Ab initio analysis of the contributions of Eley-Rideal and Langmuir-Hinshelwood mechanisms in the atomic oxygen recombination on the Al_2O_3 coating

V. L. Kovalev,,** A. A. Kroupnov,*** and A. A. Buchachenko*****
** Department of Mechanics and Mathematics, M.V. Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119991, Russia*
*** Moscow Institute of Physics and Technology State University, 9 Institutskiy lane, Dolgoprudny city, Moscow Region, 141700, Russia*
**** Institute of Mechanics, M.V. Lomonosov Moscow State University, Michurinskii prosp. 1, Moscow 119192, Russia*
***** Department of Chemistry, M.V. Lomonosov Moscow State University, Leninskie Gory 1, Moscow 119991, Russia*

Abstract

The rate coefficients of adsorption, desorption, Eley-Rideal (ER) and Langmuir-Hinshelwood (LH) reactions are determined for heterogeneous recombination of atomic oxygen on the α-Al_2O_3 surface in the 500-2000 K temperature range from the first-principle calculations on alumina clusters. These parameters are used to calculate recombination coefficients at the conditions that model the experiments at MESOX facility. Crossover from the ER-mediated to LH-mediated regime is found to occur at ca. 1100 K. Good agreement with the measurements in the 1000-1400 K temperature range attests the first-principle cluster modeling combined with the statistical methods for rate coefficient calculations as a simple and adequate approach for preliminary characterization of the prospective thermal protection coverages.

1. Introduction

Heterogeneous recombination of highly-energetic particles formed in a shock wave play one of the key roles in the thermal balance of the reusable space vehicles during atmosphere entry and flyby [1-3]. Understanding the recombination kinetics and its dependence on the surface composition provides the means for designing efficient thermal protection systems for forthcoming space missions. The cost of real flight tests and limitations of Earth-based experiments pose the first-principle modeling as the most attractive tool for preliminary assessment and modification of the perspective materials. It is not surprising that a number of different multiscale models have been developed in the past decades, first of all, for the crystal SiO_2 surfaces that imitate silica-based ceramics used and tested within the Space Shuttle program.

Heterogeneous chemistry responsible for the ñcatalyticityò of the protecting coverage is introduced in the form of the kinetics equations, which govern the composition and energy content of the gas at the interface. At an upper scale, chemical kinetics is conjugated to the flow dynamics in a standard way, see, e.g., Refs.[1,4-8]. To follow empirical approaches, it is enough to consider these two scales treating the kinetic scheme as fixed and its parameters ï as adjustable to experimental data. In contrast, first-principle models add a lower scale that, first, justifies the kinetic scheme and, second, feeds it with the elementary rate coefficients obtained from the quantum chemistry calculations or by atomistic simulations accounting for the specific structure of the material.

Despite modern theoretical chemistry offers a broad range of methods and simulation protocols for heterogeneous rate coefficient calculations, see, for instance, Refs.[9-11], experience in their application to high temperature processes involving highly reactive species is rather limited. Furthermore, different models (ideal periodic, cluster, polymorph, etc.) can be explored for a surface. The question which one better represents a real (non-crystalline, corrugated, doped) coverage remains widely open and cannot be answered without large-scale trial calculations. Our understanding of the heterogeneous kinetics mostly arises from empirical models that postulate ad hoc the simplest schemes involving adsorption and classical Eley-Rideal (ER) and Langmuir-Hinshelwood (LH) mechanisms. Recent first-principle studies in oxygen and nitrogen recombination on the SiO_2 coatings (see Refs.[12-16] and references therein) cast doubts on the adequacy of the commonly accepted empirical mechanisms revealing complex kinetics with multiple adsorption sites. Moreover, the era of empirical modeling left a controversy even in the relative importance of classical ER and LH processes. At present, any validation of the first-principle background and resulting kinetic schemes within the closed multiscale models should therefore be regarded as a valuable contribution.

In this paper, we consider heterogeneous recombination of atomic oxygen on the Ŭ-Al_2O_3 surface to demonstrate the potential of the first-principle modeling in studying new thermal protecting materials using and elucidating the catalytic mechanisms described by the commonly accepted kinetic scheme. Though the Ŭ-Al_2O_3 coverage is unlikely perspective as a thermal protection shield, this material was investigated experimentally by Balat-Pichelin and co-workers [17] at the MESOX facility [18]. Despite some controversy in thermal flux measurements and high-temperature behavior of the recombination coefficients not observed at the real flight conditions, MESOX experiments provide valuable test-ground for catalytic activity modeling. Describing the Al adsorption sites of the ideal surface within the cluster approach, we obtain the rate coefficients for adsorption, desorption, ER and LH reactions using statistical thermodynamics and reaction rate theories from the previous first-principle calculations. Good agreement with the measured oxygen recombination coefficients measured at MESOX allows to access relative importance of ER and LH mechanisms depending on temperature.

2. Model for oxygen recombination on Ŭ-Al_2O_3

2.1 Surface models and surface-oxygen interactions from the first-principle calculations

We studied the surface that corresponds to (0001) face of the hexagonal close packed α-Al_2O_3 crystal terminated by Al atoms, which is thought to be the most stable surface for the thermally grown oxide layers [19,20], see fig. 1. Carter and co-workers [21,22] performed detailed periodic density functional theory (DFT) study of the atomic oxygen adsorption and migration on this surface. A great advantage of the periodic methods is the possibility to map globally all the stationary points of a multidimensional interaction potential energy surface ï minima, describing the adsorption sites, and saddles, describing the reaction or surface diffusion barriers. Periodic calculations revealed two adsorption sites: one at the oxygen atom of the second surface layer (hereafter O-site) with the adsorption energy 2.18 eV (210.3 kJ/mol), the other at the first-layer aluminum atom (Al-site) with the adsorption energy 1.74 eV (167.9 kJ/mol). The Al-site can be viewed as the minimum on top of the barrier for surface diffusion between adjacent O-sites [22].

For the same surface, Schlegel and co-workers [23] developed the cluster model and tested it using the ab initio methods. Cluster models are attractive for their simplicity and the possibility to mimic local surface relaxation under the influence of adsorbed species, but frequently suffer from inability to treat distinct adsorption sites on an equal footing. The model by Schlegel and co-workers was adapted by us previously to study oxygen adsorption on the Al-site using the DFT method for relaxed Al_8ʃ $_{12}$ cluster that corresponds to one of the four hexagons depicted in fig. 1. The details of these calculations and their results can be found in Refs.[24-26]. The oxygen adsorption energy on the Al-site was determined as 1.75 eV (168.9 kJ/mol), in perfect agreement with the periodic calculations [21,22].

More global representation of the surface was obtained within empirical approach described in Ref.[27]. In brief, we considered the interaction between oxygen atom and four Al_8ʃ $_{12}$ clusters by summing up individual atom-cluster interactions as the functions of the O-Al distance and polar angles of the O-Al vectors with respect to the surface plane. Unfortunately, it was impossible to treat large inclinations of adsorbed oxygen towards the surface to cover the domain of the O-site formation. We therefore added a standard Lennard-Jones potential [28] between the adsorbed O and second-layer oxygen atoms. As a result, our global potential does not reveal any minimum corresponding to O-site, but shows a saddle point ï maximum of the surface diffusion barrier between adjacent Al-sites [27]. Physically, this situation can be interpreted as the assumption that at the stationary conditions O-sites remain to be occupied and do not contribute to any desorption and recombination process. This assumption is implicitly supported by the fact that periodic calculations [21,22] overestimate the compression of the outer layer of the clean surface with respect to the experimental data [19,20]. Logically, O-sites should be even more energetic and less labile than predicted by Carter and co-workers. At least surface diffusion (and therefore LH recombination process) for these sites is strongly suppressed below 2000 K [22,27].

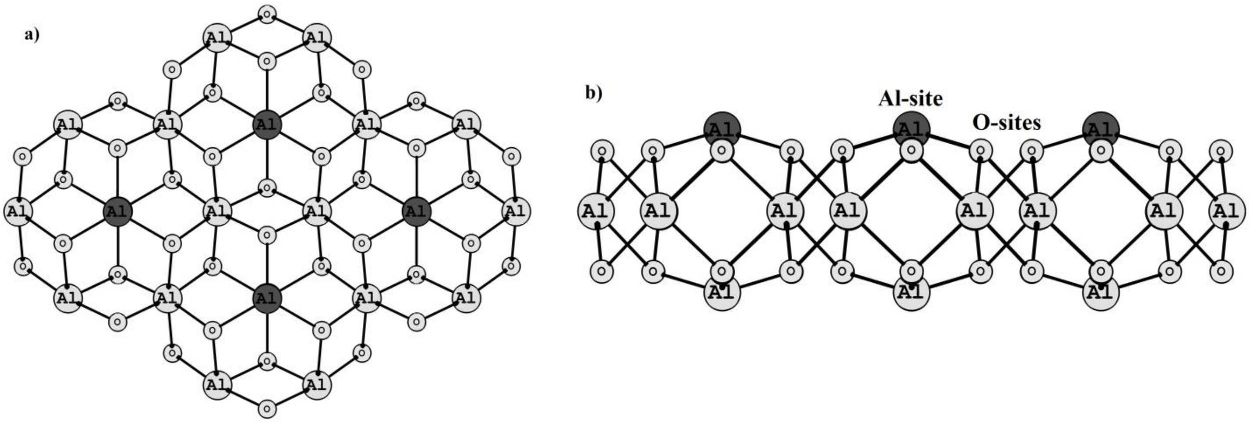

Figure 1: The (0001) face of the hexagonal close packed α-Al_2O_3 crystal. a) Top view, b) side view.

2.2 Heterogeneous recombination kinetics

Classical heterogeneous recombination kinetic scheme incorporates three elementary stages, namely, adsorption equilibrium (1), ER mechanism (2) and LH mechanism (3):

$$\mathrm{O} + (S) \xleftrightarrow{k_a, k_d} (\mathrm{O} - S)\,, \tag{1}$$

$$\mathrm{O} + (\mathrm{O} - S) \xrightarrow{k_{ER}} \mathrm{O}_2 + (S)\,, \tag{2}$$

$$(\mathrm{O} - S) + (\mathrm{O} - S) \xrightarrow{k_{LH}} \mathrm{O}_2 + 2(S)\,. \tag{3}$$

Here (S) and ($\mathrm{O}-S$) designate a free surface site and a site occupied by an oxygen atom O. The corresponding rates expressed through the rate coefficients k, partial pressure p_O and surface coverage θ_O of atomic oxygen are

$$r_a = k_a p_\mathrm{O}(1\text{-}\theta_\mathrm{O}), \quad r_d = k_d\theta_\mathrm{O}, \quad r_{ER} = k_{ER} p_\mathrm{O}\theta_\mathrm{O}, \quad r_{LH} = k_{LH} p_\mathrm{O}\theta_\mathrm{O}^2. \tag{4}$$

It is evident that all four elementary processes depend on the coverage and the system of differential kinetic equations cannot be decoupled to give, for instance, individual contributions of each recombination mechanism.

2.3 Elementary rate coefficients

The geometric parameters, energies and vibrational frequencies of the stationary points of the potential energy surfaces computed by the DFT method were used to parameterize the statistical formulas for the elementary rate coefficients in equation (4). Details of the calculations are presented in Ref.[27]. Here we only briefly describe the approaches and give resulting parameterization of the rate coefficients as the functions of temperature.

For adsorption rate coefficient the standard expression through the sticking coefficient s_0

$$k_a = \frac{s_0(T)}{S^0}\left(\frac{k_B T}{2\pi m}\right)^{1/2} \tag{5}$$

was used. Here k_B is the Boltzmann constant, m is the mass of oxygen atom and S^0 is the number of adsorption sites per unit surface area calculated geometrically from the surface structure parameters. Since our calculations revealed no activation barrier for an atom approaching the adsorption site, the well-known statistical estimate for direct activationless adsorption was accepted for sticking coefficient, see, e.g., Ref.[29].

Assuming thermal equilibrium in Eq. (1), we introduced equilibrium constant K and calculated it using the standard statistical approach [30] as

$$K(T) = \exp\left(\frac{E_{a0}}{k_B T}\right)\left(\frac{2\pi}{h^2} m k_B T\right)^{-1/2} \frac{Q_a(T)}{Q_S(T) Q_O(T)} \frac{N_A}{S^0}, \qquad \textbf{(6)}$$

where E_{a0} is the adsorption energy corrected to zero-point vibrational energy and N_A is Avogadroôs number. The ratio of partition functions of the adsorbed oxygen atom Q_a and the clean surface Q_S was estimated as the ratio of the vibrational partition functions of the clusters with and without oxygen atom attached, whereas the partition function of the gas-phase oxygen atom Q_O included the summation over the electronic states. At low temperatures it can be well approximated by the statistical weight of the ground ^{3}P state equal to 9.

Desorption rate coefficient k_d was determined by the Eqs. (5) and (6) and the definition $K = k_a/k_d$.

For the ER rate coefficient k_{ER} we made of use our previous molecular dynamics simulations [25], which can be presented in the form

$$k_{ER} = \frac{3.19}{S^0}\left(\frac{k_B T}{2\pi m}\right)^{1/2} \exp\left(-\frac{E_{ER}}{k_B T}\right), \qquad \textbf{(7)}$$

with the activation energy E_{ER} = 41.5 kJ/mol.

The LH rate coefficient k_{LH} is connected to the surface diffusion coefficient D as

$$k_{LH} = 4 N_A D(T) \exp\left(-\frac{E_{LH}}{k_B T}\right), \qquad \textbf{(8)}$$

where the activation energy is assumed to be equal to that of ER mechanism, $E_{LH} = E_{ER}$. In turn, statistical rate theory expression for D reads as [30]

$$D(T) = \rho^2 \frac{k_B T}{2\pi\hbar} \frac{Q^{\neq}(T)}{Q_a(T)} \exp\left(-\frac{E_{D0}}{k_B T}\right), \qquad \textbf{(9)}$$

where $Q^{Í}$ is the vibrational partition function of the ñactivated complexò on top of the diffusion barrier along the diffusion minimum energy path and Ɉ is the length of this path between neighboring adsorption sites. The diffusion activation energy that accounts for zero-point vibrations was found to be E_{D0} = 117.4 kJ/mol.

The results of our calculations were presented in the simple analytical form

$$k = A T^{Ŭ} \exp(-E/T) \qquad \textbf{(10)}$$

with the temperature given in degrees of Kelvin. Parameters are listed in table 1.

Table 1: Parameters of the elementary rate coefficients defined by Eq.(10)

Rate coefficient	Dimension	A	Ŭ	E, K	E, kJ/mol
k_a	cm^{3}mol^{-1}s^{-1}	3.778×10^9	1	-450	-3.7
k_d	s^{-1}	4.826×10^{11}	0	19340	160.8
k_{ER}	cm^{3}mol^{-1}s^{-1}	3.106×10^{12}	1/2	4970	41.5
k_{LH}	cm^{2}mol^{-1}s^{-1}	1.1×10^{-3}	0	19160	159.3

3. Application to MESOX experiment

The only experimental study of the oxygen recombination on the α-Al_2O_3 samples at the conditions relevant to atmosphere re-entry was performed at MESOX facility [18] by Balat-Pichelin and co-workers [17]. It covered 900ï 2400 K temperature range. Stationary diffusion layer model for MESOX experiments was developed previously [8]. We used it here considering an air with 95% and 0.001% degrees of oxygen and nitrogen dissociation, respectively, and 5% admixture of argon at the pressures from 1 to 7 kPa. The temperature at the upper layer boundary was set to 1800 K, whereas the surface temperature varied from 500 to 2000 K. Interaction of nitrogen molecules and atoms, as well as Ar, with the surface was neglected. The stationary solutions for surface coverage were used to define the recombination probabilities γ_{O} as the ratio of the recombined atom flux J_{O} to the total atomic flux to the surface:

$$\gamma_{\mathrm{O}} = (2\pi m k_B T)^{1/2} J_{\mathrm{O}} / p_{\mathrm{O}} . \quad \textbf{(11)}$$

To gain a qualitative insight into the contribution of distinct catalytic mechanisms, we considered three kinetic models, the full one with both ER and LH mechanisms present according to Eqs.(1)-(3), and partial, in which only one mechanism, either ER (2) or LH (3), is operative together with adsorption/desorption equilibrium. In all cases the rate coefficients from the table 1 were used.

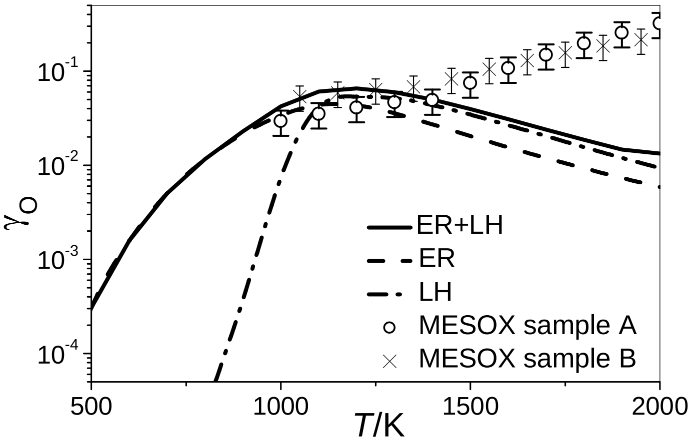

Figure 2: Oxygen recombination coefficients on the α-Al_2O_3 surface from the MESOX experiment for two samples (A, B) [17] and present calculations with different recombination kinetic schemes, full (ER+LH) and partial for the LH and ER mechanisms.

Figure 2 compares the calculated temperature dependences of the oxygen recombination coefficient at the pressure 4100 Pa (results depend on the pressure very weakly) with the measured data. Good agreement is achieved for the temperatures below 1400 K. Our calculations showed that up to T = 1000 K the ER mechanism dominates the recombination process. The contribution of LH kinetics, however, increases with temperature much faster and becomes equal to ER one at 1100 K. At higher temperatures, LH mechanism becomes favorable and provides 70-90% of the total recombination efficiency. Note that this consideration is only valid in a qualitative sense as far as the full kinetic model cannot be represented by the sum of two partial models. It is the surface coverage d_{O}, the fraction of adsorption sites occupied by oxygen atom, that couples ER and LH mechanisms. Figure 3 shows the stationary value of the surface coverage as the function of temperature calculated using the full and partial kinetic models. Results for LH mechanism clearly indicate that below 1000 K surface diffusion and thermal desorption are fully suppressed, so the loss of adsorbed atoms is only possible via ER mechanism. Crossover from ER-mediated to LH-mediated regime occurs at ca. 1100 K, when two mechanisms become equally efficient in removing adsorbed oxygen atoms (figure 3) or, equivalently, in forming gas-phase oxygen molecule (figure 2).

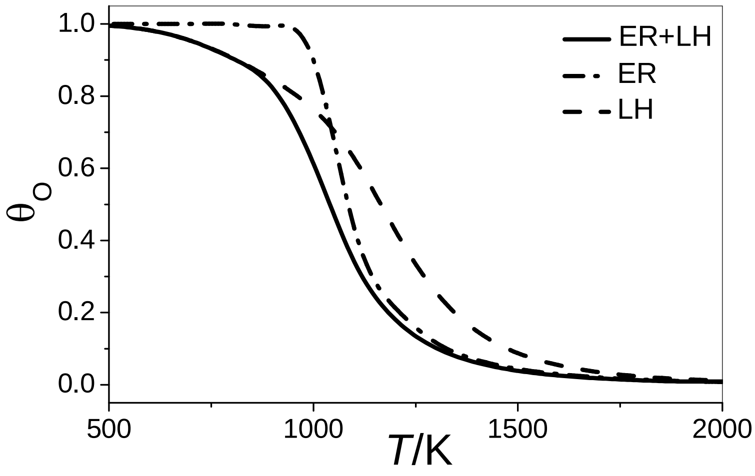

Figure 3: Stationary values of the surface coverage by oxygen atom from the present calculations with different recombination kinetic schemes, full (ER+LH) and partial for the LH and ER mechanisms.

Figure 3 may be also used to resolve the contradiction between the high-temperature MESOX data and the low-temperature measurements for plasma etching processes reviewed in Ref.[17]. For temperatures between 300 and 773 K, recombination coefficient γ_O were reported to fall within the 2×10^{-3} ï 0.06 range, at least by an order of magnitude larger than that obtained here. Moreover, there are indications that recombination proceeds through LH mechanism [31-33]. Our calculations suggest that at these temperatures LH mechanism is fully suppressed and all sites on the surface are occupied. The only possibility is the formation of the secondary adsorption layer by the gas-phase oxygen atoms having not enough kinetic energy to surmount ER activation barrier. These atoms should be able to diffuse over the surface almost freely being able to recombine by LH mechanism. The most thorough analysis of in-situ measurements of oxygen recombination from plasma [31,34] lead to the similar conclusion and estimated the second-layer adsorption energy as 40 kJ/mol. Though such mechanism was never considered explicitly in the modeling of thermal protection materials, it may be of some importance only at temperatures below 500 ï 700 K.

According to MESOX experiments, γ_O gradually increases with temperature. Moreover, at T = 1400 K one apparent Arrhenius dependence is changed to another, with larger activation energy [17]. Similar picture was observed at MESOX for some other materials, including ϐ-cristobalite and quartz [18]. Our modeling cannot reproduce this behavior: at the constant flux of the gas-phase oxygen atoms, γ_O coefficient should slowly *decrease* with temperature to a constant limit when the gas-phase atoms arriving to the surface immediately react or scatter back (zero surface coverage). It is tempting to explain the observed increase of γ_O may by another surface site(s) with higher adsorption energy, which should give the $\gamma_O(T)$ dependence similar to that shown in figure 2, but shifted towards higher temperatures (for instance, O-sites characterized in the periodic calculations [21]). However, no high-temperature increase of the recombination coefficient was found during the real-flight tests [2], so the discrepancy may originate from the difference in the composition of the gas phase under shock wave and microwave heating.

4. Summary and conclusions

The closed multiscale model based on the first-principle density functional calculations is used to interpret the high-temperature experimental data on oxygen recombination on the α-Al_2O_3 samples obtained at MESOX facility [17]. It is found that the consideration of the labile adsorption Al-sites provides good description of the measurements within the 1000-1400 K temperature range. We found that the crossover from Eley-Rideal-mediated regime to preferentially Langmuir-Hinshelwood recombination occurs at 1100 K due to surface diffusion activation. We conclude that the first-principle cluster modeling combined with the statistical methods for rate coefficient calculations can be viewed as a simple and adequate approach for preliminary characterization of the prospective thermal protection coverages.

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