Computational Materials Science 79 (2013) 634–638

Contents lists available at ScienceDirect

Computational Materials Science

journal homepage: www.elsevier.com/locate/commatsci

Role of nanoceria coatings on the high temperature oxidation of stainless steels: An atomistic simulation

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ARTICLE INFO

Article history:
Received 13 April 2013
Received in revised form 22 July 2013
Accepted 28 July 2013

Keywords:
Nanoceria coatings
High temperature oxidation
Diffusion in chromia scales
Diffusional computer simulations

ABSTRACT

Computer simulations using the Density Functional Theory and GAUSSIAN 03 were implemented in predicting potential mechanisms that can be associated with the high temperature oxidation of stainless steels. In particular, the role of nanoceria protective coatings on the induced diffusional mechanisms at 1273 K was satisfactorily predicted. Atomistic calculations were made on computed activation energies for oxygen inward diffusion and for iron outward diffusion through the nanoceria coating and the chromium oxide scale, respectively. In addition, it was assumed that when nanoceria coatings are present in stainless steels, cerium ions can be incorporated in the Cr_2O_3 scale as dopants. Computer simulations indicate that in the absence of Ce ions in the chromia scale lattice Fe outward diffusion is dominant and accounts for the relatively high oxidation rates. It was found that in a Ce-doped Cr_2O_3 scale the predicted activation energies exhibit appreciable changes. Under these conditions the activation energies for both, iron and oxygen diffusion increase in magnitude. However, the activation energy for O inward diffusion falls below the one corresponding to Fe outward diffusion. In turn, oxygen inward diffusion becomes rate limiting accounting for the role of nanoceria coatings on the high temperature oxidation resistance of stainless steels.

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1. Introduction

High temperature oxidation is in general governed by active diffusional mechanisms which control the rate of scale growth. Accordingly, there is an extensive number of works [1–3] aimed at unfolding the microscopic mechanisms associated with the diffusional processes involved in high temperature oxidation. From these works, insight on the exhibited activation energies and diffusional coefficients is often provided. Nevertheless, the experimental outcome does not always reflect the active mechanisms that occur at the nanoscale level.

In general, mass transport over relatively long diffusional distances can be described by Fick first and second laws [4]. The experimentally determined diffusion coefficients reported in the literature often constitute a global evaluation of the transport phenomena, in a crystal lattice containing numerous defects including grain boundaries and dislocations. However, it is difficult to unfold the intrinsic nature of the atomistic diffusional processes of a given crystal lattice from conventional experiments.

Theoretical studies on diffusional mechanisms have been carried out using atomistic calculations and molecular dynamics (MD) methods. MD methods can be employed to obtain information on diffusional coefficients (Einstein relation, implying an average on all times and a summation on all ions). Hence, MD is highly valuable in defining the diffusion pathways and for gaining insight into the active diffusional mechanisms in nanostructures.

In the present work, atomistic calculations were made in order to disclose possible mass transport mechanisms that are active during the high temperature oxidation of stainless steel. The steels are typically coated with a film of nanoceria particles which provides a dramatic improvement in the high temperature oxidation resistance [5–7]. The experimental outcome on the role played by the nanoceria coatings [5] was used in the present work to establish possible mass transport mechanisms across the resultant oxide scale.

Thus far, there are no detailed microscopic investigations on the oxygen mass transport in Cr_2O_3 scales nor on the role of cerium oxide as a coating in stainless steels. Haiying [5] investigated the oxidation resistance of a CeO_2 coated 304 stainless steel and found that oxygen inward diffusion becomes dominant during high temperature exposure. This in agreement with the work of Thanneeru et al. [7]. In the lack of enough information on the diffusional mechanisms involved, a methodology based on the Density

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0927-0256/$ - see front matter Published by Elsevier B.V.
http://dx.doi.org/10.1016/j.commatsci.2013.07.043

Functional Theory (DFT) was developed here. In particular, the aim of this work was the determination of possible high temperature diffusion transport mechanisms at the atomistic scale in nanoceria coated stainless steels.

2. Computer simulation method

Experimental methods using nuclear probes [8–10] such as incoherent and coherent Quasi-elastic Neutron Scattering (QENS) [8,11] and Nuclear Magnetic Resonance (NMR) [8,12] are commonly employed in establishing the microscopic aspects of diffusion. By these means, it is always possible to establish the atomic jump frequency, Γ in single crystals which constitutes the microscopic key feature for the diffusion phenomenon [13].

$$\Gamma = \nu^{*} \cdot \exp(-\Delta H/kT) = \nu \cdot \exp(\Delta S/k) \cdot \exp(-\Delta H/kT), \tag{1}$$

where ν^{*} represents the Vineyard's prefactor, ν is the effective frequency associated with the vibration of an atom in the direction of the saddle point position, k is the Boltzmann's constant, ΔH and ΔS are the enthalpy and entropy associated with the atomic displacements, respectively.

A determination of bulk diffusion from first principles can be achieved by comparing the physicochemical properties of two states characterizing the system at the microscopic scale; (a) during diffusion the *initial state* (IS) and (b) the *saddle point state* (SPS). The initial state corresponds to the system before diffusion, having a certain number of point defects such as vacancies or interstitials as bulk diffusion is caused by the existence of these defects. The saddle point state corresponds to the system in which the position of the diffusing atom is associated with the complex activated along the diffusion pathway (transition state). The energy between both states provides the microscopic activation energy for diffusion and it corresponds to the ΔH value in Eq. (1).

In a given oxide, the active diffusional mechanisms can involve various possible diffusion pathways, among which the dominant one will be characterized by the lowest energy barrier (activation energy). Hence, in this work, the Density Functional Theory (DFT) is employed in order to compute the energies corresponding to both, the initial and the saddle point states. The essence of the DFT is to minimize the total energy $E[n(\mathbf{r})]$, also known as the Kohn–Sham equation [14] given by:

$$E[n(\mathbf{r})] = T_0[n(\mathbf{r})] + E_h[n(\mathbf{r})] + E_{XC}[n(\mathbf{r})] + \int n(\mathbf{r}) V_{ext}(\mathbf{r}) d\mathbf{r}, \tag{2}$$

where $n(\mathbf{r})$ is the charge density function in terms of the non-interacting single-particle wavefunctions, ψ_i; T_0 is the kinetic energy of a set of non-interacting electrons; E_h the classical Coulomb interaction; E_{XC} is the exchange–correlation energy which is the sum of all remaining many-body contributions (including kinetic energy effects) to the total energy; $V_{ext}(\mathbf{r})$ is the external potential, which is determined by the ground-state density n_0.

$$T_0[n(\mathbf{r})] = -\frac{\hbar^2}{2m_e} \sum_{i=1}^{N} \langle \psi_i | \nabla^2 | \psi_i \rangle, \tag{3}$$

$$E_h[n(\mathbf{r})] = \frac{1}{2} \iint \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}', \tag{4}$$

and

$$n(\mathbf{r}) = \sum_{i=1}^{N} |\psi_i(\mathbf{r})|^2, \tag{5}$$

$$V_{ext}(\mathbf{r}) = V_{ext}[n_0](\mathbf{r}). \tag{6}$$

Unfortunately, the exact exchange–correlation energy functional E_{XC} dependence upon $n(\mathbf{r})$ is unknown, and the successful implementation of DFT relies on its accurate estimation. In this particular work, this aspect was treated by means of the generalized gradient approximation (GGA). From the work of Perdew and Wang [15], the exchange–correlation energy is expressed as more general functions (Eq. (7)) of $n(\mathbf{r})$ and $\nabla n(\mathbf{r})$.

$$E_{XC}^{GGA}[n(\mathbf{r})] \approx \int f[n(\mathbf{r}), \nabla n(\mathbf{r})]\, d\mathbf{r}. \tag{7}$$

Once a form for E_{XC} is assumed, the ground state energy can be found by one of two methods. The first one is based on a direct minimization of Eq. (2) with respect to $n(\mathbf{r})$, subject to the orthonormality constraint: $\langle \psi_i | \psi_j \rangle = \delta_{ij}$. Alternatively, a set of single-particle Schrödinger-like equations (Kohn–Sham equations) may be solved self-consistently for the non-interacting wavefunctions, ψ_i:

$$\left[-\frac{\hbar^2}{2m} \nabla^2 + V_{eff}(\mathbf{r}) \right] \psi_i(\mathbf{r}) = \varepsilon_i \psi_i(\mathbf{r}), \tag{8}$$

$$V_{eff}(\mathbf{r}) = V_{ext}(\mathbf{r}) + V_h(\mathbf{r}) + V_{XC}(\mathbf{r}), \tag{9}$$

where

$$V_h(\mathbf{r}) = \frac{\delta E_h[n(\mathbf{r})]}{\delta n(\mathbf{r})}, \tag{10}$$

$$V_{XC}(\mathbf{r}) = \frac{\delta E_{XC}[n(\mathbf{r})]}{\delta n(\mathbf{r})}. \tag{11}$$

Finally, in terms of the Kohn–Sham eigenvalues ε_i, the total energy can be expressed as:

$$E = \sum_{i=1}^{N} \varepsilon_i - \frac{1}{2} \int \frac{n(\mathbf{r}) n(\mathbf{r}')}{|\mathbf{r} - \mathbf{r}'|} d\mathbf{r}\, d\mathbf{r}' - \int V_{XC}(\mathbf{r}) n(\mathbf{r})\, d\mathbf{r} + \int f[n(\mathbf{r}), \nabla n(\mathbf{r})]\, d\mathbf{r}. \tag{12}$$

Thus far, the key factor is to find a solution to Eq. (8). In practice, a numerical solution for this differential equation proceeds through an expansion of the single-particle wave functions. This is achieved by employing a suitable set of basis functions and by solving the resulting secular equation for the coefficients in this expansion and/or for the eigenvalues for which it has a solution. Although several choices are possible in theory, in practice the two most common types are atomic orbitals (AOs) and planewaves (PWs).

A plane wave basis set is the most common choice for simulations of crystalline systems, particularly those containing metallic phases. Hence in the present work, PWs are considered in solving Eq. (8). PWs have the advantage of being orthonormal and complete; the accuracy of the basis can be systematically improved by simply increasing the number of basis functions, thereby making it easy to check for convergence.

Another challenge facing the simulation of condensed phases results from the large number of electrons ($\sim 10^{23}$), and, nearly infinite extent of wave functions required in simulating even a relatively small (1 cm^3) amount of matter. Both of these issues are resolved by implementing periodic boundary conditions (PBC), in which a “supercell” is replicated throughout the space. By creating an artificially periodic system Bloch's theorem [16] can be applied, thereby allowing the periodic part of the wave function $u_{\mathbf{k}n}(\mathbf{r})$ to be expanded in a discrete set of PWs whose wave vectors are the reciprocal lattice vectors $\mathbf{G}$ of the crystal structure:

$$\psi_{\mathbf{k}n}(\mathbf{r}) = e^{i\mathbf{k}\cdot\mathbf{r}} u_{\mathbf{k}n}(\mathbf{r}) = \sum_{\mathbf{G}} c\mathbf{G}(\mathbf{k}n) e^{i(\mathbf{k}+\mathbf{G})\cdot\mathbf{r}}. \tag{13}$$

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