

## Full length article

## The effect of Nb on the corrosion and hydrogen pick-up of Zr alloys

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## ABSTRACT

Zr-Nb alloys are known to perform better in corrosion and hydrogen pick-up than other Zr alloys but the mechanism by which this happens is not well understood. Atomistic simulations using density functional theory of both tetragonal and monoclinic ZrO<sub>2</sub> were performed, with intrinsic defects and Nb dopants. The overall defect populations with respect to oxygen partial pressure were calculated and presented in the form of Brouwer diagrams. Nb is found to favour 5+ in monoclinic ZrO<sub>2</sub> at all partial pressures, but can exist in oxidation states ranging from 5+ to 3+ in the tetragonal phase. Nb<sup>5+</sup> is charge balanced by Zr vacancies in both phases, suggesting that contrary to previous assumptions, Nb does not act as an n-type dopant in the oxide layer. Clusters containing oxygen vacancies were considered, Nb<sup>2+</sup> was shown to exist in the tetragonal phase with a binding energy of 2.4 eV. This supports the proposed mechanism whereby low oxidation state Nb ions (2+ or 3+) charge balance the build-up of positive space-charge in the oxide layer, increasing oxygen vacancy and electron mobility, leading to near-parabolic corrosion kinetics and a reduced hydrogen pick-up. Previous experimental work has shown that tetragonal ZrO<sub>2</sub> transforms to the monoclinic phase during transition, and that during transition a sharp drop in the instantaneous hydrogen pick-up fraction occurs. The oxidation of lower charge state Nb defects to Nb<sup>5+</sup> during this phase change, and the consequent temporary n-doping of the oxide layer, is proposed as an explanation for the drop in hydrogen pick-up during transition.

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## 1. Introduction

Zirconium is used as a cladding material for water-cooled reactors due to its good thermal and mechanical properties and low absorption of thermal neutrons. With the recent drive towards higher fuel burn-ups and therefore increased in-reactor fuel lifetimes, long term corrosion resistance and the absorption, by the cladding, of hydrogen produced during corrosion have become increasingly important [1]. As the solubility limit for H in Zr is exceeded, Zr-hydrides precipitate in the cladding alloy leading to cladding embrittlement [2,3]. This problem is particularly apparent after removal from the reactor; as the cladding cools, the hydrogen solubility drops and further brittle Zr-hydrides precipitate, which can lead to delayed hydride cracking [4]. Thus, increasing corrosion resistance and reducing the hydrogen pick-up fraction (HPUF) of fuel cladding are key aims for cladding alloy manufacturers.

The Zr alloys of choice in most current water-cooled reactor designs contain 0.5–2.5 wt. % Nb due to its beneficial effect on

HPUF [5–7]. Long term autoclave studies have demonstrated that Zr-2.5Nb exhibits near parabolic corrosion kinetics, and a lower corrosion rate than other Zr-based alloys such as Zircaloy-4 and Sn-containing alloys such as ZIRLO, as shown in Fig. 1. The reason for this improved corrosion behaviour is not fully understood, however, it has previously been suggested that in the oxide layer, Nb exists almost exclusively in a 5+ oxidation state as a substitutional defect on a Zr site. This is assumed to be charge compensated by a suppression of oxygen vacancies, lowering the oxygen ion conductivity of the oxide layer and thus lowering the oxidation rate [8]. This has also been suggested as a reason for the decreased HPUF in Nb-containing alloys; the Nb<sup>5+</sup> ion is expected to act as an n-type dopant, donating electrons to the oxide layer. The additional electrons combine with H<sup>+</sup> ions closer to the oxide/water interface, forming H<sub>2</sub> gas which can then escape into the water instead of the cladding metal [9,10].

The assumption that Nb exists only in the 5+ charge state in the oxide layer is supported by previous DFT simulation work [11]. However, several independent x-ray absorption near-edge spectroscopy (XANES) studies have identified oxidation states ranging from 5+ to 2+ (and also metallic Nb) in the oxide layer of Zr-Nb alloys [12–16]. Recently there has been some debate regarding

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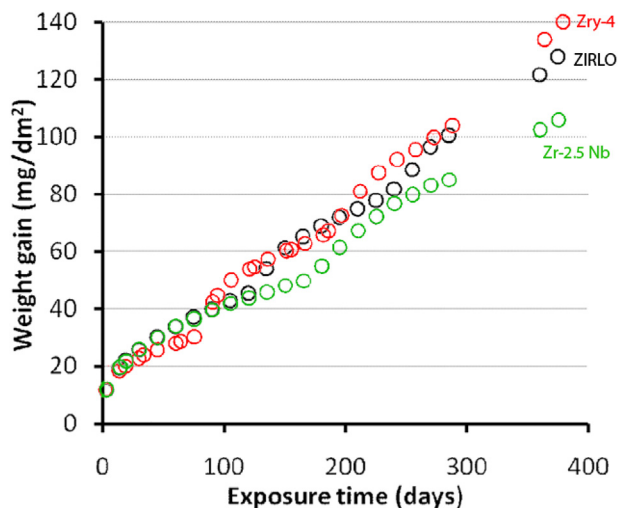


Fig. 1. Corrosion of Zry-4, ZIRLO and Zr-2.5Nb at 360 °C in de-ionised water under saturated pressure conditions at 18.7 MPa, reproduced from Ref. [7].

the location of these lower charge state Nb ions (i.e. whether they exist within the bulk oxide, or are localised in the partially oxidised Nb-containing secondary phase precipitates (SPPs) [17], the latter is reasonable, since SPPs account for around 60% of the Nb in a typical Zr-1.0Nb alloy such as ZIRLO). However, a recent study by Couet et al. [16] investigated an alloy with a sufficiently low Nb-concentration to avoid the formation of SPPs (Zr-0.4Nb), which showed that a large proportion of the Nb contained in the oxide layer was in a 3 + oxidation state or below. The assumption that Nb<sup>5+</sup> is the only Nb ion present in the oxide layer is also unable to explain the variation in HPUF observed during corrosion [18].

The corrosion model developed by Wagner and Hauffe [19,20] suggests that all Zr-based alloys should exhibit parabolic corrosion kinetics, however, this is rarely observed in experimental studies. A recent corrosion model developed by Couet et al. [16] applies the *space charge* model to the oxide layer of Zr-alloys and demonstrated that during corrosion, the limited mobility of oxygen vacancies, when compared to electrons, could lead to a build-up of non-equilibrium positive charge in the layer, inhibiting corrosion and causing sub-parabolic kinetics. This build-up of charge also inhibits the movement of electrons, reducing the electrical conductivity of the oxide and thus increasing HPUF. In Zr-Nb alloys, it is proposed that the ability of Nb to occupy charge states lower than Zr<sup>4+</sup> (i.e. to be included as overall negatively charged defects) may help mitigate the build-up of space charge, allowing near-parabolic corrosion kinetics and reducing HPUF.

The Nb-containing alloy ZIRLO exhibits near parabolic corrosion kinetics, almost identical to that of Zr-2.5Nb, but with a first transition time similar to Zircaloy-4. This reduced transition time has recently been linked to the presence of Sn in the alloy composition [21,22]. Previous investigations have considered the oxide layer to be a generally uniform structure, making no distinction between the monoclinic and tetragonal phases of ZrO<sub>2</sub> that have been shown to be present [23,24]. In this study, DFT simulations are used to study both isolated defects and clustering of Nb defects with oxygen vacancies in both tetragonal and monoclinic ZrO<sub>2</sub>, to determine the possible charge states and infer a possible corrosion mechanism.

## 2. Methodology

Simulations were performed using the DFT code CASTEP 8.0

[25], with consistent parameters and convergence criteria used throughout. Ultra-soft pseudo potentials with a cut-off energy of 550 eV were used, and the Perdew, Burke and Ernzerhof (PBE) [26] formulation of the generalised gradient approximation (GGA) was used to describe the exchange-correlation functional, since previous work has shown this to effectively describe Zr systems [4,22,27,28,46]. A k-point separation of 0.045 Å<sup>-1</sup> arranged in a Monkhorst-Pack sampling scheme [29] and supercells formed 3 × 3 × 2 repetitions of the tetragonal ZrO<sub>2</sub> unit cell and 2 × 2 × 2 repetitions of the monoclinic ZrO<sub>2</sub> unit cell in the x, y and z directions respectively, were shown to offer an acceptable compromise between simulation accuracy and computation time. All simulations employed density mixing using the method described by Pulay [30]. An energy correction calculated using the screened Madelung method [31] was used to account for the electrostatic self-interaction of defects created by the use of periodic boundary conditions and a finite supercell size. This is an improvement over the Makov-Payne method [32] as it takes into account the anisotropy of the dielectric properties of the two structures. The dielectric values calculated by Zhao and Vanderbilt [33] were used.

All defective structures were simulated using pre-relaxed pure ZrO<sub>2</sub> supercells, which were then energy minimised under constant volume. The criterion for energy convergence in self-consistent calculations was 1 × 10<sup>-8</sup> eV. The energy and displacement limits between successive iterations for each ion were 1 × 10<sup>-5</sup> eV and 5 × 10<sup>-4</sup> Å respectively, and a maximum force of 1 × 10<sup>-2</sup> eV/Å between ions was allowed for convergence to be considered achieved.

For the Nb-containing simulations in this work, a +U value of 1.5 eV was applied in order to account for the errors arising from the use of the PBE formulation of the GGA exchange-correlation functional. This value was taken from an extensive study into the behaviour of transition metals using DFT with comparisons to experimental energies, performed by Hautier et al. [34]. In this approach we follow extensive previous work using the +U parameter to account for errors simulating transition metal oxides in DFT [11,35–38].

Defect formation energies ( $E_f^i$ ) were calculated using the method outlined in Ref. [22]. All vacancy, substitutional and interstitial defects were considered (anti-site defects were not considered due to the large size and charge difference between the anions and cations). The chemical potentials of the reactive species used to plot the Brouwer diagrams were obtained from formation energies of the relevant oxides following established methods [22,39–42].

In order to ensure charge neutrality, the sum of all defects multiplied by their charge must equal zero:

$$\sum_i q_i c_i - N_c \exp\left(-\frac{E_g - \mu_e}{k_B T}\right) + N_v \exp\left(-\frac{\mu_e}{k_B T}\right) = 0 \quad (1)$$

where the first term is the sum of the charges of all ionic defects ( $q_i$  is the charge and  $c_i$  the concentration of defect  $i$ ), the second and third terms are the electron and hole concentrations respectively.  $N_c$  and  $N_v$  are the density of states for the conduction and valence bands,  $E_g$  is the band gap of the crystal,  $k_B$  is the Boltzmann constant and  $T$  the temperature. The concentrations  $c_i$  of each defect  $i$  are calculated using the approach developed by Kasamatsu et al. [43], which uses standard Boltzmann statistics to calculate concentrations but also accounts for defects competing for the same lattice site.

Tetragonal ZrO<sub>2</sub> is a wide band gap insulator, and as such the concentrations of electrons and holes are expected to be sufficiently low that Boltzmann statistics are appropriate. Self-trapping of electrons will cause a reduction in the formation energy of

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