

# Ab-initio analysis of the contributions of ER and LH mechanisms in the atomic oxygen recombination on the $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coating.

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Analysis of the heterogeneous recombination mechanisms and determination of their main kinetic parameters are of prime importance in designing the thermal shields for protection of the perspective hypersonic reusable spacecrafts [1]. Nowadays, multiscale modeling acquires increasing importance in solving these problems. Indeed, it provides the mean to describe the structure of the material and its interaction with highly energetic species from the first principles, thus opening an unbiased way to consider the whole variety of the corresponding physical and chemical processes. Only along this avenue the key heat transfer mechanisms could be reliably identified and their efficiencies could be related to the particular chemical and structural features of the coating.

To describe chemical component of the heat transfer during the spacecraft's passage through an atmosphere, multiscale models usually use the classical kinetic schemes that correspond to Eley-Rideal (ER) and Langmuir-Hinshelwood (LH) mechanisms of heterogeneous catalysis [1]. The lack of reliable experimental data frequently constitutes the main problem for such models. Indeed, flight experiments provide the information on the very few coating materials, whereas special ground-based facilities are not able to reproduce all the flight regimes and often introduce additional uncertainties in the composition of the gas mixture due to excited species and the products of their decomposition. However, even if the reach set of experimental data is available for a material, empirical approach, which adjusts elementary rate coefficients to the measured heat fluxes and other macroscopic properties, may not be reliable for assessment of a particular mechanism due to complexity of the inverse multi-parametric problem [2]. For this reason, even the simple qualitative question – what mechanism, ER or LH, dominates the heterogeneous recombination? – remains widely unanswered. Definite answer can only be found by the first-principle modeling of each perspective material.

Present report provides the detailed analysis of the contributions of ER and LH mechanisms in the atomic oxygen recombination on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coating. It is based on the quantum chemical calculations of the relevant potential energy surfaces, the molecular dynamics and statistical estimations of the elementary rate coefficients, and the diffusion layer modeling for partially dissociated air interacting with the surface that takes into account both ER and LH recombination mechanisms.

The kinetic scheme for atomic oxygen heterogeneous recombination consisted of the following elementary acts:

- oxygen adsorption/desorption equilibrium that implies the strong chemical bonding (chemisorption):



- ER (impact) recombination:



- LH (associative) recombination:



Here ( $S$ ), ( $O-S$ ) denote the empty adsorption sites and sites occupied by oxygen atoms, respectively, and all the acts are assumed to be thermodynamically and chemically consistent. Reaction rates are determined by the law of surface action,

$$r_a = k_a p_O \theta, \quad r_d = k_d \theta_O, \quad r_{er} = k_{er} p_O \theta_O, \quad r_{lh} = k_{lh} \theta_O^2,$$

where the oxygen adsorption coverage  $\theta_O$  and the fraction of empty adsorption sites  $\theta$  obey the condition  $\theta_O + \theta = 1$ . The  $r_i$  values are therefore the reaction rates per unit surface area. The coverage  $\theta_O$  enters the reaction rate expressions for both ER and LH mechanisms. It implies that their contributions cannot be exactly segregated into the simple sum. To deduce them qualitatively, the calculations were performed not only for the full scheme, but also for each individual mechanism conjugated to adsorption equilibrium. The diffusion layer model conformed the conditions typical to the MESOX facility [3]. Recombination coefficient was defined in a standard way, as the ratio of the recombining oxygen atom flux to the net oxygen atom flux towards the surface [1]:

$$\gamma_O = J_O / J_O^\downarrow,$$

where the net flux is determined by the partial pressure of oxygen atoms  $p_O$

$$J_O^\downarrow = p_O (2\pi m k_B T)^{-1/2}$$

and has the  $\text{cm}^{-2}\text{s}^{-1}$  dimension ( $m$  is the mass of oxygen atom and  $k_B$  is the Boltzmann constant).

Elementary rate coefficients  $k_i$  are the functions of physico-chemical parameters of the gas phase, as well as of the chemical composition and structure of the surface. They were determined by means of the molecular dynamics and statistical approaches using the potential energy surfaces (PESs) calculated from the first principles. Adsorption rate coefficient was expressed through the sticking coefficient calculated statistically under the assumption of direct activationless adsorption, whereas the adsorption equilibrium constant was used to evaluate the desorption rate coefficient. The activation energy for impact recombination was obtained directly from the quantum-chemical calculations, whereas the pre-exponential probability factor was calculated by the molecular dynamics method. The rate coefficient for associative recombination was expressed through the surface diffusion coefficient calculated using the activated complex theory. More detail can be found in ref. [4].

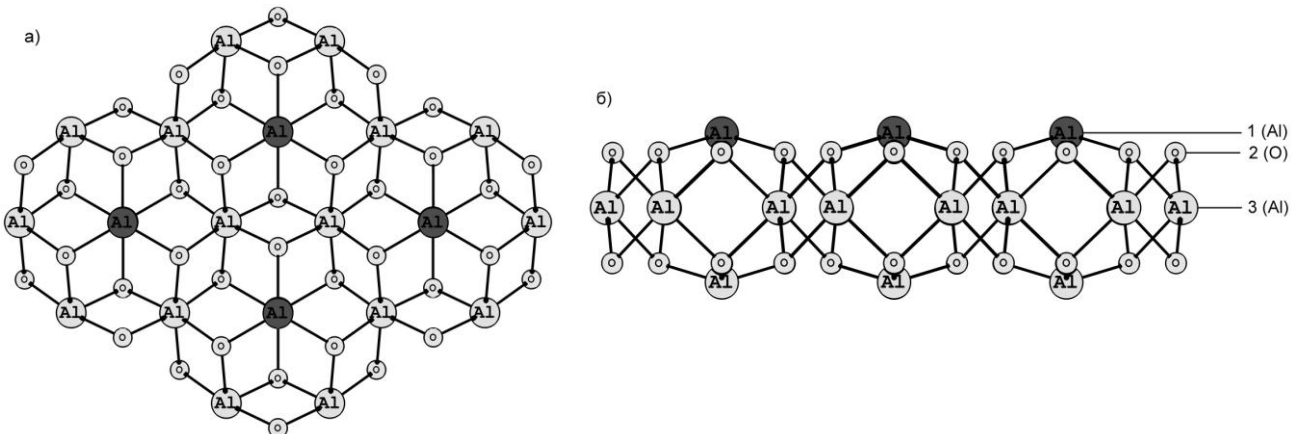


Figure 1. The model used for the  $\alpha\text{-Al}_2\text{O}_3$  (0001) surface, top (a) and side (b) views. The structural element of the surface shown is obtained by the four-fold translation of the  $\text{Al}_8\text{O}_{12}$  cluster. The Al(1) atoms of the surface atomic layer – oxygen adsorption sites – are shown in the dark gray color.

The most stable surface of the thermally grown crystal  $\alpha\text{-Al}_2\text{O}_3$  coating is the Al-terminated one corresponding to the (0001) plane of the hexagonal close packing lattice, see figure 1. Cluster models for this surface and its interactions with atomic and molecular oxygen were developed in refs. [5-7]. The density functional theory with the B3LYP functional was used in all calculations.

The PES describing atomic adsorption was calculated for the  $\text{Al}_8\text{O}_{12}$  cluster unit (one of the four hexagons shown in the figure 1(a)). Smaller cluster  $\text{Al}_4\text{O}_6$  was considered for modeling molecular adsorption and for interaction of the gas-phase O atom with the adsorption site already occupied by another atom. Adsorption of both atomic and molecular oxygen was found to proceed barrierless at the Al(1) atom of the surface atomic layer. As far as the direct quantum-chemical calculations of the several surface units were proven difficult, the extension of the cluster model was achieved semiempirically. Four  $\text{Al}_8\text{O}_{12}$  clusters were composed in the «rhomb» shown in figure 1(a) and the PES for oxygen atom moving along the surface plane was approximated as the sum of four PESs between the adatom and each cluster and Lennard-Jones potentials between the adatom and oxygen atoms O(2) belonging to the second atomic surface layer, see figure 1(b). The reaction (diffusion) paths connecting the nearest Al(1) sites and the parameters of the transition states for statistical calculations were determined using this total PES.

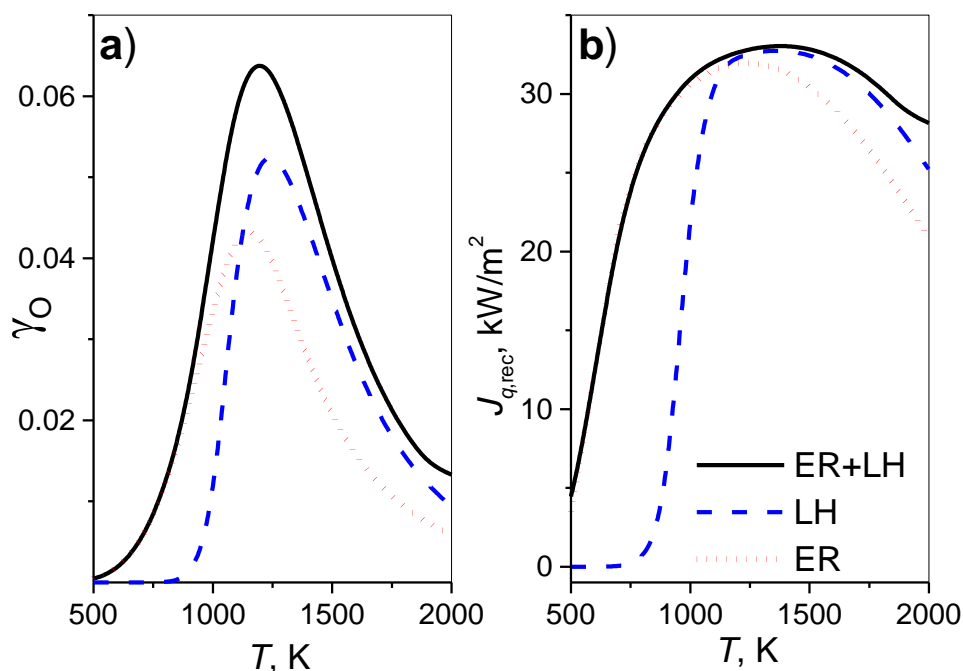


Figure 2. Oxygen recombination coefficient  $\gamma_0$  (a) and heat flux to the surface due to oxygen recombination (b) as the functions of surface temperature  $T$ . The results are presented for three schemes involving both ER and LH mechanisms and each particular mechanism individually. The total pressure was set to 4100 Pa.

Figure 2 presents the temperature dependences of the oxygen recombination coefficient  $\gamma_0$  and heat flux to the surface due to energy release in the recombination reaction. Both are calculated using three kinetic schemes introduced above: one involves both ER and LH mechanisms, the other two treat each mechanism individually. In accord with the kinetic analysis, the total quantities cannot be represented as the sum of contributions due to each mechanism. Relative importance of particular mechanism can be assessed only qualitatively, by the similarity of the particular and total results. Figure 2 points out that at the surface temperatures below 1000 K recombination mainly proceeds by ER mechanism. The limiting stage of the LH scheme is the surface diffusion of oxygen atoms. Though large chemisorption energy suppresses it at low temperatures, diffusion rate rapidly increases as the temperature grows up. As a result, associative recombination starts to dominate over the impact one above 1100 K. This qualitative picture holds for all pressure interval studied (1000-7000 Pa).

To conclude, simultaneous consideration of the Eley-Rideal and Langmuir-Hinshelwood heterogeneous recombination mechanisms does not allow the rigorous separation of their contributions into the process. For this reason empirical adjustment of the elementary rate coefficients may give unphysical rate parameters for each mechanism, even though the observed quantities are successfully reproduced. True parameters can only be deduced by the first-principle calculations of the PESs and reliable methods for the theoretical rate coefficient calculations. The model for heterogeneous recombination of atomic oxygen on the  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> coating reveals that ER recombination mechanism prevails at temperatures below 1000 K, whereas above 1100 K the LH mechanism becomes more efficient and provides about 70% of the total recombination probability.

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