



# Study of sub-oxide phases at the metal-oxide interface in oxidized pure zirconium and Zr-1.0% Nb alloy by using SEM/FIB/EBSD and EDS techniques



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## HIGHLIGHTS

- Presence of rich in tetragonal phase oxide layer in the post-transition stage have been clearly presented.
- Presented images shows: thin sublayer, columnar grains and equiaxed grains near metal/oxide interface.
- Similar behavior of pure zirconium and its alloy proves that one can consider pure zirconium as an analogous to its alloy.
- Presence of parallel and perpendicular cracks located in the rich in monoclinic phase sublayer have been evidenced.

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## ABSTRACT

Metal-oxide interfaces phases developed during high temperature oxidation on pure zirconium and zirconium alloy (Zr-1.0%Nb) were investigated. Main objective of the study was to elucidate the results coming from previous structural studies and better understand the process of zirconium alloys oxidation. Samples were prepared by high temperature oxidation at 600 °C in air under normal atmospheric pressure. Afterwards, samples were examined by combined methodology of SEM/FIB/EBSD and EDS techniques. Implementation of these techniques revealed complexity of studied systems and confirmed the presence of continuous, rich in tetragonal phase oxide layer located in the proximity of the zirconium substrate. This region is probably characterized by lower amount of oxygen than the external part of the oxide scale. According to the EDS analysis, reported oxide scale is most likely composed of stoichiometric ZrO 1:1. In order to explain observed phenomena, the combined effects of compressive stress and stoichiometry level were taken into account.

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## 1. Introduction

Due to the low thermal neutron capture cross section and very good corrosion properties in the aggressive reactor environment, zirconium alloys are considered as cladding materials for current and future generations of nuclear reactors [1]. According to the worldwide strategy, the next generation of nuclear reactors will demand safe exploitation for 60 years with a possible extension to 120 years. Those requirements are forcing the development of current materials to provide safe and long-lasting operation up to high damage levels (depending from the material up to

150–200 dpa), high mechanical load and in highly corrosive environment [2,3]. The lessons learnt from Fukushima accident also point out to the necessity of the development of accident-resistant fuels, with the special attention to reduction of risks related to hydrogen release from overheated reactor core. One of main aspects of this research is a full understanding of oxidation process of zirconium-made fuel rod cladding.

Classical zirconium oxidation process foresees two-step stage [4,5], or as some authors suggest three-step stage [6,7], depending on whether the transition period is treated as a separate period of oxidation. First stage of oxidation is characterized by a parabolic nature and can be fitted using the power law eq:  $\Delta W = Kt^n$ , where  $W$  is the weight gain measured in  $\text{mg}/\text{dm}^2$ ,  $K$  depends on alloying elements and oxidation temperature,  $t$  is the oxidation time measured in days and  $n$  has a value of 2–3 depending from

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temperature, as reported by Nagase et al. [8]. In the first stage a thin, dense zirconium oxide layer consisting mostly of the tetragonal phase is created. This phase is mainly located on the border of the metal/oxide interface (region characterized by the highest level of compressive stress) and reaches a thickness of several hundred nanometers. However, continuity and uniformity of this phase in the post-transition oxidation stage are still being questioned in the literature. Reported by several groups results, see Refs. [6, 9, 10], suggest that visible tetragonal phase is cracked and may create so-called “islands” of the tetragonal phase accumulation. However, these studies were performed at lower oxidation temperatures (generally in the region between 300 and 400 °C) and/or in aqueous environment. Therefore, they are hardly comparable with our report. It should be emphasized, that chosen in this study oxidation conditions are poorly documented in the literature [10,11].

It is commonly believed that, when the oxide growth continues, the external part of the oxide scale increases its distance from the interface, the compressive stress diminishes, which results in transition from tetragonal to monoclinic phase (schematic view of the zirconium/zirconia interface has been presented in Fig. 1). Moreover, when a total oxide thickness exceeds a given value, which for zirconia is approx. 3  $\mu\text{m}$  [11,12], the oxide layer begins to crack and second stage of corrosion occurs. Previously produced oxide loses its protective properties, and appearing cracks allow faster diffusion of oxygen into the metal which accelerates corrosion. This oxidation stage is characterized by a quasi-linear nature and can be described using equation  $\Delta W = Kt + C$  where  $C$  is the initial weight gain.

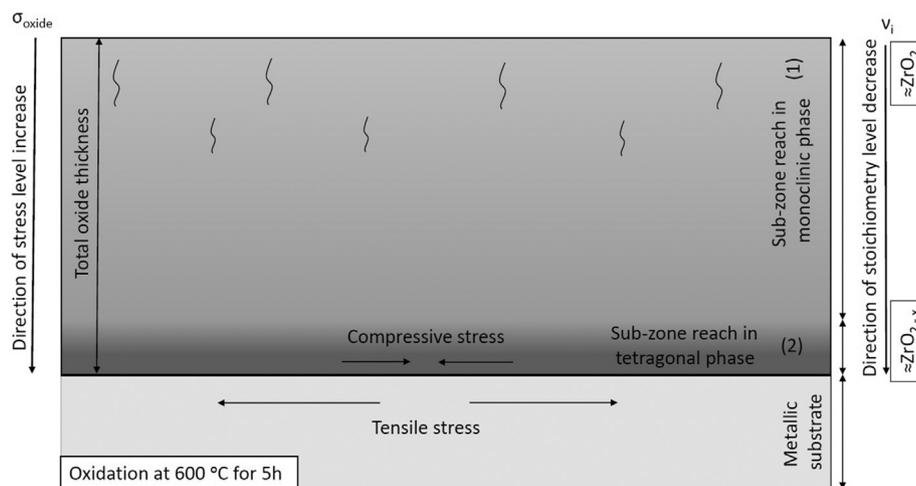
Since the corrosion process proceeds on the verge of the metal-oxide interface [11,13], one may expect that this region will play a key role in the control of zirconium oxidation. One of the first authors who confirmed that the oxygen migrates through the oxide scale and the oxidation process takes place on the metal/oxide interface were Kofstad [14] and Mrowec [15]. This type of oxygen diffusion is also known in the literature as “spinal (or core) diffusion”. As reported in Refs. [15,16], a thin oxide layer created in the proximity of the metal consists mostly of tetragonal phase. According to works of Bouvier et al. [17] and Barberis et al. [18], this phase may be stabilized by three factors such as: compressive stress, stoichiometry level and grain size. In addition, this zone is not cracked and oxygen diffusion through this zone is considerably

slowed down. For that reason, the growth control of the particular transition oxide zone can significantly increase the lifetime of cladding materials. Due to the limited access to zirconium alloys, most of the research is performed on the pure zirconium (purity level of order 99% - explained in the following paragraph). Therefore, in the first stage of this study, one must check if similar (or ideally the same kind) thin layer of zirconia, located in the proximity of metallic substrate is created in both samples, pure Zr and zirconium alloy, respectively. This will allow in the future to reference the results obtained on pure zirconium and apply them to zirconium alloys without violating publication data rules.

In this work we combined several techniques, i.e. Scanning Electron Microscopy (SEM), Focused Ion Beam (FIB), Electron Backscattered Diffraction (EBSD), Energy Dispersive X-ray Spectrometry (EDS) and Raman spectroscopy to characterize the microstructure and chemical composition of the phases located in the proximity of the metal-oxide interface grown on un-doped zirconium (purity 99.2%) and zirconium alloy (Zr-1%Nb) under the same high temperature corrosion conditions. The presence of similar sub-oxide regions have been confirmed in both studied cases. This work opens the possibility to represent (in terms of research) corroded system of zirconium alloy by using pure zirconium samples. Presented work is a part of much broader topic aiming to understand the influence of mechanical stresses, chemistry and microstructure of interface in the zirconium – zirconia system [19].

## 2. Materials and methods

The studied material (pure zirconium with 99.2% purity) was provided as 0.5 mm thick recrystallized sheet by GoodFellow Cambridge Ltd laboratory. The zirconium alloy (Zr-1%Nb) sample comes from an original piece of material planned to be used in the previous design of the nuclear reactor. In order to eliminate the stress created during manufacture preparation of the purchased starting material, all samples were heat treated at 600 °C for 1 h in air under normal atmospheric pressure. Afterwards, they were cut into 1  $\text{cm}^2$  pieces and mechanically polished with SiC papers (gradation from 320 to 4000 $\times$ ) and liquid diamond suspension until the “mirror-like” surface finish. Next, the samples prepared in such a way were oxidized in high-temperature stove at



**Fig. 1.** Schematic representation of the zirconium/zirconia interface developed at high temperature. Labeled by (1) and (2) zones represent rich in monoclinic and tetragonal phases, respectively. Marked regions are reference in the following part of the study. Visible small cracks located in the external part of the oxide, perpendicular to the metal/oxide interface. The arrows visible in the schema depict trends of stress and stoichiometry level, respectively their increase and decrease throughout the oxide scale.

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