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Electrochemical effects of isolated voids in uranium dioxide

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ABSTRACT

We present a model to study the electrochemical effects of voids in oxide materials under equilibrium conditions and apply this model to uranium dioxide. Based on thermodynamic arguments, we claim that voids in uranium dioxide must contain oxygen gas at a pressure that we determine via a Kelvin equation in terms of temperature, void radius and the oxygen pressure of the outside gas reservoir in equilibrium with the oxide. The oxygen gas within a void gives rise to ionosorption and the formation of a layer of surface-charge on the void surface, which, in turn, induces an influence zone of space charge into the matrix surrounding the void. Since the space charge is carried in part by atomic defects, it is concluded that, as a part of the thermodynamic equilibrium of oxides containing voids, the off-stoichiometry around the void is different from its remote bulk value. As such, in a uranium dioxide solid with a void ensemble, the average off-stoichiometry level in the material differs from that of the void-free counterpart. The model is applied to isolated voids in off-stoichiometric uranium dioxide for a wide range of temperature and disorder state of the oxide.

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1. Introduction

Extended defects are ubiquitous in all crystalline materials, including oxides, both under equilibrium and non-equilibrium conditions such as irradiation. Extended defects that have been widely studied in crystalline solids include interfaces and grain boundaries, dislocations lines and small dislocation loops, voids, bubbles and pores. Particle irradiation is effective in introducing extended defects such as loops, voids and bubbles [1]. Irradiation also leads, in some cases, to the formation of precipitates and it leads to evolution of the grain boundary network as in the case of grain growth and refinement in, say, nuclear fuel pellets [2]. Most of the extended defects induced by irradiation remain in the solid after the irradiation is stopped. The formation of extended defects under irradiation involves a process of nucleation and growth that is driven by the availability of point defects in excess of the thermal equilibrium concentrations. As a material of utmost technological importance in the nuclear industry, uranium dioxide, UO_2, has been investigated for its formation of extended defects with and without irradiation over many decades [1,3]. Of special importance is the formation of voids or gas bubbles (cavities) in UO_{2+x} as this process affects both the mechanical properties, swelling, and thermal transport properties. Reactor-irradiated samples showed a dispersion of bubbles which would coarsen and consolidate into larger equilibrium shaped cavities upon annealing as studied by TEM [3]. The position and size distribution of voids has been studied in the rim structure of the post-operation nuclear fuel elements [4]. More recently, mixed oxide fuel under short term irradiation was investigated by X-ray computer tomography and radiography and showed the formation of voids on the periphery of the fuel element [5]. Without irradiation, voids have also been found to form in UO_2 as part of the preparation of polycrystalline samples. Castell [6] used low voltage scanning electron microscopy for images of the equilibrium Wulff-shaped voids in UO_2. The voids were produced by spectacular grain growth process that involved inclusion of intergranular pores into the grains. The finding showed the stability of coexisting voids in the oxide. The same phenomenon have also been found in other oxides depending on the preparation methods and were tied to changes in the physical properties of the oxides, see for example [7–9].

Efforts to simulate the formation of voids and dislocation loops have been carried out by means of Molecular Dynamics simulations. Martin et al. [10] used classical molecular dynamics simulations to investigate the clustering of irradiation-induced point defect into dislocation loops and nanocavities (voids). Defect clustering in ceria and urania has also been investigated by Aidhy et al. [11,12] by molecular dynamics. As to a higher scale, continuum mechanics models were introduced to tackle the interaction of voids in solids; such models analyzed the problem from a purely mechanical point of view serving the inquiry about mesoscale elements in metals and alloys. The work by Willis and

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Bullough [13], for example, attempted modeling of the mechanical interaction of two bubbles within a solid and predicted that they would always mechanically attract. Other attempts have also been proposed to model voids in solids through mechanical stress analysis [14]. However, such models were meant for metals and hence are not representative of other aspects of the problem that may arise in the case of oxides.

In order to properly model extended defects in an oxide such as UO_2, the ionic nature of these materials must be taken into account. Charged point defects as well as electronic carriers are the building blocks of the oxides defective structures and the mediators of their evolution. The electrochemical and mechanical stress fields, both created by the defects, whether point or extended defects, dictate the stability or evolution of an oxide's defective elements. A set of investigations have been carried out in the past to take the ionic nature of oxides into consideration when modeling microstructure elements. The focus was mainly on dislocation loops [15–17]. Besides being limited to dislocation loops, such attempts have not considered the electronic structure modification in the form of intrinsic or extrinsic electronic states associated with extended defects, e.g., free surface, grain boundary, and so on; see [18,19]. To better model extended defects in oxides, we have introduced a local off-stoichiometry model that analyzed the interaction of defect fields in the presence of a flat surface exposed to equilibrium oxygen pressure [20]. The model was similar in spirit to the electrochemical and mechanical model of defects introduced by Swaminathan et al. [21], and, aside from being generalized to atomic defects and electronic charge carriers and gas reaction boundary conditions at the solid surface, it is formally equivalent to the classical space charge model of Kliewer and Koehler [22]. While there are many similarities in the electrochemical basis of this model to the ones introduced by Maier [23,24], this model, in addition to considering void effects, correlates the defect fields and the accompanying electrostatic profile to the chemical state of the oxide as controlled by the oxygen atmosphere. This effect comes into play on the bulk side by controlling the off-stoichiometry and on the surface side, in this case the void surface, as will be explained below. Here, we aim at the microstructure evolution of ionic UO_2 through interaction of mesoscale elements as mediated by defects and electronic carriers. Further, electronic structure results for the point defect formation energy and the electronic band structure was employed in application for the case of UO_{2+x}.

In light of the above, we bring into consideration the electrochemical effect of voids in oxides and their interaction with point defect fields. In this paper, we extend our model in [20] to the case of voids in UO_{2+x}. As shown in the next section, oxygen must be present inside the void as a result of chemical equilibrium of the overall material with a remote oxygen reservoir. The electrochemical effect arising due to the presence of oxygen inside voids is accounted for by the ionosorption theory. The defect fields around a void are then calculated within the framework of chemical diffusion of defects, which is based on the electro-chemical potentials of the defect and electronic species. In steady state, and in the absence of boundary fluxes, the defect concentration profiles are consistent with uniform electro-chemical potentials of all species. Such profiles represent the equilibrium profiles giving rise to the space charge profile and local off-stoichiometry of the oxide as a function of distance from the void surface.

2. Model

2.1. Oxygen pressure of isolated voids in an oxide

The uniform chemical state of a disordered oxide, such as UO_{2+x}, is controlled by the temperature and the oxygen pressure of the chemical reservoir with which the oxide is in equilibrium. The presence of a void in the oxide perturbs this uniform state of equilibrium. In particular, as argued below, a void enclosed within a disordered oxide is required to adhere to thermodynamic equilibrium with the rest of the solid. This requires the void to contain oxygen gas, the pressure of which can be found by comparing the solid oxide with an isolated void with a reference void-free oxide subject to the same thermal and chemical environment.

The sought comparison can be made by considering a void remotely placed in a semi-infinite solid with a flat surface in contact with a reservoir of oxygen at partial pressure p_0. Without loss of generality, the void is assumed to have a spherical shape with a radius R and oxygen content at pressure p. Thermodynamic equilibrium is assumed of the system. The oxygen chemical potential within the oxide equals that of the environment; that is

$$\mu_O^{\text{oxide}} = \frac{1}{2}\mu_{O_2}^0(T,\ p_0), \tag{1}$$

where μ_O^{oxide} is the potential within the solid oxide. Applying the same condition with the content of the void gives

$$\mu_O(T,p) = \mu_O^{\text{oxide}} = \frac{1}{2}\mu_O^0(T,p_0), \tag{2}$$

which gives the chemical equilibrium condition. On the other hand, mechanical equilibrium of the void surface requires

$$p - p' = \frac{2\gamma}{R}, \tag{3}$$

where p' is the mechanical pressure in the oxide just outside the void surface and γ is the oxide surface energy. Eqs. (2) and (3) furnish the necessary conditions for equilibrium [25]. A perturbation of Eqs. (2) and (3) gives

$$d\mu_O = d\mu_O^{\text{oxide}}, \tag{4a}$$

$$dp - dp' = d\left(\frac{2\gamma}{R}\right). \tag{4b}$$

The perturbation is also governed by Gibbs–Duhem equation [25],

$$sdT - \Omega dp - d\mu_O = 0, \tag{5a}$$

$$s'dT - \Omega' dp' - d\mu_O^{\text{oxide}} = 0, \tag{5b}$$

where Ω and Ω' are the molecular volumes of the gas and the oxide, respectively, and s and s' are the entropies per molecule of the gas and the oxide side, respectively. Solving Eqs. (4) and (5) for isothermal conditions yields

$$\frac{\Omega' - \Omega}{\Omega'} dp = d\left(\frac{2\gamma}{R}\right), \tag{6}$$

which upon neglecting Ω' with respect to Ω, using the gas law, $\Omega = k_B T/p$, and integration between p_0 and p gives

$$p = p_0 \exp\left(-\frac{2\gamma\Omega'}{Rk_BT}\right). \tag{7}$$

Eq. (7) gives the oxygen pressure that has to exist inside a void of radius R enclosed in an oxide in order for equilibrium to be attained throughout the heterogeneous oxide. This equation is known in classical thermodynamics as the Kelvin equation for equilibrium of a liquid (or a solid) with its vapor [25]. A plot of Eq. (7) is shown in Fig. 1 for UO_2. The plot shows that the deviation from the reservoir oxygen partial pressure dictated by Eq. (7) is small for radii within the range of those observed for equilibrium voids in UO_2 [6].

In order to appreciate the result (7), i.e., the presence of oxygen gas in voids in any oxide, let us consider the following situations.

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