was associated with the appearance of a well-defined layer of cracks parallel to the interface, from which they suggested that these cracks led to an decrease in the rate by reducing the area actively taking part.

Essentially, a pathway which provides the transportation of oxidizing species down or close to the metal-oxide interface must be provided for an accelerated oxidation rate at the kinetic transition. One of the possible microstructures are vertical cracks as observed in thick oxides such as the Zr-Nb-Ti oxide in this work or others studied before [222], and also reported for post-transition oxides only a few microns thick formed in steam [27]. However, such cracks were not generally observed in this work for samples close to or past the first kinetic transition, in agreement with many other studies, e.g. [25, 101, 122, 123, 138, 300, 301].

It is suggested from this work that a development of interconnected nano-porosity (1-3 nm in diameter when seen isolated), especially along the oxide growth direction, is one of the key mechanisms that triggers the kinetic transition, as schematically shown in **Figure 8.1b**. The nano-size pores have been considered to nucleate probably as a result of the Kirkendall effect at the metal-oxide interface, or grain boundary diffusional creep of the oxide (**section 5.3.6**). They are then embedded in the oxide and condensed into grain boundaries and become connected along the oxide growth direction. The oxidation rate decreases during the pre-transition stage and if the condensation and coarsening of nano-pores are assumed to occur at a constant rate for the oxide grown on a particular Zr alloy, it may be expected that the connected pores finally reach regions close to the metal-oxide interface. The tetragonal to monoclinic oxide transformation, which is also expected to happen first in the outermost oxide and gradually more towards the metal-oxide interface as oxide grows, may also contribute to the formation of an interconnected network of porosity. And the delayed oxidation of SPPs is therefore beneficial in stabilizing the tetragonal oxide and retarding the transformation. The smaller cracks of the first type can probably enhance the nano-porosity in

the oxide by induce pores at the tips of these cracks (**Figure 5.25**). Due to the presence of the vertical connected pores along grain boundaries, the horizontal cracks now become connected to the oxide surface. Once this happens, the parallel cracks can play a role in encouraging the transition. Interconnected path ways for oxidizing species can form effectively without the density of vertical connected pores necessarily being very high. As a result, the external oxide is short circuited in the overall electrochemical corrosion cell and the only protective layer is the thin oxide layer beneath the cracks (which have been shown to nucleate close to the metal-oxide interface) and the oxidation becomes fast, leading to the kinetic transition.

A smaller periodicity of the horizontal layers of cracks has been found to correlate with an earlier transition at a smaller oxide thickness and a higher post-transition corrosion rate [138]. In this work the first formed layer of big cracks (longer than ~ 500 nm) was about ~ 850 nm away from the oxide surface in ZIRLO oxide, and ~ 2 μm away for the slower oxidising Zircaloy-4 in qualitative agreement with [138], i.e. an earlier transition is correlated with an earlier formation of big cracks. Considering two oxides that have different crack periodicity, the oxide thickness when both are in the pre-transition stage will be similar since the pre-transition growth rates are not very different. In the light of the transition mechanism discussed here, the situation at time t when the oxide with smaller crack periodicity is approaching transition, as sketched in **Figure 8.2**, may be used to explain the effect of more frequent cracking. The oxide with smaller crack periodicity has developed layers of big cracks which can accelerate the oxidation rate when connected by nano-pores along the oxide growth direction (8.2a), while the microstructure of an oxide with bigger crack periodicity that may contain no large cracks at all will be less effective in increasing the oxidation rate (8.2b), especially if the vertical connected pores are not present at very high density. As a result, an earlier transition can be expected for the oxide which cracks earlier or shows smaller

periodicity of big cracks. If the post-transition stage then exhibit cyclic oxidation which mimics the pre-transition period, a higher post-transition rate would also be expected.

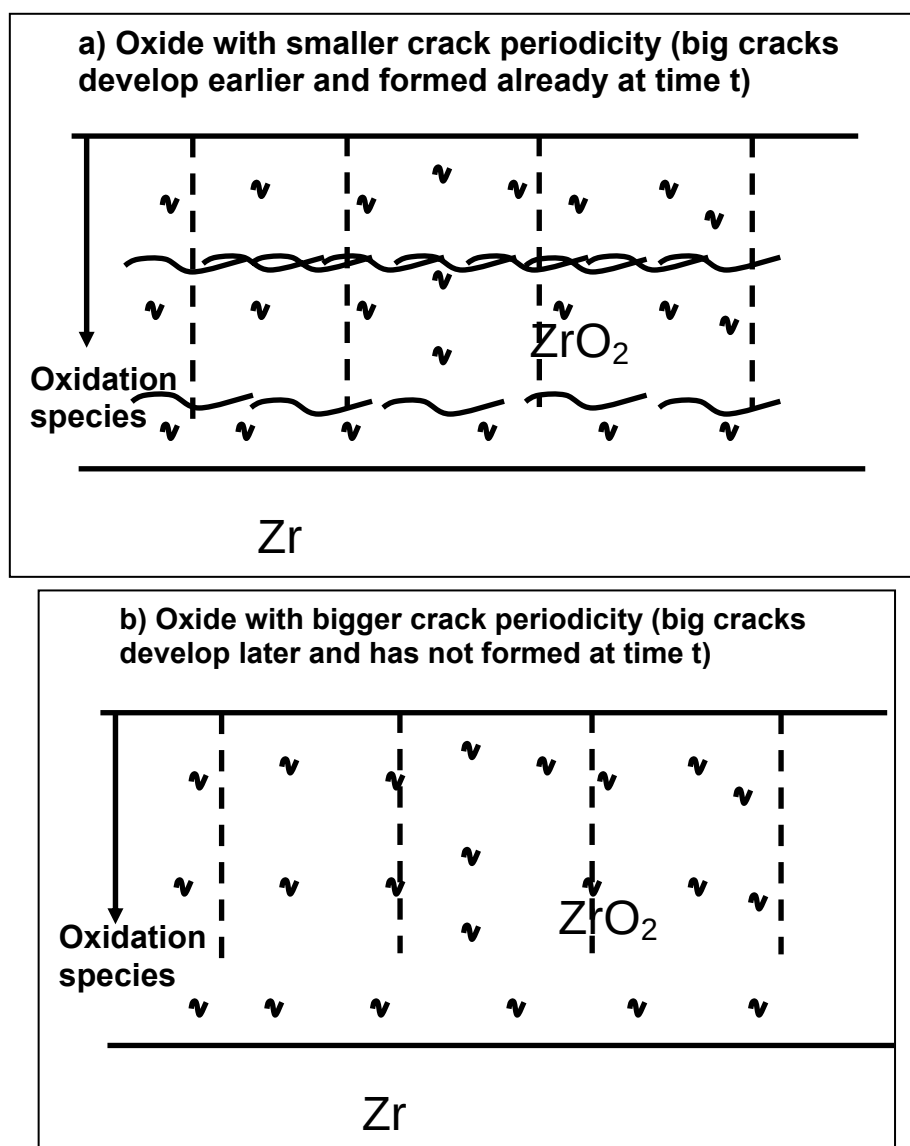
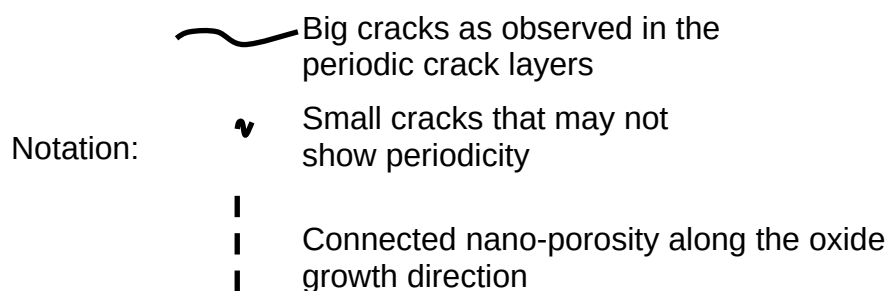


Figure 8.2 Schematics of oxides with different periodicity of cracks illustrating the possible effect of the horizontal cracks.

Although globally an increase in the oxidation rate is reflected as a kinetic transition shown in a weight gain vs. corrosion time curve, investigation of local microstructure changes

exactly at the transition point would be difficult as transition must happen inhomogeneously across the sample but should be instantaneous at any specific location. For the particular ZIRLO 120 days RXA sample that was probably at a stage around the transition, regions with connected pores along the growth direction very close to the metal-oxide interface have been observed in some part of the sample, suggesting a transition just about to happen locally. Similarly, in the black oxide of the ZIRLO SR 140 days sample, big variations were found in the thickness of the suboxide layer. The locations where no suboxide was detected may be experiencing or have just passed the transition. This also indicates that a macroscopic colour does not accurately represent the microscopic oxidation process, although it is common to correlate the colour change from black to grey with the kinetic transition [6, 10] and relate it to the formation of lateral cracks in the oxide at transition. From this work, cracking can not be considered, at least, as the only factor, as cracks were already seen with a significant density in the black, pre-transition oxides. In fact, other authors correlate the black colour to localized surface plasmon resonances (LSPR) in metallic particles, which causes absorption of light in the visible region and as a result a low reflectance. In the later stage of the oxidation, smaller precipitates become oxidized and shift the LSPR to lower wavelength so that the absorption by LSPR in the visible light is not effective any more [302]. This process, although may have an effect on the transition, should be a gradual change and has not been found to correlate exactly with a kinetic transition in time.

8.2.3 Post-transition stage

Only samples that sit in the early post-transition stage have been investigated in this work. A layer of fresh oxide has been developed at the metal-oxide interface in these samples, where the nano-pores have not developed due to the fast growth of the oxide. This has resulted in the observation of a similar microstructure to the pre-transition oxide; well aligned columnar

structure in the inner oxide and equiaxed grains in the outer part. The difference lies in that the columnar grains in the middle are now less well-developed, and are more porous due to the presence of higher density interconnected nano-pores. The volume fraction of the horizontal cracks is also increased. In all, the thickness of the protective layer, containing only horizontal cracks and non-interconnected pores, is ~600-700 nm for the samples investigated, thinner than the pre-transition oxides. The situation is schematically shown in **Figure 8.1c**.

Tupin et al. [27, 28] have shown that a rate-limiting step no longer exists in the post-transition oxidation stage of Zircaloy-4 in steam but is still present in the case of the oxidation of a ZrNbO alloy. In this work it has not been tested if a rate-controlling step is valid in the post-transition stage, but a decreasing oxidation rate after the kinetic transition seems to be happening, especially for ZIRLO. This may imply a similar mechanism in the post-transition stage as that in the pre-transition stage. The very few data points after the first transition have made it impossible to fit a kinetic curve, but it appears that the rate at the beginning of the post-transition stage is higher than that of the pre-transition stage, see **Figure 4.2**. This may be explained by the transportation of charged oxidizing species over a thinner barrier compared to that in the pre-transition stage, or related with a higher density of small cracks in this barrier layer as shown by 3D FIB characterization (**section 7.3**).

The horizontal cracks have been regarded as barriers for oxidation before the transition, but when interconnected with nano-porosity in the oxide growth direction at the transition they can accelerate the oxidation rate locally. Therefore, it would be expected in a post transition oxide that the last-formed cracks close to the metal-oxide interface will be above the delayed portion of the oxidation (**section 7.2.2**) but those at a larger distance from the interface will be more likely above the more advanced portion as the oxidation front at that portion has grown faster at the transition. A frequency histogram of the distance in the oxide growth direction separating the last-formed cracks from the delayed and advanced portions of the interface,

shown by [101] for a post-transition Zircaloy-4 oxide, seems to be in agreement with this expectation (**Figure 8.3**). The frequency of finding a last formed crack above the convex portion of the metal-oxide interface is higher than above the concave portion for the cracks within $\sim 2\ \mu\text{m}$ from the interface (roughly the transition thickness) but lower for cracks further away.

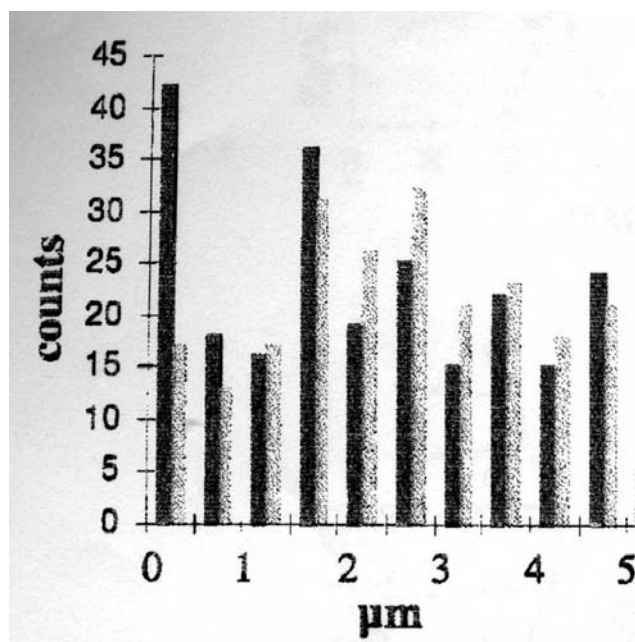


Figure 8.3 Frequency histogram of the distances, measured in the oxide growth direction, separating the last-formed cracks from the delayed convex (black) and the advanced concave (grey) portions of the metal-oxide interface on a post-transition Zircaloy-4 sample oxidized in 688K water vapour [101].

The metal-oxide interface in the samples just past the transition becomes much flatter, possibly as a result of a fast moving metal-oxide interface during the transition. Correspondingly, either no obvious (or a much thinner) suboxide layer has been found in the early post-transition oxides. On the other hand, a relatively thicker suboxide was still detected at an interface location where the oxidation rate was particularly slowed down by a crack closely above the oxidation front.

8.2.4 Post-second transition stage

The very thick oxide ($\sim 80\ \mu\text{m}$) grown on the Zr-Nb-Ti test alloy that has a very poor corrosion resistance has been considered to be a post-second transition oxide. In this stage, a

higher linear oxidation rate has been reported. The oxide exhibits a very porous scale full of interconnected pores and cracks, including vertical cracks extending to the metal-oxide interface, which has not been found for the samples past the first kinetic transition. The vertical cracks may partly be developed from the nano-porosity aligned along the oxide growth directions. This type of microstructure obviously favours a rapid and continuous growth of the oxide scale. The extremely fast moving metal-oxide interface has resulted in a low oxygen partial pressure at the metal-oxide interface and no suboxide could be detected in this sample.

8.3 Future work

This work has examined a series of oxides grown on RXA ZIRLO sheet for different exposure times up to the stage shortly after the first kinetic transition. Microstructural characterization including oxide morphology, oxide nano-porosity, crack development, and nano-scale chemical analysis at the metal-oxide interface has revealed an abrupt change at transition and, after transition, an oxidation process that more or less mimics the pre-transition stage. To better understand the oxidation mechanisms, it would be interesting to investigate longer exposed samples across the second transition period in all these aspects. The methodology used in this work including TEM sample preparation, quantitative EELS and 3D FIB slicing and reconstruction will be very useful for characterizing future zirconium oxide samples.

The nano-size porosity present in the oxide and its development during the oxidation process has been suggested to be an important factor related to the breakaway mechanism. It would be interesting to carry out an in-situ EIS measurement following the oxidation of the same alloys to gain some information about the porosity development in the oxide.

The 3D FIB slicing technique used for the study of crack evolution in the oxides has the limitation that it can not examine the development of the same cracks with time. Therefore, characterization of cracks development using in-situ techniques such as acoustic emission or X-ray tomography would be interesting.

The stoichiometry of the suboxide at the metal-oxide interface has been measured quantitatively by EELS line profiles. In comparison, EFTEM, although normally with worse noise levels, has the capacity to examine a larger area of the metal-oxide interface to reveal the inhomogeneous distribution of the suboxide layer. A quantitative EFTEM can be achieved in future using similar calibration methods employed for the quantitative EELS analysis. Combining these two techniques would be useful to gain information on the accurate composition from a larger interface area. In addition, it is also interesting to explore the features in the low energy loss region of the EELS spectrum which can be associated with the suboxide phase. Information about the atomic bonding and electronic structure of the suboxide may then be gained.

An important aspect, the oxidation of intermetallic precipitates, has been studied briefly in this work. More detailed examination on the oxidation behaviour of Zr-Nb-Fe precipitates should be interesting as there are relatively fewer studies on this type of precipitates in the literature compared to Zr-Fe-Cr SPPs. STEM-EDX analysis can be used to yield more information about the redistribution of the alloying elements when the SPPs are oxidized.

Different types of hydrides have been found in the metal part of the oxidized samples. Detailed characterization of hydride formation at different oxidation stages should be carried out in the future for developing a mechanistic understanding of its effect on the oxidation process. It is possible that the hydrides observed in this work were formed during the sample preparation process. Future characterization of hydrides using TEM should then consider the choice of sample preparation methods and evaluate the influence of different methods.

In more general aspects, it is interesting to test if a rate limiting step can be validated in the pre- and post- transition oxidation stage of the alloys studied in the MUZIC programme, and how the change in water and hydrogen pressure influence the oxidation rate, with the methods proposed and carried out in [27, 303]. This will help to yield more detailed oxidation mechanisms with specific rate-controlling process and validate the suggestions in this work. Furthermore, for a mechanistic understanding of the oxygen process, it would be very interesting to investigate the behaviour of oxygen and hydrogen species during the oxidation by carrying out SIMS characterization on specimen spiked with ^{18}O or deuterium.

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Appendix A: Error estimation on analyzing diffraction patterns and HRTEM images

I frequently needed in this work to identify the crystal structures of observed micro/nano-structures using electron diffraction and HRTEM. As the possible candidates can have very similar lattice spacings, an error analysis is necessary in order to know the level of confidence I have in my data analysis.

1 Diffraction patterns

For the analysis of micro-diffraction patterns such as in **Figure 3.8**, the error is considered to be mainly from the uncertainty of measuring the diffraction pattern. To find out the distance D between a diffraction spot G and the central spot, one usually connects spots G and -G through the central spot or using higher order diffraction spots with the same spacing (2G and -2G, 3G and -3G etc) and divide the total distance X by the number of repeat periods N to get the average length of D, i.e. $D = \frac{X}{N}$. We measure X from the number of pixels in the digital images (images taken on films are scanned into digital form for analysis) and calculate the plane spacings as:

$$d = \frac{1}{D} = \frac{N}{X} [\text{pixel}^{-1}] = \frac{N}{X \cdot P} [\text{nm}] \quad \text{Equation A.1}$$

where P is the pixel size in the unit of nm⁻¹/pixel. When deciding the position of diffraction spots on the image, we assume 1 pixel detection error, which gives $\Delta X = \pm\sqrt{2}$ because X is obtained by measuring the difference between positions of two spots. Applying the error propagation rule, the error on the measurement of d can be evaluated from the following equation:

$$\Delta d = \pm \frac{N}{PX^2} \Delta X = \pm \frac{\sqrt{2}N}{PX^2} [\text{nm}] \quad \text{Equation A.2}$$

Table A.1 gives the amount of error on determining plane spacings d under the most commonly used experimental conditions. It can be seen that the amount of error depends on the specific plane spacing d that is measured through X . The typical d spacings of monoclinic ZrO_2 and $\alpha\text{-Zr}$ are given in **Table A.2** as a reference to show the d values that are commonly measured in this work. If other parameters are kept the same, the error increases with d . Averaging the D with bigger N helps reduce the error. For the measurement of angles, I found by repeated measurement a margin of error $\sim \pm 1$ degree. Therefore, if the diffraction pattern has a good quality, the errors are quite small and a combination of measured plane spacing and angle are in most cases accurate enough to attribute the analyzed structure with confidence to one of the possible candidate structures.

2 HRTEM images

When analyzing HRTEM images, one can determine the lattice spacing either directly from the real image (**Figure A.1a**) or from the reciprocal spacing on the fast Fourier transformed (FFT) diffractogram of the real image (**Figure A.1b**). The latter approach is used in most of the cases as it is an average over the selected area. As long as the area selected is representative of the structure, this approach is preferred. The distance between diffraction spots can be measured from the intensity line profile connecting them (**Figure A.1c**). In this case, apart from the detection error that is one pixel for a spot, another term describing the blurring of the spot, which we call diffusivity ρ , is also included for estimating the uncertainty of the position of a spot. This term then deals with errors associated with any deviations from a perfect crystal lattice image due to instrument instability or other experimental and sample issues such as small thickness variation, local lattice strains etc. The diffusivity ρ is taken as

half of the peak width at half maxima of the intensity peak that represents on diffraction spots
(Figure A.1c).

Table A.1 The amount of error on determining plane spacing d for different d values. $P= 0.03743 \text{ nm}^{-1}/\text{pixel}$, which is the value for most of the micro-diffraction patterns under the experimental conditions used.

$d \text{ (Å)}$	$\Delta d \text{ (N=2) (nm)}$	$\Delta d \text{ (N=4) (nm)}$
5.0	0.0066	0.0033
4.5	0.0054	0.0027
4.0	0.0042	0.0021
3.5	0.0032	0.0016
3.0	0.0024	0.0012
2.5	0.0017	0.0008
2.0	0.0011	0.0005
1.5	0.0006	0.0003

Table A.2 The d spacings of the monoclinic ZrO_2 and $\alpha\text{-Zr}$

Monoclinic ZrO_2					$\alpha\text{-Zr}$				
No.	h	k	l	$d \text{ [Å]}$	No.	h	k	l	$d \text{ [Å]}$
1	0	0	1	5.08701	1	1	0	0	2.79800
2	1	1	0	3.69765	2	0	0	2	2.57300
3	0	1	1	3.63907	3	1	0	1	2.45900
4	-1	1	1	3.16470	4	1	0	2	1.89400
5	1	1	1	2.84063	5	1	1	0	1.61600
6	2	0	0	2.62268	6	1	0	3	1.46300
7	0	2	0	2.60618	7	2	0	0	1.39900
8	0	0	2	2.53992	8	1	1	2	1.36800
9	-2	0	1	2.49945	9	2	0	1	1.35000
10	-2	1	0	2.34250	10	0	0	4	1.28700
11	1	2	0	2.33404	11	2	0	2	1.22960
12	0	1	2	2.28450	12	1	0	4	1.16890
13	-2	1	1	2.25274	13	2	0	3	1.08420
14	-1	1	2	2.21377	14	2	1	0	1.05880
15	2	0	1	2.19188	15	2	1	1	1.03600
16	-1	2	1	2.18053	16	1	1	4	1.00630
17	2	1	1	2.02030	17	2	1	2	0.97830
18	-2	0	2	1.99101	18	1	0	5	0.96600
19	-2	1	2	1.85933	19	2	0	4	0.94740
20	2	2	0	1.84810	20	3	0	0	0.93270
21	0	2	2	1.81874	21	2	1	3	0.90030
22	-2	2	1	1.80383	22	3	0	2	0.87710
23	-1	2	2	1.78297	23	0	0	6	0.85770
24	0	0	3	1.69371	24	2	0	5	0.82920
25	2	2	1	1.67723	25	1	0	6	0.82010
26	1	2	2	1.66070					
27	3	1	0	1.65712					
28	-3	1	1	1.65245					
29	0	3	1	1.64394					
30	-1	1	3	1.61000					
31	-1	3	1	1.59235					
32	-2	2	2	1.58220					
33	1	3	1	1.54586					
34	-2	0	3	1.53932					
35	3	1	1	1.50952					
36	-3	1	2	1.49596					
37	1	1	3	1.47767					

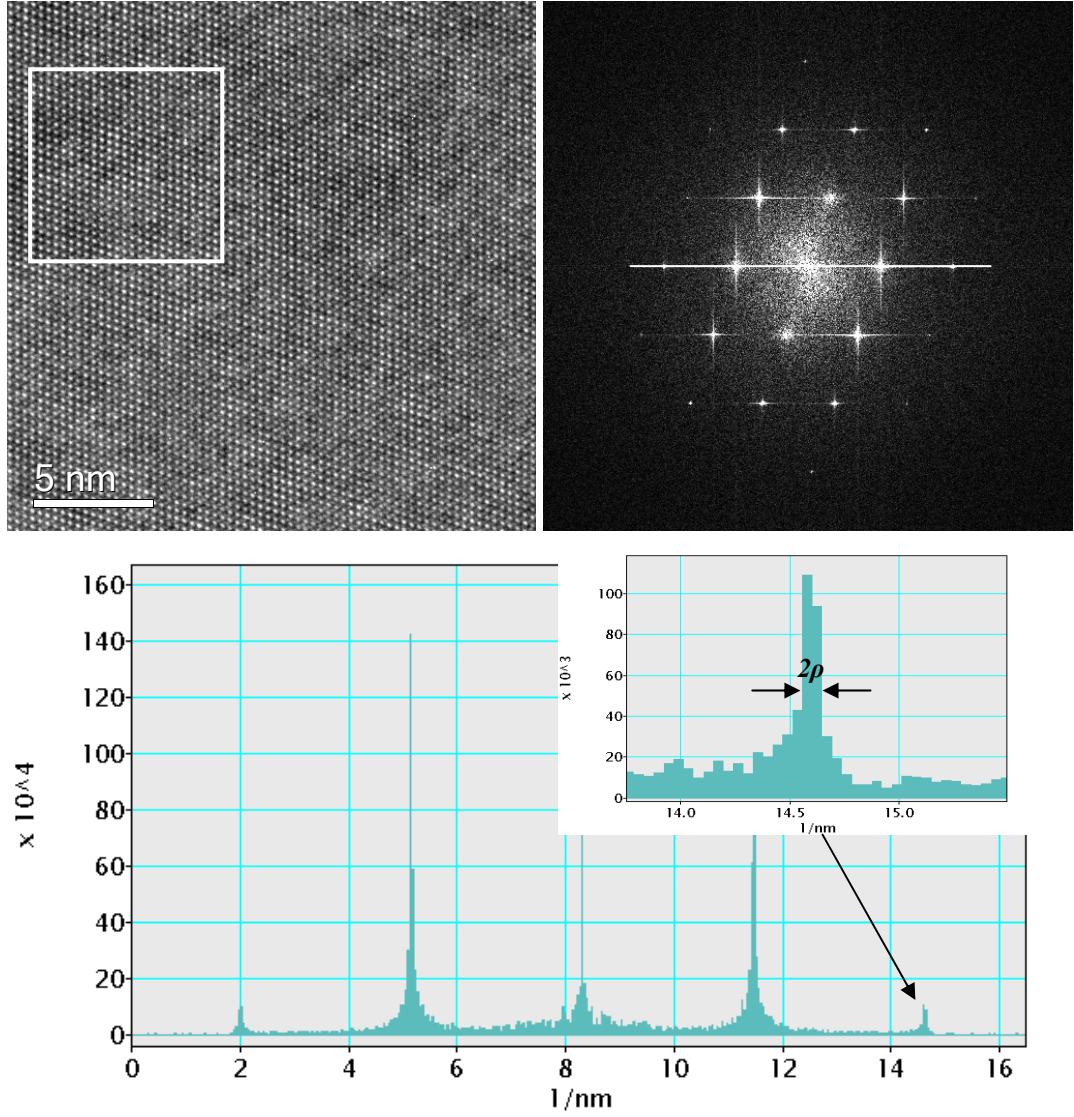


Figure A.1 a) A HRTEM image of a Si standard sample and b) the diffraction pattern obtained by the Fourier transformation of the selected area (enclosed by the white box) on the real image. This is used to measure the lattice spacing. c) The distance between diffraction spots can be measured from the intensity line profile connecting them as indicated by the line in b). The diffusivity ρ is measured as the peak width at the half maximum of the diffraction spot peak intensity (inserted figure).

As a result, the total error in deciding the position of the diffraction spots is obtained by adding the above two independent type of errors together, and this gives:

$$\Delta X = \sqrt{2(1 + \rho^2)}[\text{pixel}] \quad \text{Equation A.3}$$

and the margin of error of the lattice spacing d is given as **Equation A.2**:

$$\Delta d = \pm \frac{N}{PX^2} \Delta X = \pm \frac{\sqrt{2(1 + \rho^2)}N}{PX^2} [\text{nm}] \quad \text{Equation A.4}$$

Because $d = 1/D = X/N$, **Equation A.4** can be rewritten as:

$$\Delta d = \pm \frac{\sqrt{2(1 + \rho^2)}d^2 \cdot P}{N} [\text{nm}] \quad \text{Equation A.5}$$

The parameters here have the same definition as those used in the case of diffraction pattern analysis, since we also use the diffraction pattern obtained by Fourier transformation. From **Equation A.5**, we see that the error will decrease with decreasing P in the FFT diffraction pattern, which is the case when we decrease the magnification of the real image using a CCD camera with a fixed number of pixels. This relationship has been shown experimentally by Biskupek and Kaiser [1]. Therefore a lower magnification would be preferred for achieving a lower error. This is true when diffractograms of real images that have same size in unit of pixels are compared. However, areas that have the same size in pixel are bigger in units of nanometers at lower magnification because for real images the pixel size increases with decreasing magnification. In this work grains are typically 10-30 nm across. Therefore comparing diffractograms associated with areas of similar size in nm is more interesting. I examined HRTEM images with different magnifications of $\times 200000$, $\times 400000$ and $\times 800000$ taken from the same region of a Si standard sample and always chose a $\sim 20 \times 20 \text{ nm}^2$ area from these images. It was found that the pixel size P of the diffractogram is the same for different magnifications in this case, $\sim 4.5 \text{ \AA/pixel}$. So the conclusion is that the choice of magnification doesn't change the amount of error if we analyze areas of real images with the same size (in nm) and only consider the effect of P .

However, if too high magnification is used instrument instability plays a bigger role and gives rise to an increase in the diffusivity term ρ , on the other hand at too low magnifications the pixel size of the real image will become too big to resolve the lattice spacing effectively. Taking these points into account, magnifications of $\times 400,000$ - $500,000$ have been used for the analysis reported in this work.

Considering a specific magnification, the error increases with decreasing size of the analyzed area in the real image due to the increasing p value for the corresponding diffractogram. **Table A.3** gives an idea of the amount of error for images taken at a

magnification of $\times 400,000$ and for a range of lattice spacings d under normal experimental conditions: analyzed area of $(5-40 \text{ nm})^2$; $N=2$ or 4 ; $\rho = 1$ pixel. This type of analysis will be needed to interpret the significance of HRTEM data reported in later chapters.

In the above error analysis, other factors such as the error in the calibration of camera length and image magnification are not taken into account so the margin of error is a lower limit.

Table A.3 The amount of error for images taken at a magnification of $\times 400\,000$ and for a range of lattice spacings d at common experimental conditions assuming $\rho = 1$ pixel.

d (nm)	Δd (nm)							
	Size = $(44 \text{ nm})^2$		Size = $(22 \text{ nm})^2$		Size = $(11 \text{ nm})^2$		Size = $(5 \text{ nm})^2$	
	N=2	N=4	N=2	N=4	N=2	N=4	N=2	N=4
0.50	0.0057	0.0028	0.0113	0.0057	0.0229	0.0114	0.0457	0.0229
0.45	0.0046	0.0023	0.0092	0.0046	0.0185	0.0093	0.0371	0.0185
0.40	0.0036	0.0018	0.0072	0.0036	0.0146	0.0073	0.0293	0.0146
0.35	0.0028	0.0014	0.0055	0.0028	0.0112	0.0056	0.0224	0.0112
0.30	0.0020	0.0010	0.0041	0.0020	0.0082	0.0041	0.0165	0.0082
0.25	0.0014	0.0007	0.0028	0.0014	0.0057	0.0029	0.0114	0.0057
0.20	0.0009	0.0005	0.0018	0.0009	0.0037	0.0018	0.0073	0.0037
0.15	0.0005	0.0003	0.0010	0.0005	0.0021	0.0010	0.0041	0.0021

1. Biskupek, J. and U. Kaiser, *Practical considerations on the determination of the accuracy of the lattice parameters measurements from digital recorded diffractograms*. Journal of Electron Microscopy, 2004. **53**(6): p. 601-610.

Appendix B: Quantitative EELS analysis of oxygen content at metal/oxide interface

The methodology for a quantitative EELS analysis used to obtain reliable measurement of the oxygen content at the metal/oxide interface is described in this appendix and also can be found in our published paper [1]. This includes inelastic partial scattering cross-section calibration against a ZrO_2 powder standard, and estimation of the effective inelastic mean free path of high energy electrons in oxidised Zr-alloys with specially FIB prepared TEM samples.

TEM and EELS measurements were carried out in a Jeol 3000F microscope operated at 297 kV and equipped with a Gatan image filter (GIF). EELS acquisitions in STEM mode were performed with an incident half angle $\alpha = 11.5$ mrad and collection angle $\beta = 9$ mrad. In TEM mode, a collection angle $\beta = 1.8$ mrad was used. STEM high-angle annular dark field (HAADF) images were acquired with a collection semi-angle >70 mrad. All EELS acquisitions were performed using a spectral dispersion of 0.5 eV/channel. Ideally, a bigger collection angle in STEM mode should be used to ensure a collection over the full angular range, but the improved energy resolution provided by the 9 mrad spectrometer aperture was preferred since the data obtained in this work was also used for another on-going project dealing the differences in the fine-structure between the oxide, sub-oxide and metal phases. Therefore, these conditions were chosen for an optimized balance between energy resolution, collection efficiency and reasonable acquisition time

1 Calibration of inelastic partial scattering cross-section

Initial quantitative analysis to determine Zr and O concentrations was performed with the Gatan Digital Micrograph (DM) EELS module, using the Zr- $M_{4,5}$ and O-K edges respectively.

Inelastic partial scattering cross-sections provided by the Gatan software (from the hydrogenic model for O and the Hartree-Slater model for Zr) were used. The ideal calibration of inelastic partial cross-sections for Zr and O would require at least two standard samples of known composition containing different Zr/O ratios. Unfortunately, apart from the stable ZrO₂ oxide, all the other reported phases with different stoichiometries in this binary system are not stable (or reproducible) enough at room temperature [2], and so could not be used as standards. For this reason, a high-purity monoclinic ZrO₂ powder sample (TOSOH TZ-0) was used as the only standard. I have assumed that this standard has the precise stoichiometry Zr:O = 1:2. Rather than measuring experimentally the individual inelastic partial cross-sections for Zr and O, a “k-factor” approach was used to calculate the ratio between the two values from experimental EELS spectra obtained in STEM mode. To minimize the statistical error, five spectra were acquired from different areas in the powder sample. A typical spectrum is shown in **Figure B.1**. Atomic ratios were deduced following the quantitative procedure described in [3], which is also implemented in Gatan’s DM software. Settings for the selection of pre-edge and post-edge windows are given in **Table B.1**. The choice of window width and position was selected empirically as a good compromise between integrated intensity (to achieve good statistics), good reproducibility and background extrapolation uncertainty (for the choice of pre and post-edge windows). The calculation of the k-factor k_{ZrO} was based on the following formula [3, 4]:

$$\frac{C_{\text{O}}}{C_{\text{Zr}}} \approx \frac{I_{\text{O-K}}(\beta, \Delta)}{I_{\text{Zr-M 4,5}}(\beta, \Delta)} \cdot \frac{\sigma_{\text{Zr-M 4,5}}(\beta, \Delta)}{\sigma_{\text{O-K}}(\beta, \Delta)} = \frac{I_{\text{O-K}}(\beta, \Delta)}{I_{\text{Zr-M 4,5}}(\beta, \Delta)} \cdot k_{\text{ZrO}} \quad \text{Equation B.1}$$

where C_{Zr} and C_{O} are respectively the atomic concentrations of Zr and O in the sample, $I_{i-j}(\beta, \Delta)$ is the j^{th} shell core loss intensity of atom i integrated over an energy region of width Δ starting at the edge onset, and $\sigma_{i-j}(\beta, \Delta)$ is the partial inelastic scattering cross-section for j^{th} shell of atom i integrated over a collection angle β and an energy range Δ beyond the threshold. Using $C_{\text{O}}/C_{\text{Zr}} = 2$ for the stoichiometric ZrO₂ standard powder and I values obtained

from the spectrum in **Figure B.1**, the k-factor k_{ZrO} is calculated to be 7.27 ± 0.01 if only statistical errors from the area integrations are considered. When this experimental ratio is used for quantification of the sample composition, we found that the atomic concentration of O measured from the bulk oxides far from the metal/oxide interface on both cross sectional samples of the kind shown in **Figures 6.1** and **6.2** was 67.6 ± 1.2 at. %, in satisfactory agreement with the theoretical oxygen content of what is expected to be stoichiometric monoclinic ZrO_2 .

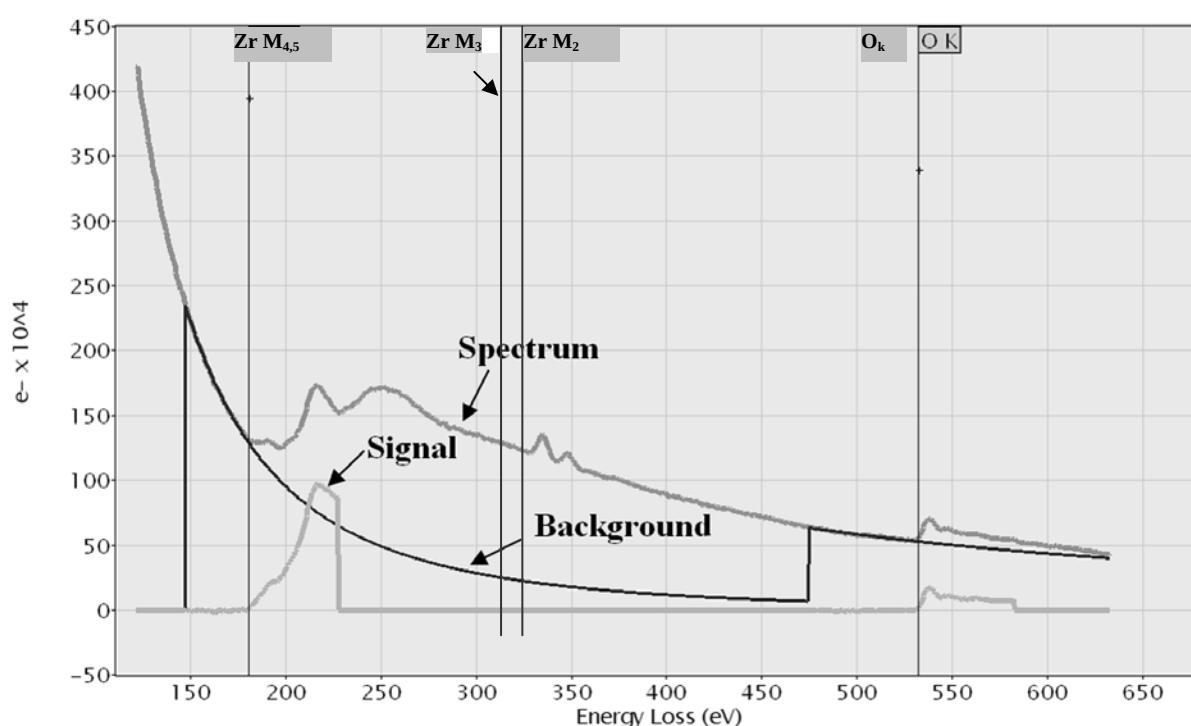


Figure B.1 A typical EELS spectrum from the stoichiometric ZrO_2 powder standard. The inverse power-law curve used for the background subtraction is shown, together with the background subtracted signal.

Table B.1 Optimized values for background subtraction and edge setup for the calculation of the sample composition from EELS spectra. The thickness of the stoichiometric ZrO_2 powder used for the calibration has been checked to be ~ 65 nm.

	Edge Position (eV)		Window (eV)	Offset	Window (eV)	Width
Zr-M ₄₅	180	Background Subtraction	-33.5		30	
		Signal	-3.0		50	
O-K	532	Background Subtraction	-84.5		50	
		Signal	0		50	

2 Estimation of effective inelastic mean free path

In order to evaluate the influence of multiple scattering, the effective inelastic mean free path, λ , under our experimental conditions ($\alpha=11.5\text{mrad}$ and $\beta=9\text{mrad}$) was estimated. For this purpose, a wedge-shaped TEM specimen (1° wedge angle) (**Figure B.2a**) was prepared by focussed ion beam milling from the black oxide of the 140 days ZIRLO SR tube sample. The limited pixel density provided by our FEI 200 FIB (1024x1024) was found to be insufficient, and produced distinct step changes in thickness in the wedge-shaped TEM sample. The Zeiss NVision 50 FIB, with a maximum patterning resolution of 6144x4608, produced satisfactory TEM samples without any observable steps. **Figure B.2b** is the HAADF image of a sample prepared on this instrument. The brightness and contrast settings of the HAADF detector were set to maximize signal contrast, and the dark current was set to zero at the hole at the left hand side of the image. Therefore no dark current correction was required. The HAADF image intensity (I_{HAADF}) can be assumed to be proportional to the sample thickness (t) for the thickness range of interest and can be expressed as:

$$I_{\text{HAADF}} = a \cdot t \quad \text{Equation B.2}$$

where a is the pre-factor and depends on several parameters including atomic number, density of the material and detector acquisition parameters. Along a horizontal line across this wedge sample, as shown in **Figure B.2b**, the thickness (t) and distance (x) should follow a linear relationship, with x_0 being the distance from the virtual point in the sample with zero thickness to the starting point of our horizontal line profile:

$$t = \tan(1^\circ) \cdot (x + x_0) \quad \text{Equation B.3}$$

So we have

$$I_{\text{HAADF}} = a \cdot \tan(1^\circ) \cdot (x + x_0) \quad \text{Equation B.4}$$

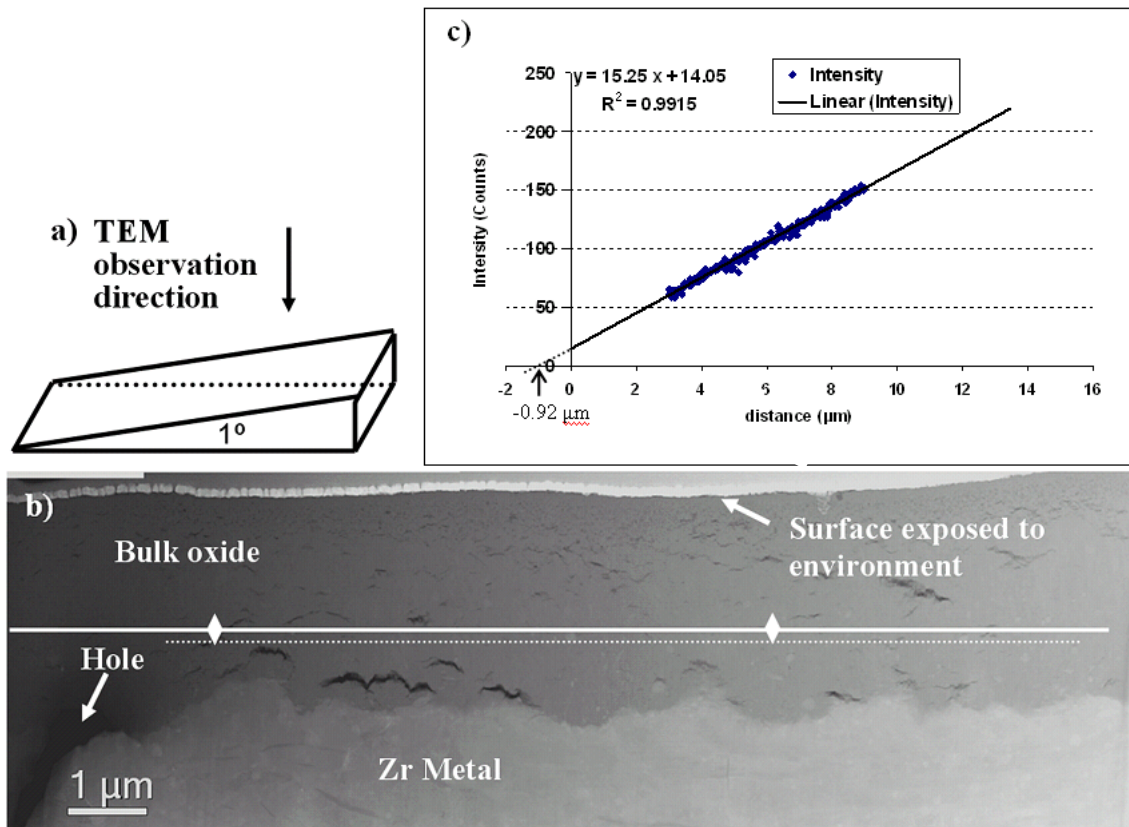


Figure B.2 a) Schematic diagram of the FIB-prepared, wedge-shaped TEM sample extracted from the black oxide of the 140 days ZIRLO SR sample. b) HAADF image of the wedge sample. The darker elongated features parallel to the metal/oxide interface are cracks always observed in this type of oxide. c) Linear fitting of the HAADF intensity line profile across the solid horizontal line. Only part of the data (from the region between the two markers in the solid line) was used for the calibration. The interception with the x axis gives the absolute zero point.

Therefore, when the intensity vs. distance profile across the horizontal solid line shown in **Figure B.2b** was measured, the value of $a \cdot \tan(1^\circ)$ equals the slope of a linear fit of this line profile, which was found to be 15.25 ± 0.07 counts/μm (**Figure B.2c**) and yields for **Equation**

B.4 $a = \frac{15.25}{\tan(1^\circ)} = 0.873 \pm 0.004$ counts/nm and $x_0 = 0.92 \pm 0.03$ μm. Knowing the value a , the

absolute thickness of the sample t at any point can be determined from the intensity of each point in the HAADF image according to **equation B.2**. In **Figure B.2c**, only part of the data (from the region between the two markers in the solid line) was used for the calibration because in the thinner part of the sample (left) a hole was formed during the FIB milling process. At the thicker end of the sample (right) the linear relationship between the intensity and the sample thickness no longer holds due to multiple scattering.

For the experimental estimation of the mean free path, λ , a series of EELS spectra were acquired from different sample locations in TEM mode using the same dispersion of 0.5eV. The STEM mode could not be used for this purpose since our hardware was not capable of acquiring spectra containing zero-loss peaks (ZLP) due to their high intensity. A selected area (SA) aperture with ~230 nm diameter was used during the acquisition. The relative log-ratio sample thickness (t/λ) was computed from the EELS spectra using the following formula [5]:

$$\frac{t}{\lambda} = \ln \frac{I}{I_0} \quad \text{Equation B.5}$$

where I is the total integrated area under the EELS spectrum and I_0 is the area under the zero-loss peak. I_0 was extracted using the different fits offered by DM. The “2 Gaussian” model, which fits two Gaussian functions to the ZLP, was found to give the best results, and has been used throughout this work. The absolute thickness (t) of the corresponding area was determined from the HAADF image intensity using **Equation B.2**. The resulting plot of t vs. t/λ is shown in **Figure B.3**. A good linear relationship is obtained up to a value of $t/\lambda \approx 1$. From the slope of the linear fit of the curve, the experimental λ value is found to be 105.2 ± 0.8 nm.

3 Evaluation of the influence of sample thickness

An EELS profile along the horizontal dash line in the wedge sample shown in **Figure B.1** was acquired to evaluate the influence of sample thickness on the measurement of chemical composition. The oxygen concentration was calculated using the experimental k-factor k_{ZrO} , and the thickness at the starting and end points of the line was determined by the method described in **section B.2** and that of any points in between was obtained by interpolation. The resulting concentration vs. thickness plot is shown in **Figure B.4**, which is a profile of quantified oxygen content as a function of sample thickness in the black bulk oxide of the 140

days ZIRLO SR sample far from the metal/oxide interface. It was found that the oxygen content deviates from the expected Zr/O ratio for stoichiometric bulk ZrO_2 above sample thicknesses of about 75 nm. Therefore, to ensure previous calibration was done on the sample with right thickness, the thickness of the stoichiometric ZrO_2 powder standard was re-checked by EELS using the same acquisition conditions (and the experimentally determined value of λ) and found to be ~65 nm.

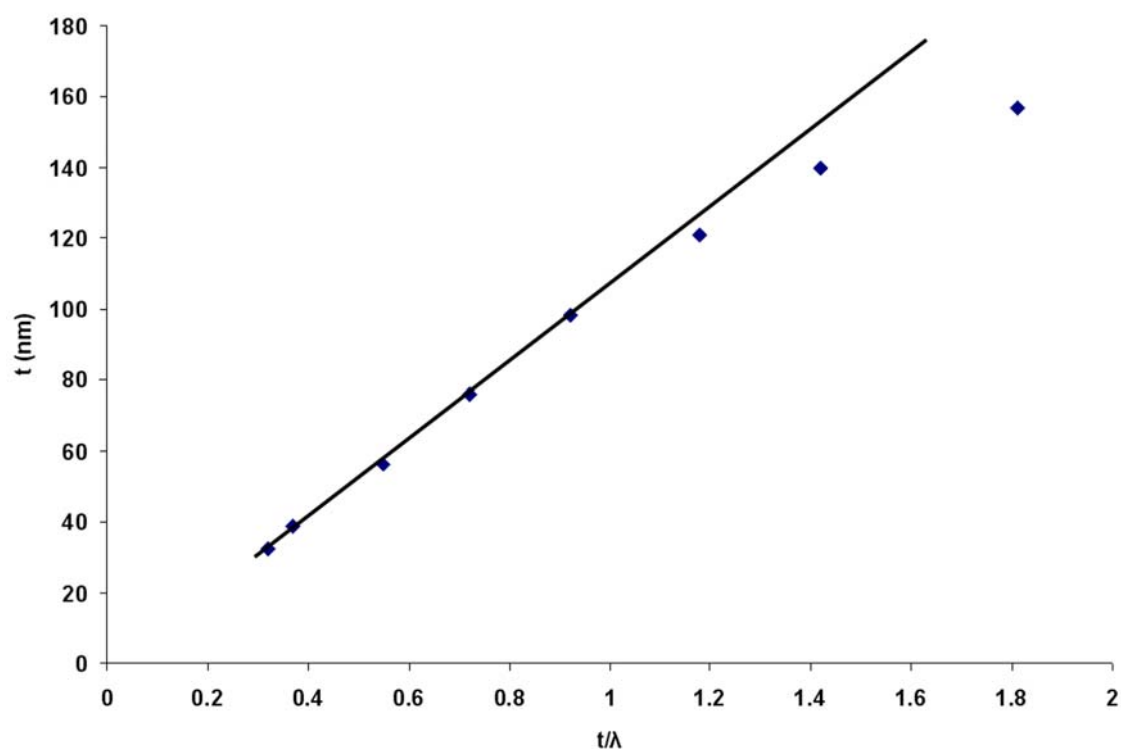


Figure B.3 Estimation of electron mean free path, λ , by linear fitting of t/λ vs. t . Values of t/λ at positions with different thickness were obtained by SA EELS in the TEM mode and values of t for the corresponding positions were obtained from the calibration of the STEM-HAADF data in **Figure B.2**.

Fourier-based deconvolution methods could not be applied with the available experimental facilities since it was not possible to acquire EELS spectra containing the zero-loss peak in STEM mode (due to shutter speed limitations). For this reason, thickness measurements were performed for all the samples under the same experimental conditions. The thickness dependence of oxygen quantification obtained from **Figure B.4** has been used as a reference to ensure that only samples sufficiently thin so that multiple scattering is unlikely to be an issue were used for quantitative analysis.

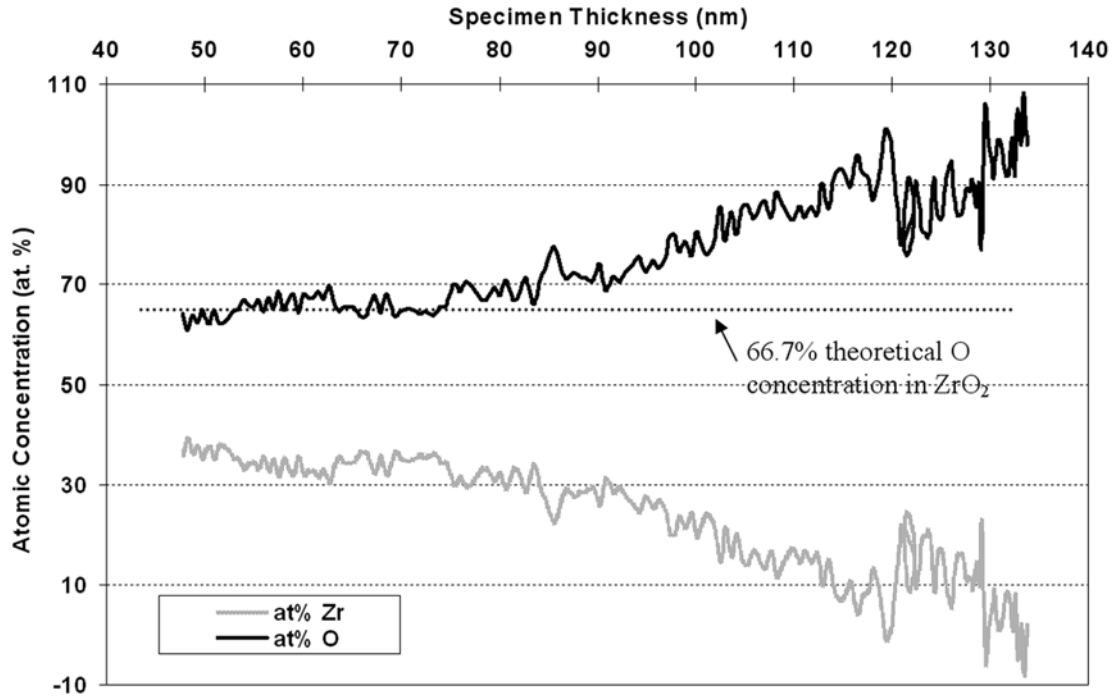


Figure B.4 Quantified oxygen content as a function of sample thickness in the bulk black oxide of the 140 days SR ZIRLO sample far from the metal/oxide interface. The profile is taken along the dashed horizontal line shown in **Figure B.2**.

4 Discussion

Without the inelastic cross section calibration (and use of the “k-factor” approach), an attempt at quantification on the commercial ZrO_2 powder that we have used as a standard gives an oxygen composition of ~ 79 at. %, which deviates significantly from the expected value of $\sim 67\%$. It is assumed that this is a result of the use of incorrect σ values for Zr and O in the calculation, where the theoretical Hartree-Slater model is used for Zr and the hydrogenic model for O. Here instead the value of k_{ZrO} has been calculated from raw data for the same ZrO_2 standard material using a method similar to that described in [6]. The experimental value of the k -factor, k_{ZrO} , is found to be 7.27 ± 0.01 , which is much smaller than the value of 17.5 derived from the σ_{Zr} and σ_{O} values calculated by the two models in the Gatan software. The inelastic scattering cross section is a direct measure of the intensity of scattering from the electrons of sample atoms, and many models deal with the theoretical calculation of this parameter by use of either classical physics or wave mechanics. The hydrogenic model is

good for the quantification of K ionisations and the Hartree-Slater model can be applied to give reasonable predictions for inner shell excitations of heavy elements. However for delayed M_{45} edges, which result from the centrifugal potential in multi-electron atoms and depend sensitively upon the assumed atomic potential, it has been shown that when the Hartree-Slater model is used there is considerable overestimation of σ values for Ag and Te [7]. In this study I found that the calculated $\frac{\sigma_{Zr}}{\sigma_o}$ ratio (k_{ZrO}) is higher than the experimental value, which also indicates an overestimation of σ_{Zr} if σ_o is assumed to be more reliably predicted by the hydrogenic model.

To achieve an optimum calibration, a sample with a perfectly known shape is essential. In this work a carefully fabricated wedge sample has been used for the calibration of specimen thickness based on the linear dependence of HAADF image contrast up to a certain thickness [8, 9]. An alternative sample geometry that can be used for this type of thickness calibration is a conical needle also fabricated by FIB milling [10]. As the needle has a circular cross-section, the width of the needle at any point is equal to the maximum thickness of the same cross-section when the needle is observed perpendicular to its long axis. This method therefore can benefit from a more direct measurement of sample thickness, but the approach using a wedge-shaped sample as described above has the advantage of providing a much larger electron-transparent area.

The λ value for ZrO_2 was experimentally calculated to be 105.2 ± 0.8 nm, which agrees reasonably well with the calculated value of 115 nm using Egerton's equation [11, 12]. Several different zero-loss peak fitting models implemented in Gatan's software, including "2 Gaussian", "Reflected Tail", "Gaussian & Lorentzian" and "Gaussian & Lorentzian²", were used to extract the counts from the zero loss peak and to compute the log-ratio relative thickness, t/λ . In **Figure B.3**, the intercept of the linear fitting must be fixed to zero, as t/λ should equal zero if t is zero. The λ values obtained by fitting the t vs. t/λ plot and the degree

of fitting confidence for the different models are listed in **Table B.2**. A rather small difference of less than 9 nm in the λ values was found between these models. The best fitting was achieved when using the “2 Gaussian model”, which does not seem to overestimate the extension of the tail on the peak. The linearity between t and t/λ is maintained here up to a value of $t/\lambda \approx 1$, while previous studies have reported linearity up to ~ 5 for Al [13] and 0.5-0.6 for Ni, Al₂O₃, SiO₂ and Si [9]. This discrepancy might be related to differences in material properties or the precise calculation methods used. It should also be noted that the presence of an amorphous layer caused by FIB milling is expected on both sides of the TEM sample. This layer can be as thin as ~ 3 nm after low-energy milling (2 keV Ga⁺) (c.f. **section 2.2.**), so I only expect it to affect our λ estimations for the thinnest regions of the sample. The influence of the amorphous layer has not been taken into account for the calculation of λ . In addition, I did not consider the influence of the finite size SA aperture, the choice of zero-loss peak model and/or choice of spectral dispersion. Therefore, the uncertainty in the composition value might have been underestimated, but the accuracy of the compositional analysis of bulk ZrO₂, which is unlikely to deviate very far from the ideal stoichiometry, suggests that these inaccuracies are not significant in this case.

Table B.2 The λ values obtained by fitting the t vs. t/λ plot, fitting confidence and examples of zero-loss peak integral for different zero loss peak fitting models used in the calculation of log-ratio relative thickness.

Zero-Loss Fitting Models	λ obtained by fitting the t vs. t/λ plot (nm)	Fitting Confidence (R^2)	Zero-loss peak integral of EELS spectra for 32.5 nm sample thickness ($\times 10^6$ e)
2 Gaussian	105.25	0.9981	3.4386
Gaussian & lorentzian ^2	109.23	0.9949	3.5863
Reflected Tail	110.9	0.9932	3.6324
Gaussian & lorentzian	113.76	0.9888	3.6933

The calibrated oxygen concentration in the bulk oxide far from the metal/oxide interface (which I have assumed to be stoichiometric ZrO_2) deviates from the expected value (67 at. %) when the sample thickness is larger than ~ 75 nm (**Figure B.4**), i.e. $\sim 0.7 t/\lambda$, which is likely to be a result of the onset of multiple scattering events in the sample. This is in reasonable agreement with other work which reports that multiple scattering starts to occur at $t/\lambda \sim 0.55$ [14].

The measured oxygen concentration after calibration is estimated to have an error around ± 1 -2 at.% when only statistical error is considered. It should be noted that I have not taken into account the statistical fluctuations in atomic concentration observed in some of profiles (c.f. **Figure 6.4b**) as a source of uncertainty. This should certainly increase the errors estimated for the quantification of oxygen content by another ± 1 -2 at.% depending on the degree of fluctuation. In all the error should be smaller than ± 5 at.%, which should allow us with confidence to detect large stoichiometry variations at the metal/oxide interface.

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Abstract

The current work is part of the EPSRC MUZIC project, which established the collaboration among several universities to carry out a multidiscipline study on the breakaway oxidation of zirconium alloys. The overall goal of the project is to further understand the mechanisms of the oxidation and breakaway process of zirconium alloys. This thesis describes the nano/micro-structural study and nano-analysis of the corroded zirconium alloys using up-to-date TEM and 3D focused ion beam (FIB) slicing and reconstruction techniques. The work mainly focused on the characterization of ZIRLO.

The oxide morphology in general comprises an inner columnar layer and an outer equiaxed layer, except for a post-second transition oxide grown on a Zr-Nb-Ti test alloy with a very poor corrosion resistance, which exhibits generally only equiaxed grains throughout the whole oxide scale. Detailed investigation reveals oxides in a slower oxidation stage exhibit better developed columnar grain structure. All the oxides, independent of different corrosion stages and alloy types, contain predominantly monoclinic oxide and a small amount of tetragonal oxide.

Defects at different length scales were examined. In stead of a sudden burst of crack nucleation at the kinetic transition, a gradual introduction of cracks parallel to the metal/oxide interface throughout the pre-transition stage is found, suggesting no direction correlation between the formation of cracks and the transition. Besides cracks, the oxide also contains different forms of nano-porosity: isolated pores of 1-3 nm or interconnected pores at grain boundaries. The density of interconnected porosity, especially those along the oxide growth direction, increases towards the oxide surface, evolving over time. It is suggested that the kinetic transition is related to the development of an interconnected porosity down to the metal/oxide interface, providing easy pathways for the transportation of oxidation species.

The metal-oxide interface has a wavy morphology both in the micrometer and nanometer scale. The roughness develops to a maximum just before the first kinetic transition. An intermediate suboxide layer with complex 3D morphology between the bulk oxide and the metal substrate is found. Quantitative EELS analysis shows the composition of this layer to be 40-50 at. % oxygen. The suboxide appears to develop in thickness with increasing oxidation time for the pre-transition oxides, while is very thin or absent in the post-, and post-second transition oxides. In the suboxide region, multiple phases including α -Zr, ω -Zr, tetragonal

oxide and a phase with an unidentified structure were found, suggesting different structures can coexist in the suboxide layer.

Second-phase particles (SPPs) of β -Nb and hexagonal Zr(Fe,Nb)_2 types were found in ZIRLO samples and FCC Zr(Fe,Cr)_2 was the predominant type in Zircaloy-4. The SPPs showed delayed oxidation compared to surrounding Zr. In ZIRLO, those containing high Fe contents were found to be oxidized and transform into an amorphous state much earlier than β -Nb. Hydrides of different types (γ , δ and ϵ) were observed in the metal and metal/oxide region for both Zircaloy-4 and ZIRLO samples. A higher density of hydrides was seen in post-transition oxides of ZIRLO than in pre-transition oxides.

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Other authors' contributions to this thesis

Jianfei Wei, University of Manchester. Optical microscopy in Figures 4.1, 4.3 and 4.4.
Corrosion testing in Figure 4.2 and Table 4.1

Peng Wang, University of Manchester. In-situ EIS in Figure 5.26b

The work of these authors is also acknowledged alongside these figures and tables in the text.

Preface

The research described in this thesis was carried out by the author in the Department of Materials at the University of Oxford between January 2008 and March 2011, under the supervision of Prof. Chris R. M. Grovenor, Prof. John M. Sykes and Dr. Sergio Lozano-Perez. All of the work is original, and where the work of others is included it has been referenced and acknowledged. No part of this thesis has been submitted for any other degree at this university or elsewhere.

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2011

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Oral and/or poster presentations have also been given at the following meetings:

2010

“Quantitative EELS analysis of zirconium alloy metal/oxide interfaces”, Microscopy and Microanalysis annual meeting, Portland, Oregon, USA, 1st-5th August 2010

“3D Microstructure Study of Zirconium Oxide Using FIB Sectioning Reconstructions”, Microscience 2010 conference, 28th June- 1st July 2010

“Characterization of Oxide on Zirconium Alloys for Understanding Corrosion Mechanisms”, 3rd year DPhil competition at the Department of Materials, University of Oxford, UK, 23rd February 2010.

2008

“Examination of FIB Prepared Specimens of Oxide on Zirconium Alloys”, Microscopy of Oxidation 7 conference, 15th-17th September 2008